Assessment and Exploitation of the Inherent Value of Waste Electrical and Electronic Equipment (WEEE) for Circular Economy

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Abstract

Waste electrical and electronic equipment (WEEE) represents a global environmental and resource-efficiency crisis. However, WEEE is a valuable urban mine of economically, strategically and environmentally important materials e.g. precious metals (PMs) and critical raw materials (CRMs). Economic value derived from WEEE can drive solutions to the 'WEEE problem' which are conducive to circular economy, enhance global resource-efficiency, and generate environmental and social benefits. This thesis examines the value of WEEE, and methods for its exploitation to the benefit of global sustainability. The 'WEEE problem' is examined in the context of global sustainability, considering environmental & resource-efficiency implications and linear resources use by the electrical & electronic equipment (EEE) industry. Solutions are considered which exploit WEEE as an 'urban mine' and embrace circular economy.

Within this context, recycling potential of future WEEE is evaluated through projections of PM & Cu content of PCBs, based on temporal trends in historic RAM modules. CRMs are then identified in WEEE and methods of enhancing their recovery through intervention in pre-processing stages of recycling are evaluated. An industrial symbiosis process which recovers Pt from waste thermocouples for use in solar cells is presented as an example of the greater value generation potential offered by circular economy and the potential of such processes to overcome barriers to CRM recovery. Challenges and opportunities in lifecycle optimisation of printable photovoltaics for circular economy is considered as a means of enhancing the industrial ecology of this industry to avoid WEEE generation, reduce primary materials demand and enhance the value derived from these technologies at all stages of their lifecycles. Appropriate battery selection for solar off-grid systems in South Africa is then considered, demonstrating that greater value can be derived from EEE for local economies if compatibility of technologies with local skills and infrastructure for in-use and EoL management.

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This thesis is dedicated in loving memory to Mrs Pauline Elizabeth Holley (1930-2017)

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Abbreviations

3GPV	3rd Generation Photovoltaics		**EVA**	Ethylene Vinyl Acetate
AAS:	Atomic Absorption Spectroscopy		**FPM**	Fast Page Mode (RAM)
AATF	Approved Authorized Treatment Facility		**GHG**	Greenhouse Gas
			HCL	Hollow Cathode Lamp
ABS	Acrylonitrile Butadiene Styrene (plastic)		**HDD**	Hard Disk Drive
			HDI	Human Development Index
BATRRT	Best Available Treatment, Recovery and Recycling Techniques		**HIPS**	High Impact Polystyrene
			HTM	Hole Transport Material
			IC	Integrated Circuit
BIPV	Building Integrated Photovoltaics		**ICP-OES**	Inductively Coupled Plasma – Optical Emission Spectroscopy
BFRs	Brominated Flame Retardants		**ICP-MS**	Inductively Coupled Plasma – Mass Spectrometry
CBA	Cost-Benefit Analysis			
CCFL	Cold Cathode Fluorescent Lamp		**IPA**	Isopropyl alcohol
			IPR	Individual Producer Responsibility
CE	Circular Economy			
CFC	Chlorofluorocarbon		**ITO**	Indium Doped Tin Oxide
CIGS	Copper-Indium-Gallium-Diselinide (PV)		**LCA**	Lifecycle Analysis
			LCD	Liquid Crystal Display
cps	Counts per Second		**LCOE**	Levelised Cost Of Electricity
CRMs	Critical Raw Materials		**LED**	Light Emitting Diode
CNCs	Cellulose Nanocrystals		**LFP**	Lithium-Iron-Yttrium-Phosphate Battery
COGs	Cut-Off Grades			
CRMs	Critical Raw Materials		**LIB**	Lithium-Ion Battery
CRT	Cathode Ray Tube		**MAI**	Methylammonium Iodide
DDR	Double Data Rate (SDRAM)		**MFA**	Material Flow Analysis
DEHP	Di(ethylhexyl) Phthalate		**MLCCs**	Multi-Layer Ceramic Capacitor
DfRR	Design for Reuse, (Refurbishment) And Recycling		**MSSCs**	Mesosuperstructured Solar Cells
			NIB	Neodymium-Iron-Boron (alloy permanent magnets)
DIMMs	Dual In-line Memory Modules			
DMF	dimethylformamide		**OPV**	Organic Photovoltaics
DRAM	Dynamic RAM		**P3HT**	3-hexylpolythiophene
DSSC	Dye-sensitised Solar Cell		**PA**	Polyamide
EDO	Extended Data Output (RAM)		**PBB**	Polybrominated Biphenyls
EDS	Energy Dispersive X-Ray Spectroscopy		**PBT**	Poly(Butyleneterephthalate)
			PC	Polycarbonate
EEE	Electrical and Electronic Equipment		**PCB**	Printed Circuit Board
			PCBM	Phenyl-C61-Butyric Methyl Ester
EoL	End-of-Life			
EPBT	Energy Payback Time		**PCE**	Power Conversion Efficiency
EPR	Extended Producer Responsibility		**PDPE**	Polybrominated dipheyl ethers
			PET	Polyethylene terephthalate
ETL	Electron Transport Layer		**PM**	Precious Metal
ETRD	Emerging Technologies Raw Material Demand		**PMR**	Material for Precious Metal Recovery
EU	European Union		**POM**	Placed on the Market

PP	Polypropylene
PPE	Polyphenylene ether
PS	Polystyrene
PPV	Printable Photovoltaics
PV	Photovoltaics
PVC	Polyvinyl Chloride
PVD	Physical Vapour Deposition
PVDF	Polyvinyldiene Fluoride
R2R	Roll-to-Roll (production)
REEE	Reusable EEE
RSA	Republic of South Africa
REMs	Rare Earth Metals
RSD	Relative Standard Deviation
SD	Standard Deviation
SDA	Small Domestic Appliances
SDR	Single Data Rate (Sdram)
SDRAM:	Synchronous DRAM
sem	Standard Error on the Mean
SEM	Scanning Electron Microscopy
SIMMs	Single In-Line Memory Module
SMD	Surface Mounted Device
ssDSSC	Solid-State DSSC
TBBA	Tetrabromo-Bisphenol-A
TCO	Transparent Conductive Oxide
wDIMMS	Waste DIMMs
WEEE	Waste Electrical & Electronic Equipment
wPCs	Waste PCs
WRAP	Waste & Resources Action Programme
WTC	Waste Thermocouple
XRF	X-Ray Fluorescence Spectroscopy

1 Introduction

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Chapter summary

WEEE represents a considerable sustainability challenge for humanity. Most of the WEEE generated around the globe unaccounted for and its improper treatment by informal sectors has resulted in significant impacts on the environment and human health. In addition, the linear throughput of materials used by the EEE industry to manufacture new products to replace WEEE, including critical raw materials which are recovered with low efficiency or not at all from WEEE, represents a resource-efficiency crisis which must be urgently addressed. The ever-growing volumes of WEEE around the globe are also a significant secondary resource of important valuable materials. If exploited effectively, WEEE presents opportunities to address global resource-efficiency challenges and mitigate materials criticality. Significant economic, environmental and social benefits can be derived by exploiting the inherent value of WEEE, particularly through reuse and efficient recovery of valuable metals such as precious metals, PGMs and copper.

Circular economy represents a solution to the global WEEE problem and a means to enhance the industrial ecology of the EEE industry through reuse & recycling of EEE and its components, and through provision of secondary raw materials/components for manufacturing. This provides a means of exploiting greater value from WEEE through novel methods of valorisation which present economic, social and environmental benefits over traditional recycling processes. To drive circular material flows sufficient economic value must be derived from WEEE to cover costs incurred throughout recycling process chains. This requires suitable recovery processes to be available; product design to accommodate circular practices; and appropriate reverse logistics, business models and legislation to be in place. Much progress has been made around the world in establishing suitable legislation to govern WEEE management. This has resulted in establishment of collection systems, and efficient recovery processes for economically and environmentally important metals, particularly

precious metals and copper concentrated in PCBs. However, much progress is still required to address low collection rates and exports to regions where WEEE is recycled by the informal sector resulting in significant impacts on populations, ecosystems and the environment. Losses of potentially recoverable materials in pre-processing and recovery stages of recycling which limit derivable value from WEEE and the ability to efficiently recover 'high-tech' metals must also be addressed in the interests of global resource-efficiency.

To overcome these issues, greater knowledge of the composition of items within the waste stream and the available value therein is required to plan future EoL management. In addition, recovery processes which derive greater value and are more conducive to circular economy are required for viable recovery of materials which are currently lost in recycling. For the future, optimisation of product design and whole product lifecycles is necessary to ensure problems encountered in managing WEEE today are avoided, and greater value can be derived from material resources contained in WEEE. Greater education and awareness of the material content of items and available end-of-life processes is necessary to enable consumers to make informed decisions when selecting technologies that will result in better outcomes at end-of-life.

1.1   The nature of WEEE

Electrical and electronic equipment (EEE) has permeated into all aspects of our lives resulting in prosperity for billions. EEE includes the smartphones in our pockets, toys and computer games with which our children play, tablets and laptop computers. The internet itself upon which society has become increasingly dependent is hosted on a global network of servers. Low-carbon technologies for global sustainability are being rapidly and widely deployed around the world. EEE has enabled the digital revolution and provides the means of addressing the global knowledge gap, energy access gap, and to mitigate global climate change. But for all the benefits of EEE, its use leaves mankind with a considerable problem: waste electrical and electronic equipment (WEEE) – the planet's fastest growing waste stream.[1, 2]

1.1.1   WEEE by definition

WEEE, electronic waste (e-waste) and e-scrap are terms used interchangeably to describe electrical and electronic equipment (EEE) which has been discarded by its owners and is perceived to be useless.[3] However, due to inconsistency in the global use of these terms, numerous definitions of WEEE exist *(Table 1.1)*.[4-8] In an attempt to reconcile some of these

inconsistencies and introduce global conformity, the StEP initiative recently published guidance on the use of a new non-legal global definition of EEE…

> *"Any household or business item with circuitry or electrical components with power or battery supply."*

and e-waste…

> *"E-waste is a terms used to cover items of all types of electrical and electronic equipment (EEE) and its parts that have been discarded by the owner as waste without the intention for re-use."[6]*

Table 1.1 Definitions of WEEE

Source	Definition of WEEE
EC[4, 9]	*"Electrical or electronic equipment which is waste within the meaning of Article 3(1) of Directive 2008/98/EC, including all components, sub-assemblies and consumables which are part of the product at the time of discarding"* and *"electrical and electronic equipment' or 'EEE' means equipment which is dependent on electric currents or electromagnetic fields in order to work properly and equipment for the generation, transfer and measurement of such currents and fields and designed for use with a voltage rating not exceeding 1 000 volts for alternating current and 1 500 volts for direct current"* - WEEE directive, 2012/19/EU. *'waste' means any substance or object which the holder discards or intends or is required to discard"* - Waste framework directive, 2008/98/EC.
StEP Initiative.[6]	*"A term used to cover almost all types of electrical and electronic equipment (EEE) that has or could enter the waste stream. Although e-waste is a general term, it can be considered to cover almost any household or business item with circuitry or electrical components with power or battery supply."*
OECD.[7]	*"Any appliance using an electric power supply that has reached its end of life."*
Basel Action Network.[8]	*"E-waste encompasses a broad and growing range of electronic devices ranging from large household appliances such as refrigerators and air-cons to hand-held cell phones and personal stereos."*

All definitions suggest that EEE becomes 'waste' EEE once the user chooses to discard it. Therefore, it is the owners of EEE, their perception of its value and functionality, and the decisions they make regarding what to do with items for which they no longer have a use, which determine the point at which EEE becomes 'WEEE'. The situation can best be described diagrammatically (*Figure 1.1*). EEE is manufactured and distributed to users. Once the user no longer wishes to keep the device they make a decision about whether or not to discard it. If the device has been leased, it may be returned to the company from which it was leased for re-use with another user. Likewise, items owned by current users which are perceived to have retained value can be sold, traded or donated for use by another user. If the owner chooses not to sell, donate or return items to lease companies then they discard items (i.e. get rid of it as

waste), at which point EEE enters the end-of-life (EoL) phase of its lifecycle and becomes WEEE. Once received by the waste management sector, a decision is made whether the item is suitable for reuse or not. Reusable EEE (REEE) may be refurbished and sold to a new user. WEEE that has no value for re-use is recycled for recovery of valuable materials and disposal of hazardous and non-recyclable components.
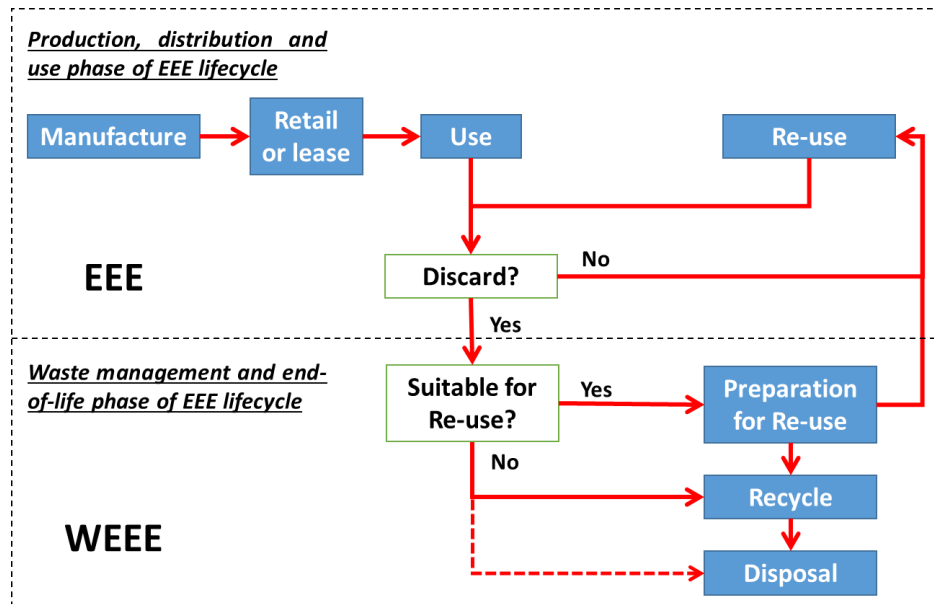
Figure 1.1 Flow of EEE into WEEE (adapted from StEP, 2014)[10]

An enormous variety of items fall within the definitions of EEE & WEEE, which are often grouped into categories such as those used in the EU for statutory reporting of quantities of EEE placed on the market and WEEE collected and treated (*Table 1.2*). A breakdown of WEEE collected in the EU by category is shown in *Figure 1.2*, and quantities of WEEE collected in each member state are given in *Figure 1.3*.

Table 1.2 Categories of (W)EEE used in the EU as set out in Annex I of the WEEE directive[4]

Category*		Example items
1	Large household appliances	White goods (ex. cooling equipment)
2	Small household appliances	Vacuums, toasters, irons
3	IT and telecoms equipment	Computers, printers, phones (screens included)
4	Consumer equipment & PV panels	Radios, electronic musical instruments,
5	Lighting equipment	Fluorescent lamps, discharge lamps
6	Electrical and electronic tools	Drills, sewing machines, saws
7	Toys, leisure and sports equipment	Games consoles, coin slot machines
8	Medical devices	Dialysis machines, ventilators
9	Monitoring and control instruments	Smoke detectors, thermostats, scales
10	Automatic dispensers	ATMs, vending machines

* for a non-exhaustive list of items that fall in each category refer to Annex II of the WEEE directive
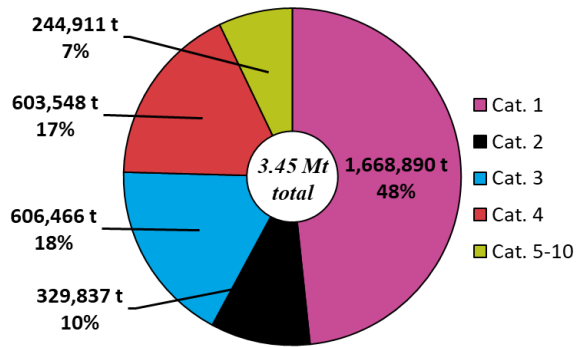
Figure 1.2 *Breakdown by category of WEEE collected in the EU in 2014 (data from Statistical Office of the EC, 2016)[11]*
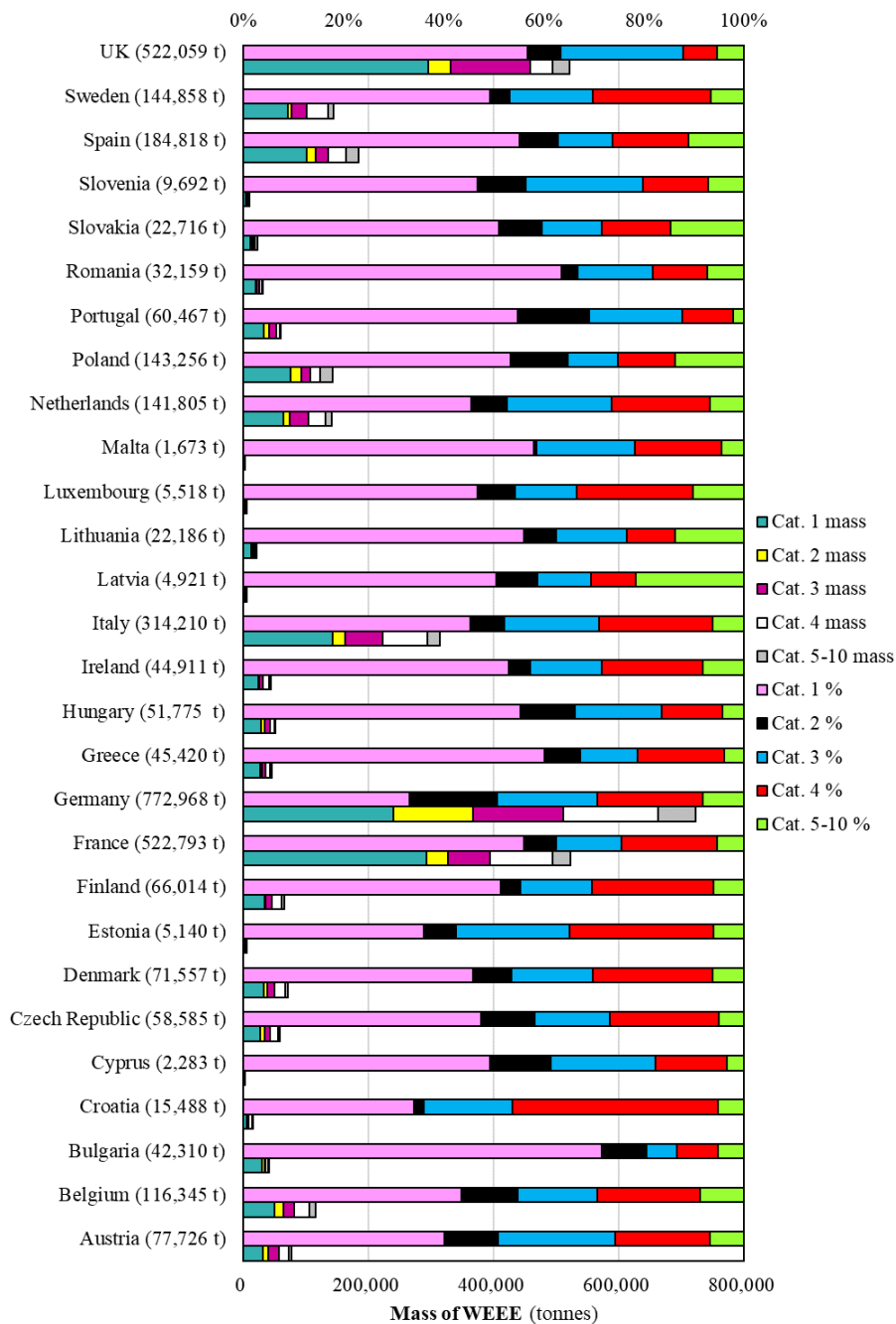
Figure 1.3 *Masses of WEEE collected in EU member states in 2014 with compositional breakdown by category (data from Statistical Office of the EC, 2016)[11]*

Each category, and different kinds of equipment within each category, often require distinct and specific waste management strategies at EoL, because of differences in design, structure and material compositions.

1.1.2 Material composition of WEEE

It is difficult to determine an overall composition for WEEE, due to compositional differences between WEEE types, the rapidly evolving nature of items in the waste stream and lack of available data from many regions of the world. However, some general compositions which have been proposed are shown in *Figure 1.4*.
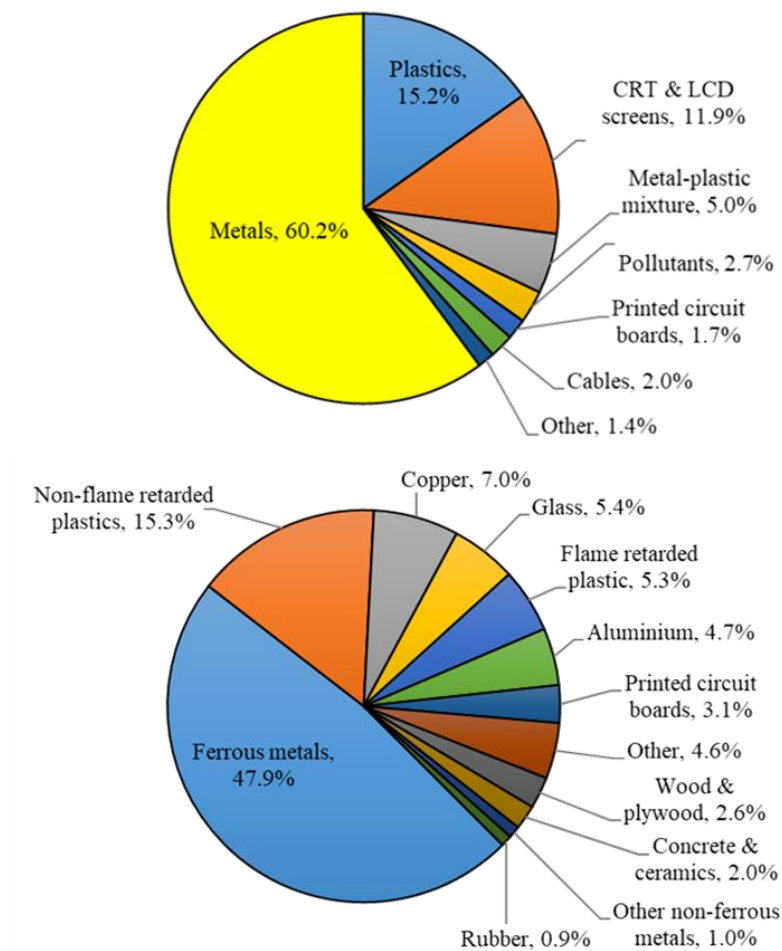
Figure 1.4 *General material compositions of WEEE by mass given by EMPA, Switzerland (top); and the European Topic Centre on Resource and waste management (bottom)[3]*

It is easier to give general compositions for WEEE categories or particular items (*Figure 1.5*). The material composition, even of the same kind of WEEE (e.g. different mobile phones or PCs), varies enormously, **and** WEEE is a complex heterogeneous combination of materials,[12]

the major mass fractions being bulk metals (aluminium, copper and ferrous), plastics [13-15] and glass. Individual items can contain up to 60 elements.[16]
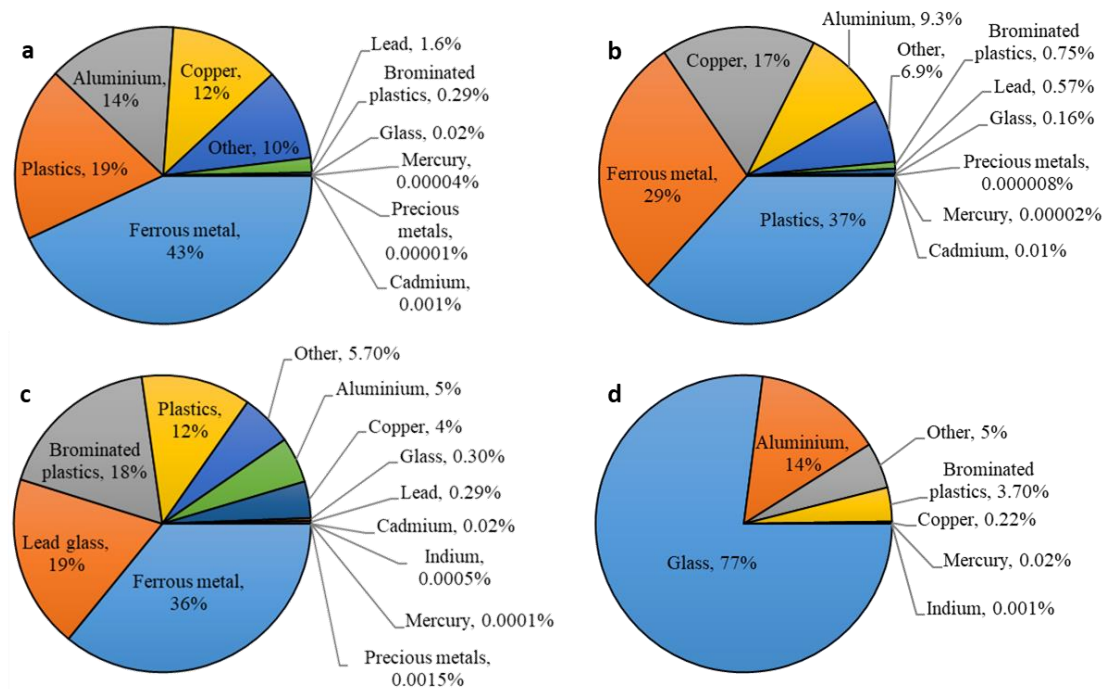
Figure 1.5 *Material composition by mass of four e-waste categories: a) large household appliances; b) small household appliances; c) ICT and consumer electronics; d) lamps*[17]

Metals – A large number of metals are found in WEEE. In addition to bulk metals and alloys such as, aluminium, brass, copper, and steel, which are used in structural components of EEE, cables, motors, heat sinks etc. and which form the major mass fraction of the waste stream, there are also trace amounts of 'high-tech metals.[18] These are metals which are vital components of EEE and typically used in high-tech applications. These include precious metals (PMs) and critical raw materials (CRMs). [19, 20]

Critical Raw Materials - In recent years, demand has risen for CRMs such as rare earth metals (REMs) used in permanent magnets, indium used in LCD screens; and metals in printed circuit board components such as tantalum, gallium and platinum group metals (PGMs). Although only used in small quantities in EEE, these metals are often crucial to the functionality of devices with few viable options for substitution. Global demand for these materials is rising rapidly due to growth in demand for EEE and use of these metals in many emerging technologies including 'green' technologies (*Table 1.3*). Economic impacts associated with supply shortages of these elements would be significant. This fact, coupled with rising demand and the possibility of supply bottlenecks has resulted in these elements gaining 'critical' status

from numerous studies in recent years.[21] (Materials criticality is discussed further in *Section 1.2.2*)

Table 1.3 *'High-tech' metals' and their driving emerging technologies[22]*

Raw Material	Emerging Technologies
Ga	Thin layer photovoltaics, ICs, LEDs
Li	Li-ion batteries
Nd	Permanent magnets, laser technology
In	Displays, thin layer photovoltaics
Ge	Fibre optic cable, IR optical technologies
Pt	Fuel cells, catalysts
Ta	Micro capacitors, medical technology
Ag	RFID, lead-free soft solder
Co	Lithium-ion batteries, synthetic fuels
Pd	Catalysts, seawater desalination
Ti	Seawater desalination, implants
Cu	Efficient electric motors, RFID
Nb	Micro capacitors, ferroalloys
Sb	Flame retardant, dopant in silicon wafers
Cr	Seawater desalination, marine technologies
REMs	Permanent magnets for wind turbines & electric vehicles

Plastics - Plastics are widely used in EEE for insulation, noise reduction, sealing, housings, interior structural parts, functional parts and interior electronic components (*Table 1.4*). [14] [15] Acrylonitrile butadiene styrene (ABS), polycarbonate (PC), PC/ABS polymer blends and high impact polystyrene (HIPS) are used predominantly in housings and make up the majority of plastics in WEEE. (*Figure 1.6*). Polypropylene (PP) is commonly used for internal components of household appliances such as dishwashers, and PVC is used for insulating cables & wiring.[14] Of the plastics used in WEEE, about a third are flame-retarded, ~60% with non-halogenated flame retardants and ~40% with halogenated flame-retardants.[15]

Table 1.4 *Applications of plastics in WEEE items[14]*

Polymer	Application
ABS	Housings of phones, SDA; microwaves; flat screens & certain monitors
	Enclosures & internal parts of ICT equipment
HIPS	Internal refrigerator components (liners, shelves)
	Housings of SDA, data processing and consumer electronics
PC	Housings of SDA & ICT equipment
Epoxy resins	PCBs
PP	Internal components of dishwashers & washing machines, castings of SDA
PPO (HIPS/PE)	Housings of TVs, monitors and some SDA
	TV, computer, printer & copier components
PC/ABS	Housings of ICT equipment and some SDA (e.g. kettles, shavers)
PVC	Cable sheathing

SDA: small domestic appliances; **PCBs**: printed circuit boards
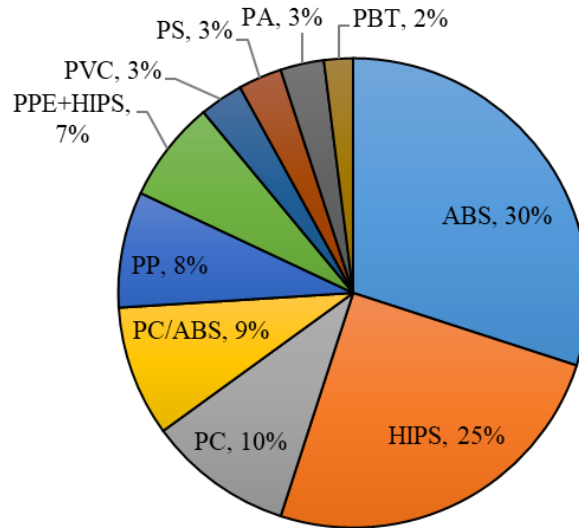
Figure 1.6 *Mass proportions of polymers found in WEEE plastics (ABS: acrylonitrile-butadiene-styrene; HIPS: high impact polystyrene; PA: polyamide; PBT: poly(butyleneterephthalate); PC: polycarbonate; PP: polypropylene; PPE: polyphenylene ether; PS: polystyrene; PVC: poly(vinyl chloride)*[15]

Hazardous materials - WEEE is hazardous because it contains a variety of toxic substances including heavy metals such as Hg, Cd and Pb, and halogenated flame retardants such a polybrominated diphenyl ethers (PBDEs) and tertrabromobisphenol A (TBBA).[23, 24] A list of hazardous substances in WEEE and their location in items is given in *Table 1.5*.

Table 1.5 *Non-exhaustive list of hazardous substances found in and arising from WEEE*[23]

Contaminant	Relationship with WEEE
Halogenated compounds	
Brominated flame retardants (BFRs):	
• Polybrominated diphenyl ethers (PDPE)	
• Polybrominated biphenyls (PBB)	Thermoplastic components & cable insulation. TBBA is widely used in PCBs & ca
• Tetrabromo-bisphenol-A (TBBA)	
Polychlorinated biphenyls	Condensers, transformers
Chlorofluorocarbon (CFC)	Cooling units (fridges, air-cons), insulation foam
PVC (polyvinyl chloride)	Cable insulation; Encapsulating material for SMDs
Plasticisers	
Phthalates e.g DEHP	Plasticiser in PVC
Metals	
Antimony (Sb)	Flame retardants in plastics & PCBs (SbO_3); CRT & lamp phosphors; Diodes
Arsenic (As)	Dopant for Si; doping agent in transistors and PCBs; GaAs semiconductor in LEDs
Barium (Ba)	Getters in CRTs; vacuum tubes of CRT displays
Beryllium (Be)	Power supply boxes containing silicon controlled rectifiers; X-ray lenses; motherbo
Cadmium (Cd)	NiCd batteries, phosphor in CRTs (CdS); printer inks/toners; plastics; contacts & sv
Chromium VI (Cr VI)	Data tapes; floppy disks; corrosion inhibitor and hardening element for metallic hou
Gallium (Ga)	Semiconductors e.g. GaAs in LEDs & ICs
Indium (In)	Indium doped tin oxide ITO for LCDs and thin-film photovoltaics (PV); transistors
Lead (Pb)	PbO as radiation shield in CRT glass; Pb-acid batteries; solder on PCBs; stabilisers
Mercury (Hg)	LCD backlights; alkali batteries; mercury wetted switches/relays in old mainframe
Nickel (Ni)	NiCd &NiMH batteries; electron gun in CRTs; surface plating for PCBs and electri
Selenium (Se)	Rectifiers; photo drums in older photocopier; PCBs
Silver (Ag)	Wiring, switches, numerous SMDs; Connectors; Pb-free solder
Tin (Sn)	Solder; LCD screens (ITO)
Zinc (Zn)	Zinc sulphide mixed with rare earths in fluorescent layer of CRT screens; used in P
REMs	Y, Eu, La, Tb used in phosphors of lamps and CRTs; Nd, Dy, Sm in permanent ma
Radio-active substances	
Americium (Am)	Smoke detectors (active sensing element); medical equipment

For details of hazards associated with materials found in WEEE see EMPA, 2009; Greenpeace, 2005; and Robinson, 2009.[17, 25, 29] l

PCBs - Printed circuit boards are components of nearly all EEE. Although PCBs account for a small proportion of the mass of WEEE overall, they represent the most valuable portion of the waste stream because they contain precious metals which can be present at 40-50 times higher concentration than naturally occurring ores.[30] According to UNU, 320 tons of gold and 7500 tons of silver are consumed annually in the manufacturing processes of PCs, cell phones, tablets and other items, adding a value of $21 billion to the urban mine.[31] Generally, PCBs are composed of 40% metals, 30% plastics and 30% ceramics[32] The most common PCBs, used in higher value items such as phones and computers, are FR-4 PCBs made from fibre glass reinforced epoxy resin. FR-2 boards are common in lower value items and power boards, and are composed of cellulose paper reinforced with phenolic resin.[33] The most common metal in PCBs is copper, used to form the electrical circuits on the PCB, present in ~15-30 wt% depending on the nature of the item.[22, 34]. Nickel and zinc are also present in significant quantities, along with lead and tin in solder alloys used to attach surface mount device (SMD) components to boards.

1.2   The 'global WEEE problem'

1.2.1   The scale of the problem - global WEEE generation

WEEE is the fastest growing waste stream on the planet [1, 2], it accounts for 5% of all municipal solid waste[3] with global generation currently at 48.9 million tonnes/year[31] and increasing by 3-5% annually.[35] Within the EU, annual WEEE generation has exceeded 10 million tonnes/year with a projected increase to 12 million tonnes/year by 2020.[36] In the UK WEEE generation has reached ~1.5 million tonnes/year.[37] A breakdown of global e-waste generation by continent and per inhabitant in each continent is given in *Table 1.6.* This data highlights that WEEE is a global problem and that WEEE generation is concentrated in regions of greatest economic development. Per region, the most WEEE is generated in Asia, however per capita Europe leads WEEE generation, followed by Oceania. There is a direct correlation between GDP per capita and WEEE per capita.[38] However, although the majority of WEEE is generated in OECD member countries, growth in the rate of WEEE generation in the developing world exceeds that in developed regions where consumer electronics markets are saturated. Rapid market penetration of electronics in developing nations with high populations will significantly increase the rate of WEEE generation in these regions, with WEEE generation in developing countries likely to soon exceed that in the developed world.[3, 39]

Table 1.6 *Annual e-waste generation broken down by continent*[38]

Continent	Amount (million tonnes)	Amount (kg/inh)
Africa	1.9	1.7
Americas (north & South)	11.7	12.2
Asia	16.0	3.7
Europe	11.6	15.6
Oceania (Australia)	0.6	15.2

Why is WEEE generated?

The reasons that EEE enters the waste stream as WEEE are numerous. Damage to items and malfunctioning components is a common cause. Obsolescence is another. This is exemplified by trends for TV and display equipment in recent years. CRT displays have been replaced with flat screens (plasma and LCD technologies), which has driven generation of waste CRTs with many devices discarded by users while still functional. This rapid replacement of CRTs has occurred due to a combination of factors. Despite being available since 1988, rapid decreases in the price of flat screens since 2003 made them more affordable to consumers, resulting in rapid growth in sales.[40] Another reason for rapid replacement of technology is shorter lifetimes of new technologies. The lifespan of flat screens is only one third that of CRTs. Aesthetics changes such as the screen size may also result in replacement, with increasingly large screens becoming ever more popular as costs fall. Upgrade of existing technologies with new functionality and upgrade of peripheral technologies results in rapid replacement of devices by consumers who view current products as outdated. Continuing with the example of TVs, new video formats e.g. 4k replacing 1080p, which previously replaced 720p; storage media e.g. Blu-ray replacing DVD which replaced VHS; and signal transmissions changes e.g. the digital switchover,[2] and the use of internet cables, WiFi or satellite in place of the traditional roof mounted TV aerial and cable have all resulted in replacement of functioning equipment. Incorporation of new functionality is also a driver for replacement as was seen following incorporation of VHS and then DVD players into CRT TVs. The increasing popularity of 'smart' TVs and 3D TVs as their cost falls will no doubt result in replacement of functional TVs into the future.

It has been suggested that consumer perception of their products in light of new updated products hitting the market may result in replacement of EEE. This has been proposed as the cause for the increase in the frequency with which the term 'iPhone slow' is searched on Google at the time new iPhone models hit the market; the 'slow iPhone phenomenon' (*Figure 1.7*).[41] Interestingly, the same trend is not observed for Android based devices such as the Samsung Galaxy. This suggests user perception of iPhone performance is not psychological, but rather devices are really running more slowly. Devices which have been in use for a period

of time can be slowed down if basic 'housekeeping' is not periodically conducted. Additionally, the release of the iPhone always coincides with an update to Apple's operating system (iOS), which may be optimized for newer hardware and therefore result in a 'slowing' of older devices which receive the OS update.[42] This is an example of how software development can result in consumer perception that devices are outdated, which could be an important factor in WEEE generation from computing products such as tablets, laptops and PCs.
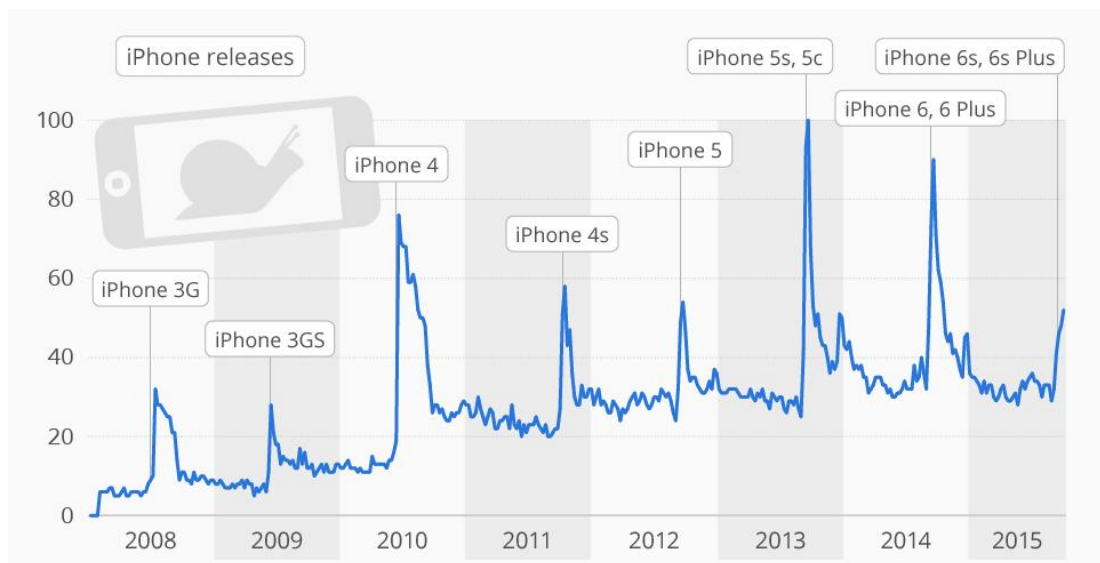
Figure 1.7 *Worldwide Google searches for the term 'iPhone slow' correlated with release dates of new iPhone models (100=peak search volume) (Figure used with permission from statista.com)[41]*

1.2.2 The nature of the 'WEEE problem'

Impacts on human health & the environment

The majority of WEEE is either landfilled or exported to parts of the world where it is recycled in a crude and inappropriate manner.[43] When this occurs, hazardous components of WEEE accumulate in the environment and within food chains.[25, 44] Persistent hazardous chemicals such as dioxins and other hazardous substances are generated as combustion products from 'open burning' of circuit boards and cables, a practice common in the developing world to recover valuable metals (*Table 1.7*). As a result, the improper treatment and management of WEEE possess considerable risks to human health and the environment.[24] Much research has been conducted to determine the impacts on human health associated with WEEE, and this has been reviewed by Grant *et al*.[45]

Table 1.7 Toxic combustion products from WEEE[29]

Hazardous compound	Generation mechanism
Polycyclic aromatic hydrocarbons (PAHs)	• Combustion product
Polyhalogenated aromatic hydrocarbons (PHAHs)	• Low temperature combustion product
Polychlorinated dibenzo-p-dioxins (PCDDs) Polychlorinated dibenzofurans (PCDFs)	• Low temperature combustion products of PVC & other plastics

Nowhere have the detrimental impacts of poor recycling practice impacted the environment and local population to a greater extent than in Guiyu City and its surrounding region in Guangdong province, China. This is the largest WEEE recycling site in the world. Here environmentally detrimental 'backyard' WEEE recycling practices are widespread, including open burning to reduce volumes and recover metals, and open acid digestion of components to recover precious metals. Waste acid containing high levels of heavy metals is dumped directly into the soil and rivers. Solder containing Pb and Sn is melted over makeshift coal grills to liberate valuable components form PCBs. These ongoing practices have resulted in contamination of the air, soil and water systems. Elevated levels of dioxins have been found in human milk, placentas and hair at sufficient levels to pose a serious health risk. Transfer of polychlorinated biphenyls via the food chain and water system to humans has been observed. Recycling workers have been shown to have median PDBE levels of 126 ng/L in their blood serum, with local residents in Guiyu at 35 ng/L, ~13 and 3.5 time higher than residents in nearby regions. respectively. Samples of human hair from towns in the region demonstrate high levels of PBBs, PBDEs and polychlorinated biphenyls. Tragically, children in the region have significantly elevated blood levels of Pb and Cd, and lower cognitive abilities than children from nearby areas. Elevated levels of polychlorinated biphenyls are also found in breast milk. Elevated levels of Cr in umbilical cord blood due to exposure of mothers' to WEEE recycling correlates with DNA damage, which may result from exposure to Cr or other toxic substances from WEEE. Recycling workers in the region have a twenty times higher chromosomal aberration rate than normal. This all suggests that WEEE has been a source of genetic mutation and cytogenetic damage for the population.[25]

A major factor contributing to such impacts around the world is illegal exports of WEEE from the developed countries to Africa and Asia where it is treated in an inappropriate manner by the informal sector.[8, 24, 25, 43, 46] Such practices persist due to a lack of education on the impacts of such practices, high unemployment rates, and a lack of regulation and enforcement of WEEE management. Proper management of WEEE, particularly when hazardous materials need to be properly processed, is costly and for this reason much material is illegally exported.

Implications for global resource-efficiency

Currently the EEE industry is based primarily on linear economic models, with growth in the sector coupled to the linear throughput of material resources (*Figure 1.8*). Like all manufacturing based on the 'take-make-use-dispose' model, creation of new EEE requires finite natural resources to be mined and refined, which are then used in manufacturing to create products which find their way to consumers who dispose of them as waste at the end of their useful life. This process reduces natural capital, and at each stage of the process energy produced from fossil fuels is consumed and environmental emissions and waste energy and materials are generated. This contributes to global warming and climate change, as well as acidification of the oceans.[47] Such models are no longer sustainable i.e. they fail to meet the needs of the present while maintaining the ability of future generations to meet their own needs.[48]
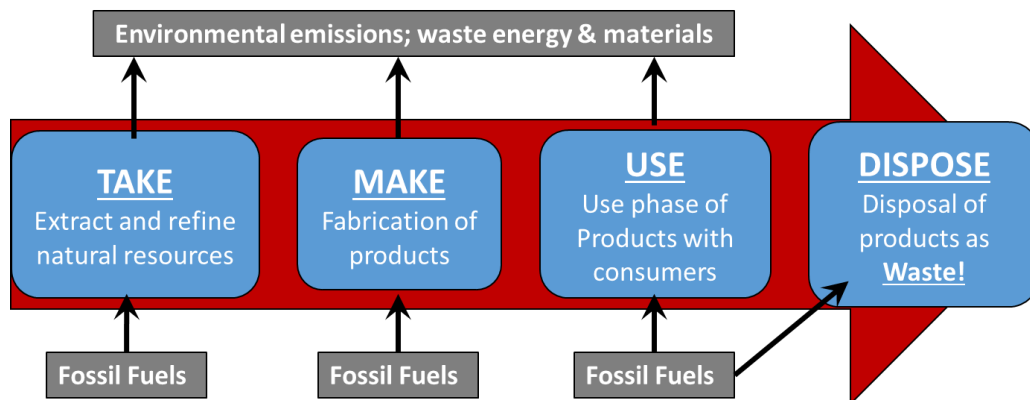
Figure 1.8 Material flows in the linear 'take-make-use-dispose' economy

Figure 1.9 indicates the position of countries according to their human development index (HDI), roughly equivalent to standard of living, and ecological footprint per capita. The dashed horizontal lines represent the planet's available biocapacity per person. As countries have developed economically they have moved across the plot according to the trend indicated by the red arrow. The increasing environmental impact with increasing HDI correlates strongly with resource use as demonstrated by *Figure 1.10*.[49] For global sustainability, all nations must be within the green area highlighted in *Figure 1.9*, in which citizens would be living well, within the limits of the planet. The data suggests firstly, that current levels of resource consumption are unsustainable, and secondly, that a resource-efficient alternative to linear economic models, which decouples economic development from the use of finite resources, is necessary.
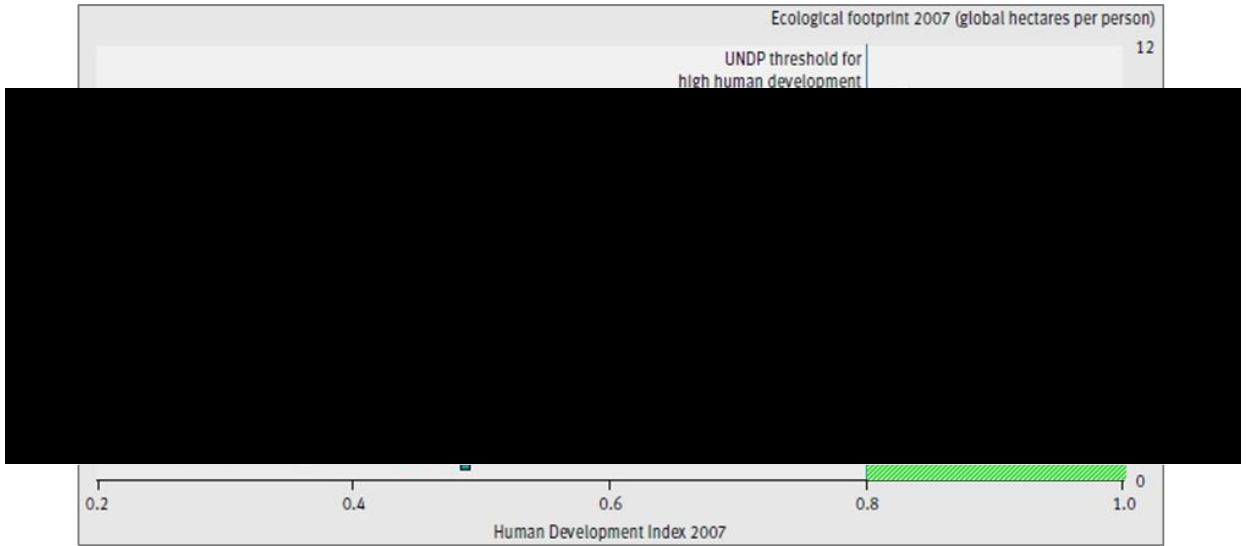
Figure 1.9 *Human Development Index vs Ecological Footprint of the World's Nations in 2007. Taken from UNEP, 2012.*[50]
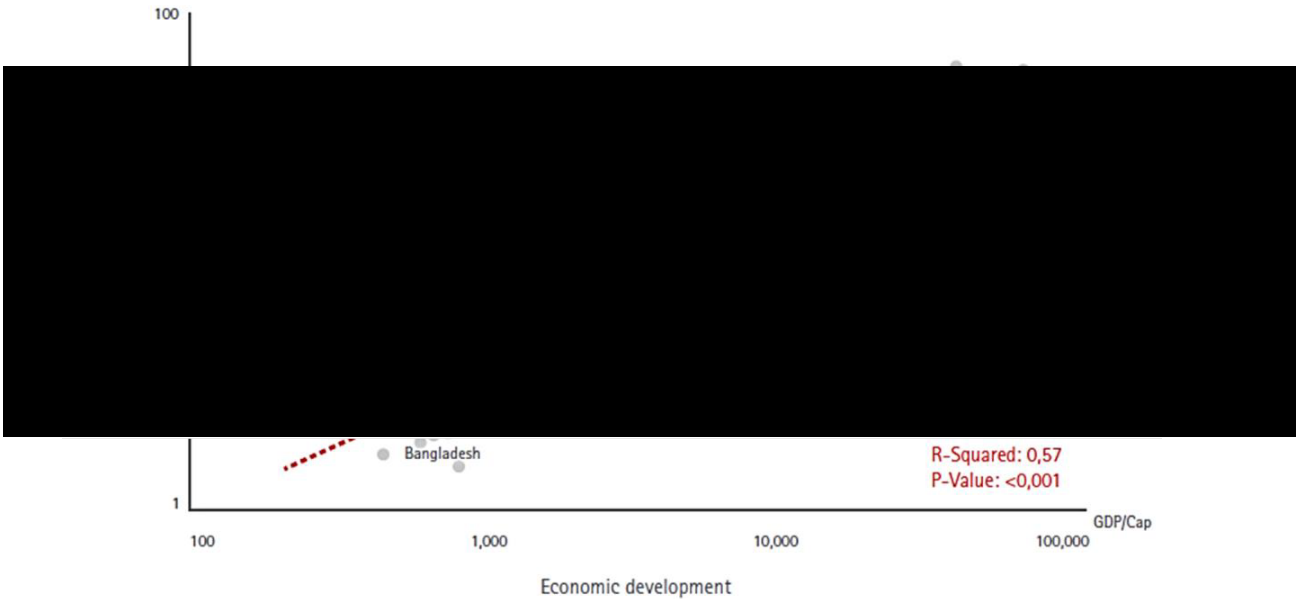
Figure 1.10 *Correlation between resource use and GDP/captia of countries(image courtesy of Accenture, permission pending)*[49]

The correlation between resource consumption, economic development and WEEE generation is clear. As the planet's fastest growing waste stream, the contribution of WEEE to the unsustainable use of resources by society must be addressed. The rate at which EEE is discarded contributes to global resource depletion; discarded items must be replaced with new ones manufactured from raw materials resulting in accelerated resource consumption and pollution.[2] For example, producing a single 32 MB RAM module requires 32 L of water, 1.6

kg of fossil fuels, 700 g of gasses and 72 g of various different chemicals.[36], and at least 240 kg of fossil fuels are consumed in manufacturing a whole PC and monitor.[50]

Materials criticality

In recent years, the issue of materials 'criticality' has received a great deal of attention from governments and industry around the world in light of growing concerns over global resource security. Numerous assessments have been conducted to evaluate the economic importance of particular materials to economies, sectors and organisations, and the risk of future supply bottlenecks for each material (*Figure 1.11*). [21, 51, 52] Those materials found to have high risk to supply and high economic impacts associated with supply shortage are determined to be '*critical*' raw materials (CRMs). A prominent example of a criticality evaluation is the recent 2013 evaluation by the EC which generated the 'EU20' list of critical raw materials (Table 1.8).[53]
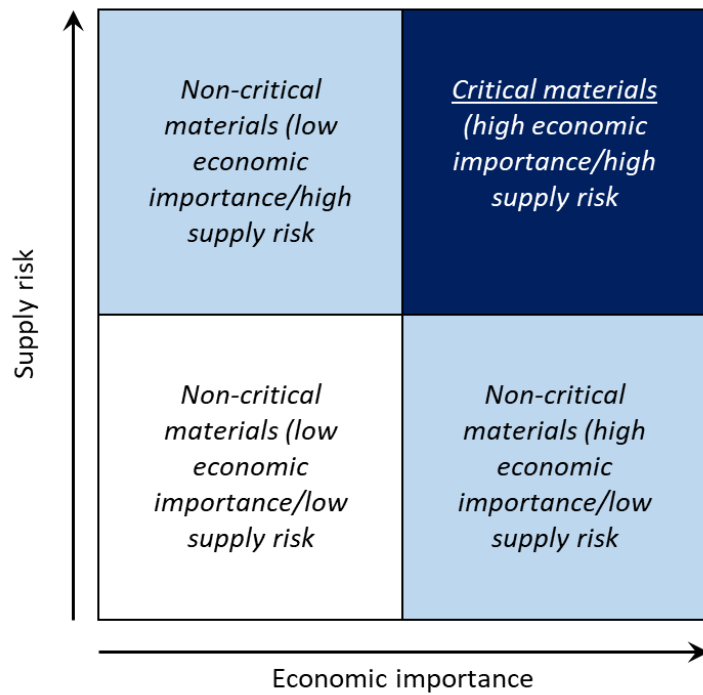
Figure 1.11 *Schematic criticality plot for evaluation of materials criticality (adapted with permission from Frenzel et al., 2017)[54]*

Table 1.8 *The 'EU20' list of critical raw materials*

Antimony	Beryllium	Borates	Chromium	Cobalt
Coking coal	Fluorspar	Gallium	Germanium	Indium
Magnesite	Magnesium	Natural Graphite	Niobium	PGMs
Phosphate Rock	REMs (Heavy)	REMs (Light)	Silicon Metal	Tungsten

REMs: Rare earth metals; **PGMs**: platinum group metals

Technology metals are consistently found to be critical, for a number of reasons. Some are scarce in the earth's crust, such as Ga, In, and Sb which are used in smartphones (*Figure 1.12*).

Selected elements found in smartphone electronics, batteries & screens

Years remaining until depletion of known reserves

- 5-50
- 50-100
- 100-500
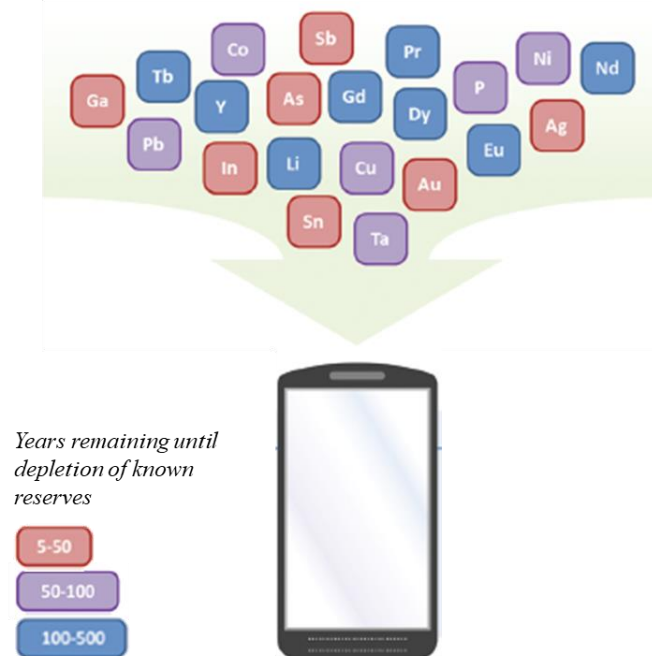
Figure 1.12 *Elemental resources used in smartphones and times until their depletion based upon current rates of extraction from known reserves (adapted from Clark et al., with permission)*[55]

Global reserves for these metals are likely to be exhausted within the next decade based on current rates of consumption and known reserves.[55] Production for many CRMs is concentrated in single regions of the globe, for example China is responsible for >95% of rare earth metals (REMs) production and has recently imposed export restrictions. Secondly, these materials are often produced as by-products of other mining operations e.g. indium which is a by-product of refining Zn and Pb sulphide ores (*Figure 1.13*). For this reason, global production cannot easily respond to rising demand. Rather, the production of these materials is dependent upon the markets of the major target metals mined.[56] Often CRMs are produced in regions of conflict or political instability, which adds to supply risk e.g. over half of the world's cobalt is supplied from DRC.
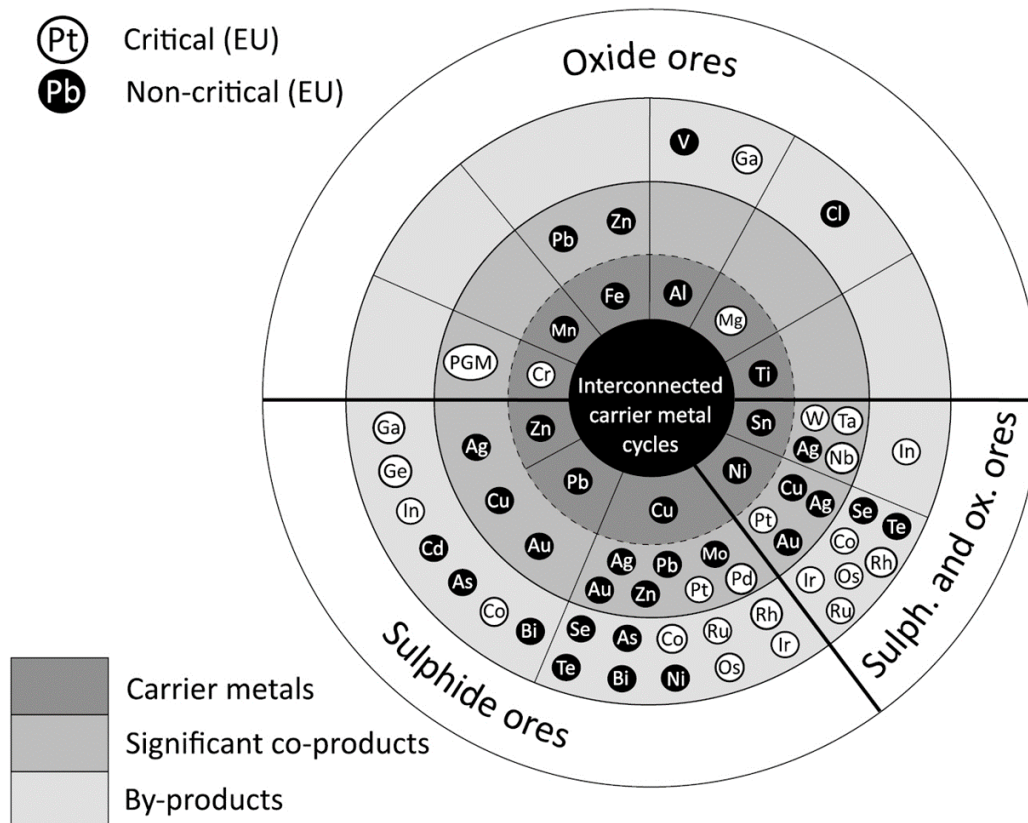
Figure 1.13 *The metal wheel—a schematic illustration of the geological relationships between different industrial metals and their co- and by-products; criticality is assigned according to the EU20. (© IOP Publishing. Reproduced with permission. All rights reserved)*[54]

Table 1.9 *Growth in element use projected to 2030 in emerging technologies. The 2006 and 2030 indicators show the proportion of demand compared to 2006 production e.g. Ga: indicator 2006 = 28/152 = 0.18 and indicator 2030 = 603/152 = 3.97*[57]

Raw material	Production[A] (t)	Demand 2006 (t)	Demand 2030 (t)	Indicator 2006	Indicator 2030
Gallium	152[E]	28	603	0.18[A]	3.97[A]
Indium	581	234	1,911	0.40[A]	3.29[A]
Germanium	100	28	220	0.28[A]	2.20[A]
Neodymium[F]	16,800	400	27,900	0,23 [A]	1.66[A]
Platinum[G]	255	very small	345	-	1.35[A]
Tantalum	1,384	551	1,410	0.40[A]	1.02[A]
Silver	19,051	5,342	15,823	0.28[A]	0.83[A]
Cobalt	62,279	12,820	26,860	0.21[A]	0,43[A]
Palladium[G]	267	23	77	0.09[A]	0.29[A]
Titanium	7,211,000[C]	15,397	58,148	0.08	0.29
Copper	15,093,000	1,410,000	3,696,070	0.09	0.24
Ruthenium[G]	29[E]	0	1	0	0.03
Niobium	44,531	288	1,410	0.01	0.03
Antimony	172,223	28	71	<0.01	<0.01
Chromium	19,825,713[B]	11,250	41,900	<0.01	<0.01

[A] Data updated by the BGR based on new information; [B] Chromite; [C] Ore concentrate; [D] Consumption; [E] Estimation of full production in China and Russia; [F] rare earth metal; [G] platinum group metals

Table 1.9 sets out estimates of demand for various scarce technology metals and their compounds used in emerging sustainable technologies; its final column shows how 2030 demand for such metals compares to 2006 demand and 2006 production for all uses. At current rates of production, by 2030 demand for Ga, In, Ge, Nd, Pt and Ta will have exceeded levels of production as they were in 2006.

Many CRMs are not easily substituted and recycling rates of most CRMs from WEEE are low,[58-60] which means that use of these metals in EEE results in considerable depletion of finite CRM reserves. This is a problem not only for economies that rely on continued supply of CRMs, but also for humanity's ability to deploy existing and emerging green technologies which are vital to strategies for achieving sustainability with our planet.[61, 62]

1.3   The value of WEEE

The ever-growing quantities of WEEE present a considerable opportunity if properly managed. WEEE itself is a source of reusable EEE, and a rich secondary material resource. For this reason WEEE is considered an 'urban mine' or 'mine above ground'.[63-65] If effectively exploited, WEEE can help enhance global resource-efficiency, reduce global emissions, mitigate materials criticality, and generate economic and social value.[34]

WEEE has an ***economic value***. This is derived from financial returns following the sale of reusable equipment and components, or recovered materials. The ***material value*** of an items is based upon the revenue generated from sale of materials recycled from WEEE which is dependent upon market values of those materials. *Figure 1.14* indicates the estimated value of major metals contained within WEEE in Australia, 50% of which is attributable to precious metals and copper. In PCBs, the proportion of the value represented by these metals is higher still. Recovery of these metals has historically provided ~95% of the revenue from WEEE recycling (*Figure 1.15*), and exploitation of this material value has been the essential financial driving force for WEEE recycling to date.
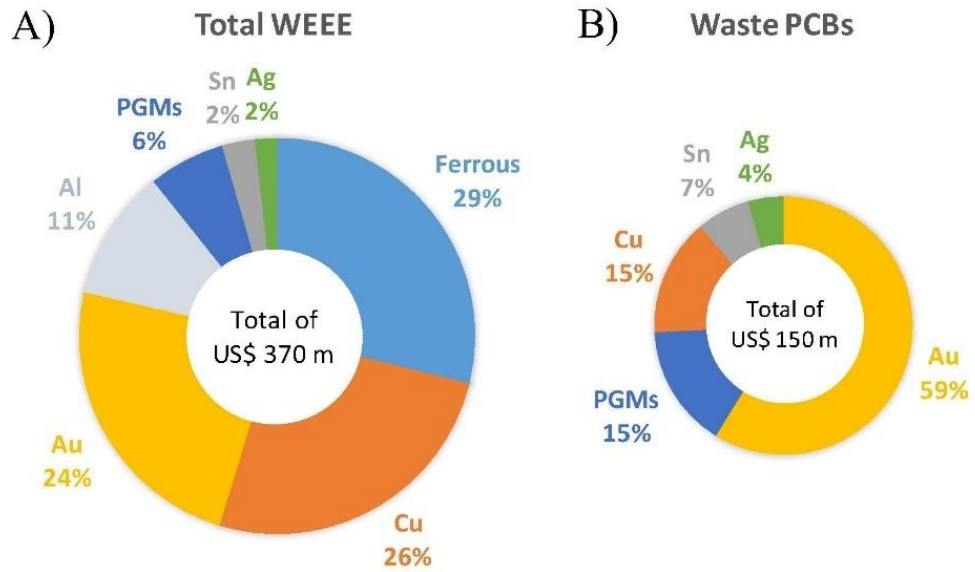
Figure 1.14. *Estimated value of major metals contained in WEEE in Australia in 2014: (A) total WEEE; (B) waste PCBs (reused with permission from Elsevier)*[66]

Silver, 1.5%
Palladium, 5.5%
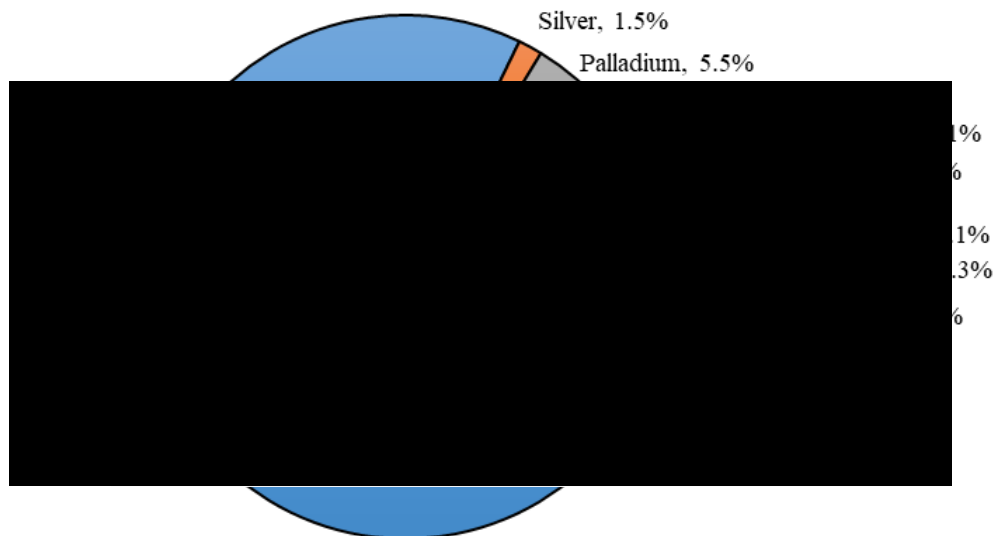
Figure 1.15 *Revenue breakdown by material from WEEE adapted from (Sodhi and Reimer, 2001.*[30]

Reusable equipment & components have a value greater than their material value, this is their *utility value.* The functionality of items grants higher economic value, for example, a functioning reused laptop is worth more than its material value.

There are additional aspects to the value of WEEE, which are not necessarily linked to its economic value. WEEE has *strategic value* by virtue of its CRM contents. Although the

material value of CRMs is low, access to such materials mitigates materials criticality and increases economic resilience. Although sale of recovered CRMs will not deliver high financial returns, access to these materials is of importance for reasons previously outlined.

WEEE also has *environmental value*. Within each item of WEEE, considerable embodied environmental costs exist, associated with lifecycle impacts of its production from primary resources. Reuse of whole items offsets demand for new EEE and avoids the necessity to incur these impacts during the production of new EEE. Recycling of materials represents a lower environmental value as environmental impacts result from the manufacturing process. However, many materials can be recovered at lower environmental cost than producing them from primary resources. This is particularly true for metals with high primary production environmental impacts such as precious and platinum group metals (*Table 1.10*).[67, 68] Recovery of 70,000 tonnes of metals at Umicore Precious Metals Refining (Hoboken, Belgium) has resulted in a saving of 1 Mt of CO_2, i.e. 79% of the CO_2 that would have been generated by primary production.[69]

Table 1.10 *Primary carbon footprint of selected elements in WEEE goods[16]*

Metals used in EEE	Primary production intensity (t CO2/t metal)	Demand for EEE (t/a)	CO2 emissions (Mt/a)
Au	16,991	327	5.56
Pt	13,954	8	0.11
Ru	13,954	16	0.22
Pd	9,380	30	0.28
Ag	144	4,917	0.71
In	142	717	0.10
Sn	16	129,708	2.09
Co	8	16,470	0.13
Cu	3	7,174,000	24.39

WEEE represents a source of *social value*. The exploitation of the economic value of WEEE will provide employment opportunities within the waste management sector. Finally, WEEE has *intangible/emotional value*. Despite owners ceasing to need EEE due to replacement with updated technology, they will often be reluctant to part with devices, perhaps because of some emotional attachment or the idea that it 'may come in handy sometime'. In this way WEEE has a unique value to its owner, and many homes have a stockpile of unused EEE. A recent customer behaviour survey conducted in the UK by the Waste & Resources Action Programme (WRAP) revealed over 60% of 4,000 participants purchasing new EEE have items at home they no longer use.[37] 'Stockpiling' of WEEE in this way represents a barrier to recycling.[2]

These elements of economic, social and environmental value are synergistic; as value in one area is derived from WEEE, so benefits will be afforded in other areas. Addressing the global WEEE problem and enhancing the sustainability of the EEE sector overall relies upon the ability to exploit economic value from WEEE, and the magnitude of benefits afforded will be related to the economic value derived.[48, 70]

1.4 Solutions to the 'global WEEE problem'

Any solution to the 'global WEEE problem' must address two issues. Firstly, how can the increasingly large volumes of existing WEEE and EEE in the market place which will soon reach end-of-life (EoL) be managed in a sustainable and responsible manner; and secondly, what can be done to enhance the industrial ecology of the EEE industry and ensure that the complex issues associated with managing current WEEE are avoided when new EEE, yet to emerge on the market, reaches EoL? Any solution must result in maximum possible resource-efficiency whilst minimising environmental impacts.

1.4.1 Circular economy – the optimum future scenario

Circular economy (CE) is a concept which describes a sustainable manufacturing economy inspired by natural systems which is restorative by design.[47] CE is regenerative by design and replaces the concepts of 'end-of-life' (EoL) and 'waste' with 'restoration' and 'resources'. Wastes therefore are viewed as valuable raw material. This represents an alternative to linear economic models with growth decoupled from consumption of finite material resources, and materials retained in circular flows within economies, cycled repeatedly in successive product lifecycles thereby remaining economically productive (*Figure 1.16*).

In a circular economy products are designed for longevity so that they may be maintained, repaired and upgraded by users to extend their useful life for as long as possible. Products may also be leased to users with ownership maintained by a service provider for collection and take-back for re-use once users cease to require them. If re-use is not possible, products may be sent back to manufacturers for refurbishment or remanufacturing to retain components in new products. Only when re-use of components is no longer possible are they recycled to recover materials for manufacturing new components. Leakage of materials from the economy as waste is minimised through efficient collection of items at EoL. Industrial symbiosis in which by-products of manufacturing in one organisation become the raw materials for manufacturing in another,[71] is used to minimise demand for primary raw materials. This presents new opportunities for valorisation of WEEE and exploitation of its inherent value.
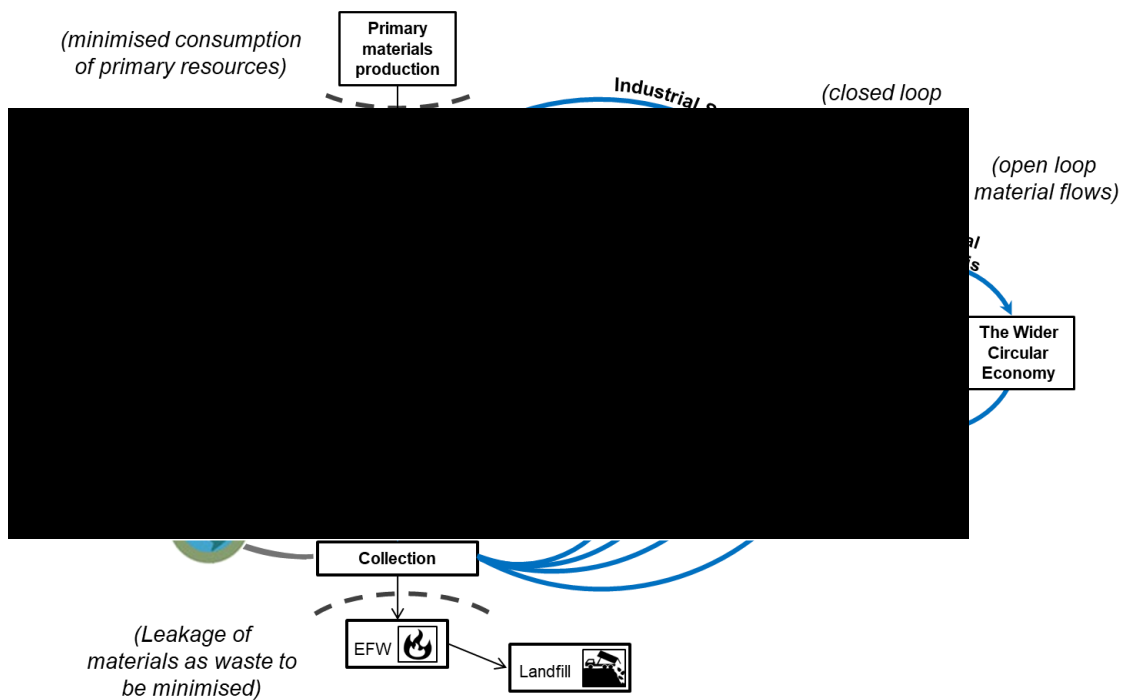
Figure 1.16 *Material flows within the circular economy (adapted from Ellen MacArthur Foundation)*[47]

Cascading components and materials across multiple product lifecycles presents alternative, often higher value routes for materials compared to traditional recycling, and in this way greater economic value may be derived. Primary raw materials may be replaced with biological materials which are renewable and can go back to the biosphere without negative environmental impacts. Product design to accommodate effective refurbishment, remanufacturing, and efficient disassembly and materials recovery are optimised. Elimination of hazardous materials which are detrimental to human health & the environment and add high cost to EoL treatment; and the use of renewable energy are key features of circular economy. A conducive legislative environment, appropriate business models which valorise products past their point of initial sale, and appropriate reverse logistics which ensure effective return of products from users are also important for a viable circular economy.[49]

Figure 1.16 shows the circular economy in diagrammatic form. The smaller the closed loop the greater material resources retained, the greater their economic productivity, and the greater retention of embodied economic and environmental value. It has been estimated that a smartphone can be resold for reuse at ~60% of its original price, far greater value than can be derived through recycling.[47] In addition, the longer that EEE and its materials are cycled within the economy, the greater the economic, environmental and social benefits. Recovered materials and components are usually obtainable at lower cost than virgin ones, and so materials cost savings for manufacturing will result from circular economy. The economic and

social potential of circular economy is significant. In Wales alone, a transition to an advanced state of circular economy has been predicted to be worth £2bn to the economy and is projected to deliver 30,000 jobs.[72, 73] Recently the EMF conducted a circularity analysis of products with different lifecycles and concluded that medium lived products (including EEE) represent the 'sweet spot' for circularity interventions i.e. it is from these goods that greatest benefits can be derived in a circular economy.[47]

The EC adopted 'the circular economy package' on 2/12/15, which included amendments to waste directives and set long term targets to divert material from landfill and increase reuse & recycling. In the interests of achieving closed loop product lifecycles the package included an action plan to support circular economy at each stage of product lifecycles through manufacturing, use and waste management with emphasis on feeding secondary raw materials back in to the economy. This aims to add momentum to the transition towards circular economy.[74]

1.4.2   *Management of WEEE, the current scenario*

Although product lifecycle optimisation and design to support circular practices may in the future provide the means to overcome the global WEEE problem, the transition to circularity will be gradual. However, the way in which WEEE is currently managed is conducive to circular economy in many respects. Legislation is in place which has resulted in infrastructure for collection and recycling of WEEE. Reuse of many items is common, particularly higher value items such as ICT equipment as a result of political impetus and recognition of the economic and social value.[75, 76] Efficient recovery processes for many materials in WEEE are in place, particularly for copper and precious metals.[12, 14, 77-82] Through recovery of these materials from WEEE, much economic value is derived with associated social and environmental benefits. On the other hand, there is much room for improvement in many areas of WEEE management. This is partially due to the fact that recycling of WEEE has been established as a means of dealing with the potential hazards of WEEE, rather than its efficient exploitation as a material resource. The following sections outline the status of legislation, collection and recycling, with a focus on recovery of 'high-tech' metals and identifying areas for improvement in resource-efficiency.

Legislation and policy

In light of the issues associated with WEEE the EU introduced and recently recast the WEEE directive[4, 5] and the RoHS directive,[83, 84] which aim to enhance the industrial ecology and resource-efficiency of the EEE industry. The WEEE directive aims to establish infrastructure for appropriate management of WEEE by diversion from landfill to authorised approved

treatment facilities (AATFs) employing best available treatment, recovery and recycling techniques (BATRRT).[85] It achieves this by banning landfilling of WEEE, and establishing statutory targets for collection, recycling and preparation for reuse. The WEEE directive places emphasises on the waste hierarchy, prioritising reuse (*Figure 1.17*). This is all conducive to circular economy, in fact amendments to the directive were a crucial part of the recent EC 'circular economy package' (along with amendments to the waste framework directive, batteries directive and other waste legislation) designed to stimulate progression towards an advanced state of circular economy.[86] The directive also imposes extended producer responsibility (EPR) on manufacturers and importers of EEE, implementing the 'producer pays' principle by making producers & importers of EEE responsible for their product EoL costs. This aims to ensure that cost is not a barrier to recycling and also provides a financial incentive to producers to improve product design for reuse, refurbishment and recycling (DfRR) which should reduce EoL costs and the financial burden of compliance. Progress in this regard has been slow however, in part because of the way in which EPR is implemented in member states. This is done in one of two ways: as individual producer responsibility (IPR), or as collective producer responsibility (CPR) as is the case in the UK. IPR makes individual producers directly responsible for the EoL costs of their products, whereas CPR makes producers collectively responsible for EoL costs of all collected WEEE in the categories which their products fall. CPR is less effective in encouraging DfRR than IPR, and therefore represents a barrier to circular economy.[72]
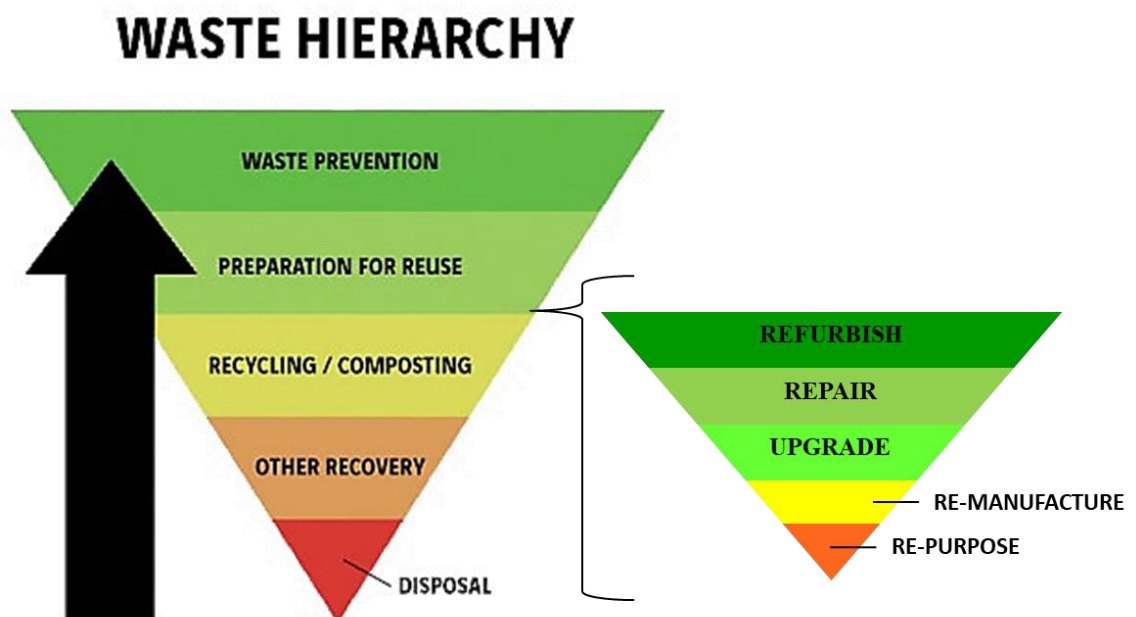
Figure 1.17 *The waste hierarchy with refurbishment, repair, upgrade, remanufacturing and repurposing operations incorporated.*

The RoHS directive limits the use of toxic substances in EEE imposing maximum permissible concentrations in new EEE placed on the market. This includes toxic heavy metals such as Hg, Cd and Pb, and brominated flame retardant compounds. In addition to health and environmental improvements, reduced hazardous material content will also reduce recycling costs[87] and make illegal export less likely. This improves the chances of WEEE treatment with best practice in terms of resource-efficiency and environmental outcomes. Globally, many governments have introduced their own WEEE legislations which in the main are based on the WEEE and RoHS directives.[31, 88-96]

The 'Resource Efficient Europe Flagship Initiative' is a key pillar of the Europe 2020 strategy for sustainable growth.[97] More efficient recycling of materials from WEEE is an important component of this initiative.[98] Much attention has been focussed on WEEE as a secondary resource of CRMs.[19, 20, 51, 53, 99-105]

WEEE management

WEEE is managed via the recycling process chain (*Figure 1.18*).It is collected and delivered to pre-processing facilities (AATFs) where items are sorted, depolluted and disassembled to separate components into distinct material streams (e.g. bulk metals, plastics, batteries, LCDs, cables etc.) rich in target materials of the subsequent recovery processes to which they are sent.[106, 107] Items identified as suitable for reuse are diverted from the recycling stream for direct reuse, or reuse following refurbishment/repair. At this time, little remanufacturing of electronics takes place. Hazardous components such as CRTs, batteries, and fluorescent lamps, are diverted to processes for safe treatment and disposal. Pre-processing is carried out manually, or with automated or semi-automated processes. Precious metal, PGM and copper containing fractions are recovered using pyrometallurgical and/or hydrometallurgical processes.
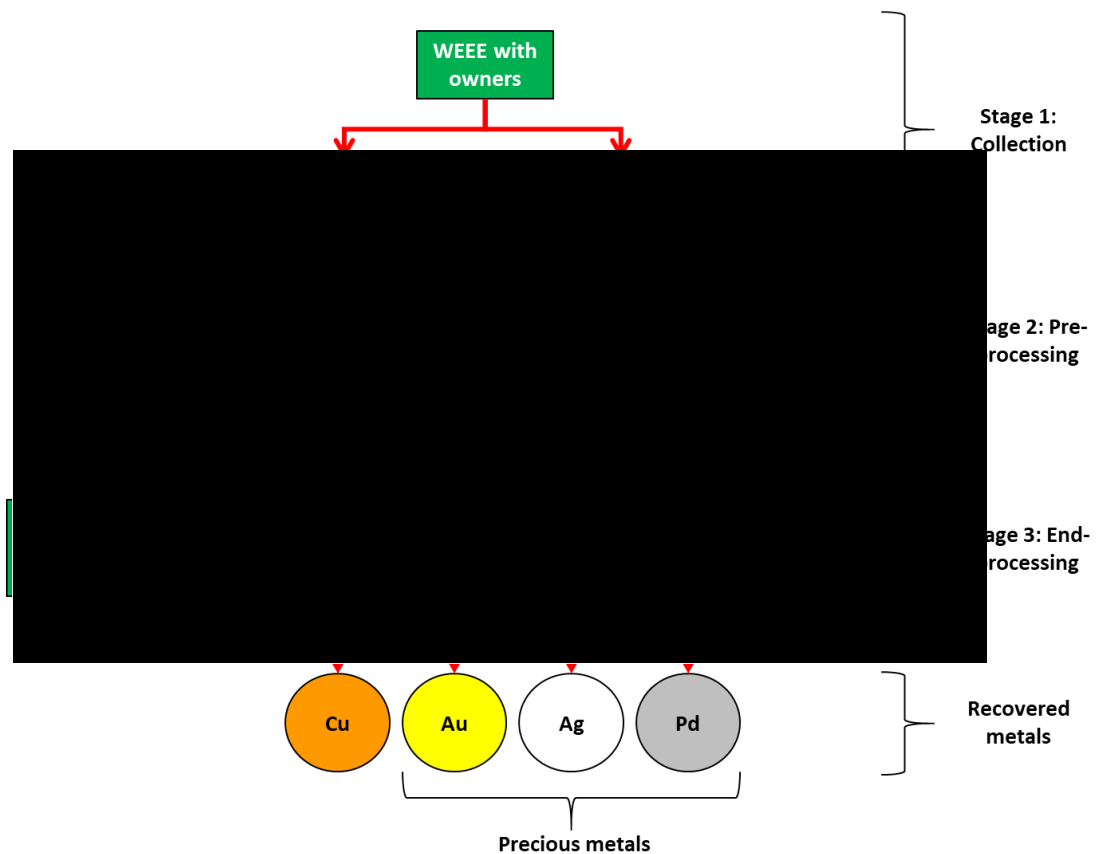
Figure 1.18 *The recycling process chain with special focus on recovery of precious metals and copper (adapted from Chancerel et al.)*[106]

The efficiency with which WEEE is either reused, or materials are recovered is determined as the product of the efficiencies of individual stages of the process. Inefficiencies in any one stage may have a dramatic impact on bottom-line recovery efficiency of materials.[106] As shown in *Figure 1.19*, low collection rates in the EU have been the limiting factor in the rate of reuse and recycling of WEEE. In the developing world, collection rates tend to be high, as the informal sector is generally very efficient in this regard. However, despite high collection rates, bottom-line recovery efficiencies of materials tend to be low due to the poor recovery efficiencies which are achieved with the crude and often hazardous recycling practices used in the informal sector.[108]

A 2012 study conducted by Oakdene Hollins for WRAP examined PM and CRM flows and associated value flows for these materials in WEEE within the UK. This highlighted that uncontrolled disposal of WEEE in residual waste streams results in considerable losses of materials and value from the urban mine. Shredding was shown to result in considerable loss of value, precious metals and CRMs. The report highlights that many CRMs present in materials sent to Europe for recovery are lost in the these recovery processes.[109]
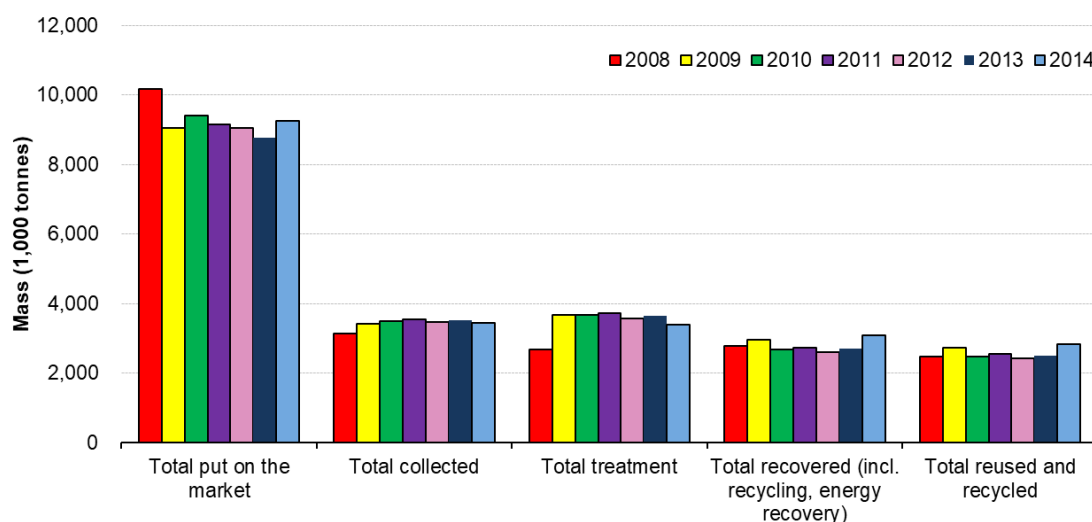
Figure 1.19 *Electrical and electronic equipment (EEE) put on the market and waste EEE collected and treated in the EU from 2008–to 2014)*[110]

Collection In Europe, EPR and statutory targets for member states imposed by the WEEE directive have resulted in establishment of collection infrastructure. EPR based reverse logistics systems are also operated around the world, with examples in Australia, Japan, Taiwan, South Korea and many of the US states, with numerous other countries, such as India, exploring how EPR may be incorporated into current regulations.[111, 112] Despite this, global collection rates remain low. Much of the world is still to develop sufficient reverse logistics systems and recycling infrastructure, and even those countries which have done so see low collection rates due to illegal exports of WEEE for 'reuse', stockpiling, and loss of items in residual waste streams.[113] It is estimated that 80% of global WEEE is exported to Asia, with significant further quantities exported to Africa where BATRRT is not employed.[2] Much of the UK's household WEEE, particularly small domestic appliances which are easily concealed within household residual waste streams, is still landfilled despite infrastructure for collection. It was estimated that 154,372 tonnes of WEEE was disposed of as residual waste in England during the 2010/11 financial year,[114] equivalent to about one third of WEEE collected throughout the whole UK during that period.[115] A 2012 study of residual waste arising in Denmark revealed that WEEE and batteries present constituted 16% and 39% of quantities being collected through proper channels at that time, respectivley.[113]

The UK WEEE collection rate in 2016 was 35.6%. Household WEEE is collected through distributor takeback schemes, or household waste recycling centres (civic amenities sites). The majority of WEEE generated is still unaccounted for. *Figure 1.20* Indicates that despite infrastructure for collection, few EU member states have exceeded 50% collection, with many

considerably lower. Where WEEE is not collected, its inherent material resources and potential economic, social and environmental value are permanently lost.
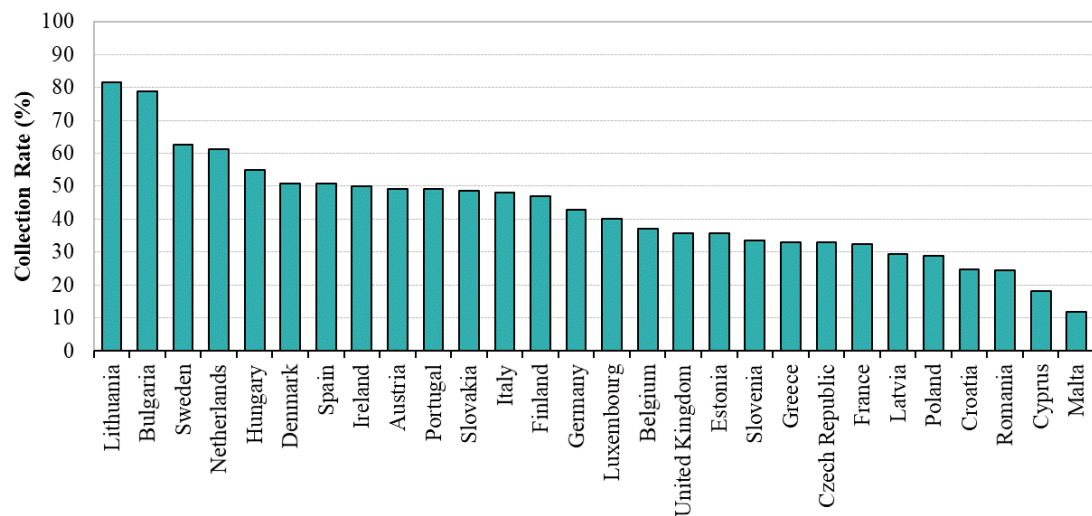
Figure 1.20 *Total collection rate for WEEE in 2014 as a percentage of the average weight of EEE put on the market in the three preceding years (2011-13), (2014 collection data estimated for Cyprus)[110]*

The WEEE treatment process

WEEE treatment consists of two distinct stages: i) pre-processing; and ii) materials recovery. Pre-processing serves a vital function. Items are separated into their constituent material/component fractions, which are then diverted to appropriate processes for materials recovery and hazardous waste disposal. At this stage in recycling, decisions are made about whether items or their components will be reused, and to which processes materials for recovery should be sent. These are critical decisions in determining the value that can be exploited from WEEE.

Materials separation can be conducted with automated, manual or semi-automated processes. Manual pre-processing is relatively costly as it is labour-intensive. Products are manual disassembled into their component parts. This provides the opportunity to harvest components for reuse, and to isolate circuit boards and other components which contain concentrations of precious metals.[116] Greater value can be recovered from items with high concentrations of precious metals in their PCBs with manual processing than through automated processes, justifying high process costs. Manual processing also gives the opportunity to isolate components in which small amounts of CRMs are present.

Automated recycling involves shredding items (following depollution) with subsequent automated separation of material fractions i.e. magnetic, eddy-current, electrostatic and

density separation to give ferrous, aluminium, stainless-steel, glass, copper, brass and plastic fractions.[12, 111] Items processed in this way have no chance of reuse. Such processes are relatively cheap, with high throughput and minimal labour requirements. However, they result in significant losses of precious metals as a result of the 'grade recovery function', a principle which applies to ore & minerals processing and is equally applicable to the processing of WEEE for the recovery of metals (*Figure 1.21*). As target material content is upgraded in a material flow by separation of non-target materials, the overall recovery yield diminishes. Shredding disperses particles of trace amounts of precious (and critical) materials present throughout the mass of the shred where they adhere to the surfaces of larger particles. At each stage in separation, these metals are lost through unintended co-separation with bulk fractions. Recovery processes for these bulk fractions do not target precious and critical materials and so these are permanently lost. From a resource-efficiency point of view, such processes should be avoided where possible in favour of semi-automated or manual pre-processing.[116] Grinding also results in dispersal of hazardous materials throughout larger mass fractions, resulting in higher potential toxicity of output fractions than WEEE items prior to shredding.[117]
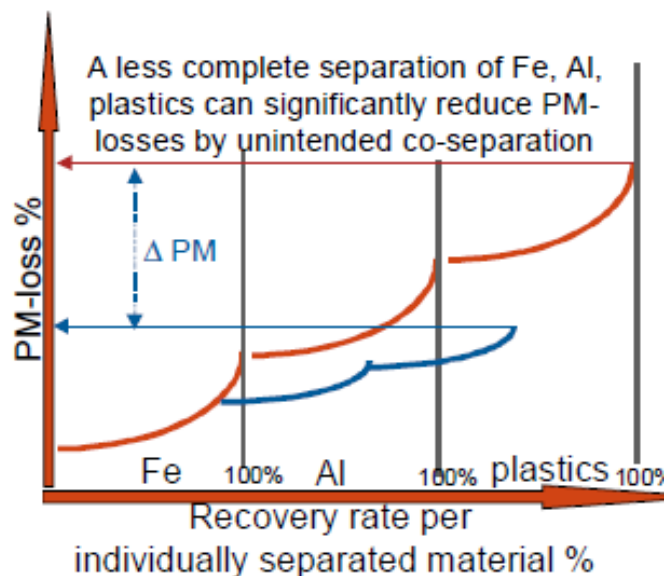
Figure 1.21 *The 'Grade-Recovery Function' which results in losses of target precious metals and other trace elements as larger bulk fractions are removed from shredded WEEE in automated pre-processing, ©2006, IEEE (re-printed, with permission, from Hagelüken, 2006)[18]*

The choice of process is largely determined by the recoverable material value of items. Low value WEEE with low precious metal content (e.g. toasters, hair dryers etc.), is recycled with automated processes, and items with high inherent value (e.g. PCs) are processed manually.

Within the UK, treatment of WEEE is largely dictated by the hazardous materials contained and the specialist processes required to deal with them as required by the WEEE directive. As a result, poor recovery of metal values is a major challenge to the recycling operation. CRMs are often lost due to their dispersion during shredding.

Europe, particularly Germany and Belgium, is using advanced technologies for refining precious metals with very good recovery rates for secondary recovery (>98% for Au). Umicore's integrated smelting (pyrometallurical) facility in Hoboken, Belgium is the most advance plant of its kind, smelting PCBs to recover precious metal enriched copper bullion, which is then further refined in hydrometallurgical processes (*Figure 1.22*). Considerable plant capacity is available which is currently being expanded. Total hydrometallurgical recovery processes are more common in Asia. Many recovery processes require a further mechanical pre-treatment to upgrade materials prior to recovery. This enhances the concentration of target materials, which improves the cost benefit of recovery. However, the 'grade-recovery' function applies, and so losses are also incurred in this upgrading process. WEEE is pre-processed to give the optimum cost-benefit taking account of processing costs, and value of recovered materials (*Figure 1.23)*
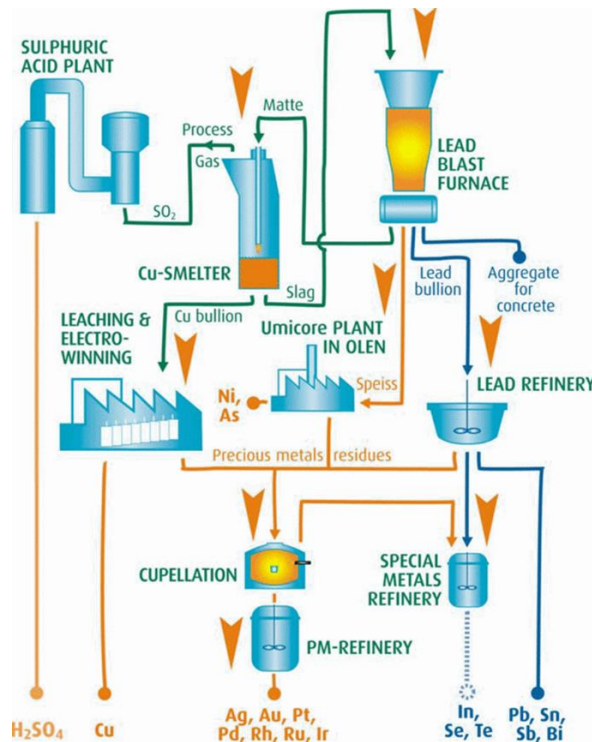
Figure 1.22 *Flowsheet of Umicore's integrated metals smelter/refinery. ©2006, IEEE (reprinted, with permission, from Hagelüken,2006)[18]*
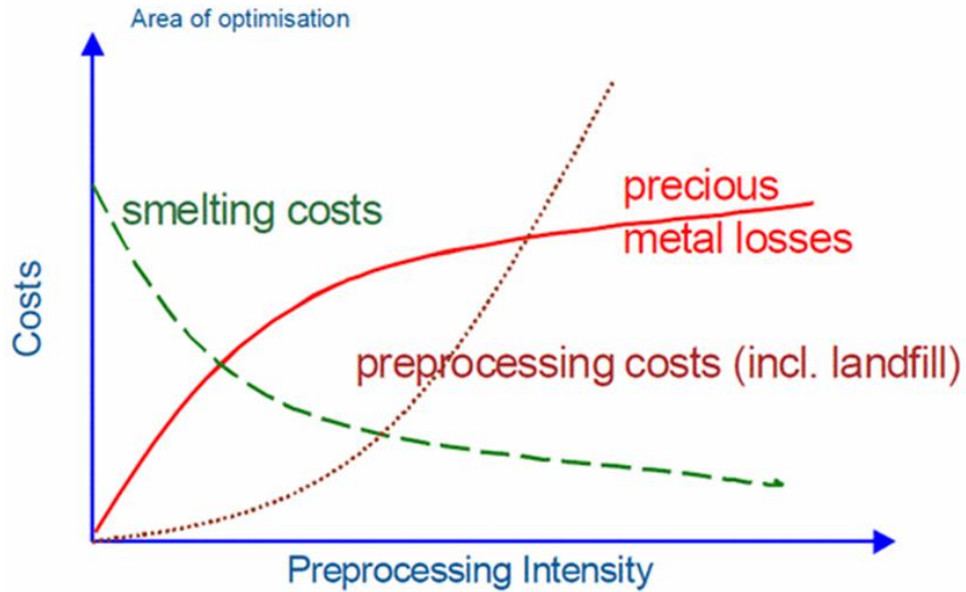
Figure 1.23 Qualitative cost function in WEEE recycling interface optimisation, IEEE (Reprinted, with permission, from Hagelüken, 2006)[18]

Despite high recovery efficiencies for target metals in these processes, many of the other materials present are not recovered either because they are of low value and therefore recovery is uneconomical, or there are thermodynamic limitations to recovery e.g. tungsten which is present in ICs as an interconnect material is lost in slag during smelting. Similar losses will be incurred for other low value critical materials in recovery processes, as indicated by the Oakdene Hollins study.[109, 118]

1.5 Economics of reuse and recycling

To drive circular material flows in EEE, it is essential that sufficient cost-benefit is achieved through reuse, refurbishment, remanufacturing and recycling. It has been stated by Cossu & Williams regarding urban mining of WEEE:

> *"As for natural ores, extraction and processing of anthropogenic stocks is necessary and the generation of an economic benefit is essential."*[119]

The revenue obtained through sale of reused equipment, or recovered components and materials must be sufficient to cover all costs associated with generating those materials/products. This includes costs of collection and transport between processing sites, process costs and operational overheads, as well as any costs associated with disposal of hazardous materials. In pre-processing, isolating components and materials for downstream processing must be achievable at a cost which can be recouped by sale of these materials for

recovery. The revenue received for PCBs at precious metal refineries is often the equivalent of the value of recovered materials less treatment and refining charges applied for processing the material (e.g. *Table 1.11*).

Table 1.11 *Example breakdown of revenue received for PCBs by Metech Recycling UK*[22]

Mass	**328.7 kg**
Treatment Charge	£0.525/kg = £172.57
Gold recovered	25.3 g
Gold less minimum deed	20.4 g
Silver recovered	262.9 g
Copper recovered	36 kg
Gold treatment charge	£180/kg = £3.67
Silvertreatment charge	£20/kg = £4.99
Copper treatment charge	£0.80/kg = £28.80
Gold Value	£33.141/g = £676.07
Silver Value	£0.63708/g = £159.07
Copper Value	£4.899/kg = 176.36
Total charges	£210.03
Total net revenue	**£801.47**

Although other metals present e.g. Ru may be recovered by refineries, no value from these materials is returned to the pre-processor. This means that the viability of manual pre-processing is determined by the PM and copper content of PCBs. If this value is insufficient to recoup these costs, automated pre-processing must be conducted, resulting in losses of potentially recoverable value and poorer resource-efficiency outcomes. It is therefore essential that items are pre-processed in the most cost-effective manner possible, with precious metal and copper losses minimised to ensure the maximum value from WEEE is always exploited through efficient recovery of the most valuable constituent materials. In the future, eco-design and DfRR will reduce manual pre-processing costs.[120-123] As a current solution, the 'best of two worlds' approach has been advocated, whereby WEEE would be manually processed in the developing world where labour costs are low, and material fractions would be recovered in advanced recovery processes in the developed world.[124] Another option is to automate disassembly with robots, a strategy which has been explored by Apple and by the University of New South Wales seperately.[125-127] Technological innovations in pre-processing such as this, which reduce processing costs, will be essential to support a viable circular economy for EEE.

1.6 Conclusion

WEEE represents a considerable sustainability challenge which must be urgently addressed in the interests of mitigating the impacts of WEEE on human health & the environment, and as a means of enhancing global-resource-efficiency. WEEE is a rich secondary source of materials and reusable EEE & components, and exploitation of economic value from this 'urban mine' will yield synergistic environmental and social benefits. Recovery of materials and components will off-set demand from primary raw materials with which to manufacture new EEE, resulting in preservation of natural capital and avoidance of emissions and waste. WEEE is also rich in critical raw materials which face global supply risks from primary sources, and for which continued supply is essential for sustainable economic growth and meeting demand from emerging technologies.

Circular economy represents a solution to the global WEEE problem and a means to enhance the industrial ecology of the EEE industry through reuse & recycling of EEE and its components, and through provision of secondary raw materials and components for manufacturing new EEE. This provides a means to exploit greater value from WEEE through novel methods of valorisation which present economic, social and environmental benefits over traditional recycling processes. Driving these circular material flows requires sufficient economic value to be derived from WEEE to cover costs incurred throughout recycling process chains; availability of suitable recovery processes; appropriate product design to accommodate circular practices; and appropriate reverse logistics, business models and legislative environments.

Much progress has been made around the world in establishing suitable legislation to govern the management of WEEE. In addition, collection systems and efficient recovery processes are available for the most economically and environmentally important metallic components of WEEE i.e. precious metals and copper, predominantly concentrated in PCBs. However, much progress is still required. In regions with advanced systems for managing WEEE, much is lost in residual waste streams or illegally exported. Much of the world is still without appropriate infrastructure for the management of WEEE, and great volumes are shipped to such regions where WEEE is recycled by the informal sector using crude 'backyard recycling' operations which have resulted in significant impacts on populations, ecosystems and the environment. Losses of potentially recoverable materials in shredding processes where manual pre-processing is prohibitively expensive, and during recovery processes, limits the economic value that is derived from WEEE and the ability to efficiently recover 'high-tech' metals. To enhance recovery, greater optimization of the interface between pre-processing and recovery is required.

In order to overcome these issues, greater knowledge of the composition of items within the waste stream and the available value therein is required to plan future EoL management. In addition, recovery processes which derive greater value through circular economy are required for viable recovery of materials that are currently lost due to low economic value. For the future, full lifecycle optimisation of products with their manufacturing and end-of-life processes will be necessary to ensure that problems associated with WEEE management today are avoided in the future, and that greater value can be derived from material resources contained in EEE at end-of-life. Greater awareness of the material content of items, available infrastructure for end-of-life treatment, and education about the 'global WEEE problem' and its solutions is also necessary to help consumers make more informed decisions when selecting technologies for superior resource-efficiency and sustainability outcomes at EoL.

In the following chapters of this thesis the inherent material and economic value of WEEE is investigated, as well as methods of improving resource-efficiency and the derivable value of WEEE at end-of-life. Most cases presented address industrial challenges encountered by Metech Recycling (UK) Ltd. at their AATF in Hirwaun, South Wales.

Chapter 3 discusses the recycling potential of WEEE based on derivable value from precious metals (PMs) and copper in PCBs of items and presents an evaluation of future recycling potential of WEEE through evaluation of temporal trends in PM and copper content in historic PC RAM modules. Identified trends are applied to other WEEE items to project temporal changes in PCB compositions. This data is considered in conjunction with projections of future WEEE arisings in Europe to estimate recoverable value from the waste stream in the future.

Chapter 4 presents the results of an industrial trial conducted on behalf of WRAP which investigated potential techniques for increasing the value derived from treatment of WEEE in Wales through recovery of critical raw materials. This chapter identifies occurrences of CRMs in WEEE, and evaluates processes for isolation of CRM bearing components for downstream recovery. The recycling potential of identified CRMs is discussed and processes for component isolation are evaluated based on cost and revenue generated through sale of material fractions produced. Identified barriers to CRM recovery are discussed with methods to overcome these in the future.

Chapter 5 presents an industrial symbiosis process in which platinum from waste thermocouples filaments is converted to chloroplatinic acid for fabrication of dye-sensitised solar cell (DSSC) counter electrode catalysts. Recovery of platinum from these thermocouples is not viable through traditional recycling routes due to the dissipative nature of the use of the CRM platinum in this application, which exemplifies a major barrier to CRM recovery from

WEEE. The process developed is used to demonstrate the potential that circular economy holds for enhancing derivable economic value from CRMs in WEEE to drive recovery, the materials costs savings and waste valorisation opportunities afforded to industry, and the environmental and social value resulting.

Chapter 6 details findings of a multi-disciplinary cross-sector sandpit organised and hosted by the author to establish a framework for future research to optimise the lifecycles of printable photovoltaics (PPV) for circular economy. The advantages of lifecycle optimisation for PPV are examined with key aspects of design and materials selection; manufacturing; likely applications of PPV and implication for EoL management; and potential recycling & refurbishment strategies. Features conducive to circular economy, identified barriers to circularity and priority areas for future research are discussed. This provides a pathway through which the industrial ecology of the PPV industry may be enhanced and growth for the industry decoupled from consumption of material resources resulting in superior resource-efficiency outcomes when these emerging technologies reach end-of-life.

Chapter 7 examines the issue of selection of appropriate battery technologies for off-grid solar energy systems for rural South Africa. During a workshop arranged and co-hosted by the author in Durban, South Africa, which aimed to develop a pan-African multi-disciplinary collaboration of stakeholders for the development of circular economy around off-grid solar systems for rural Africa, batteries selection was considered the most crucial element in solar home system design. A framework for selection of batteries is discussed which takes account of materials content, cost, local available knowledge and infrastructure for management and processing of batteries during use and at EoL in a manner conducive to circular economy which benefits local South African economies. This exemplifies how educated and informed selection of EEE can result in avoided negative impacts at EoL and sustainable economic development with superior resource-efficiency outcomes.

2 Experimental

Chapter Summary

This chapter outlines materials and methods used in the experimental work presented in this thesis. Details of chemicals and standard materials used, methods of sample preparation and conditions for analyses are outlined. Necessary theory underpinning analytical techniques necessary to interpret results presented is also included. References to the thesis sections to which details apply are included throughout the chapter.

2.1 Sample preparation

2.1.1 Grinding

All grinding was conducted with an IKA-A10 cutting mill with tungsten carbide cutting blade, suitable for effective grinding of PCBs.[128] Samples were ground for 15 minutes in a water cooled grinding chamber to prevent overheating. This method is suitable for producing a reasonably homogenised powder[129] of particle size <0.2 mm, sufficient for complete leaching of metals from samples.[32, 34, 130, 131] In general, three 0.1 g sub-samples of the homogenous powder were taken and subjected to acid digestion.

2.1.2 Digestions

To analyse samples by AAS, ICP-OES and ICP-MS, acid digestions were conducted and analysis performed directly on leachate solutions, or dilutions of these solutions to an appropriate concentration range for analysis. The specific conditions for digestion in each case are detailed in subsequent sections.

2.2 Analytical Techniques

2.2.1 Flame atomic absorption spectroscopy (AAS)

Atomic Absorption Spectroscopy (AAS) was used for determination of metal concentrations in solution. AAS has been used to quantify CRMs in samples discussed in *Chapters 4&5*.

Theory - The technique is based upon the phenomenon of atomic absorption i.e. ground state electrons of atoms will absorb visible and/or UV light of energy E causing them to be promoted from ground state (E_0) to an excited state (E_1) *(Figure 2.1)*. The wavelengths (λ) and energies of absorbed photons are characteristic of particular elements.
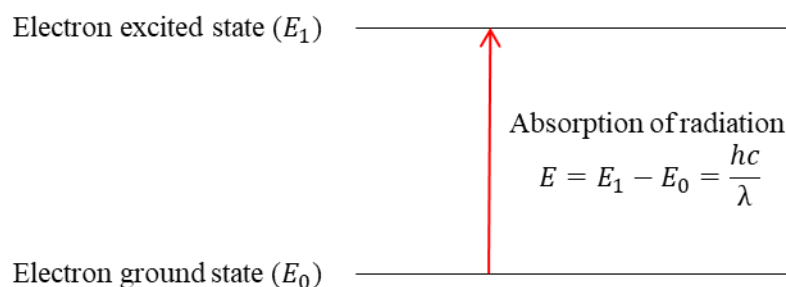
Figure 2.1 *Electronic transition from ground state (E_1) to an excited state (E_1) resulting from absorption of a photon of energy E and wavelength (λ)*

Following oxidative digestion of samples, a solution containing metal ions is obtained. The solution containing analyte is aspirated through a nebulizer forming an aerosol which is combined with high pressure acetylene and air in a burner chamber. The mixture is carried through a burner head into a reducing flame where combustion of the mixture occurs. As the sample exits the burner head and enters the flame, desolvation of the nebulized sample occurs, followed by vaporization and reduction of metallic ions to gas phase atoms which are able to absorb incident UV/visible light at characteristic wavelengths (λ). A hollow cathode lamp with a cathode made from metal of the analyte of interest is used as a radiation source. This emits all characteristic wavelengths in the absorption spectrum of the analyte. The emitted radiation is focused into a beam which passes through the path length of the flame and then through a monochromator to the detector which measures the intensity of radiation which has passed through the flame. As the beam passes through the flame, some of the radiation is absorbed by atoms of the analyte according to the Beer-Lambert law (*Equation 2.1*) where ε is the molar extinction coefficient of the analyte species, c is the concentration of analyte in solution and l is the path length of the flame. This results in reduced intensity of the detected beam (I) in comparison to the intensity in the absence of analyte species (I_0). The absorbance of the sample is then calculated from the intensities of detected radiation in the presence and absence of samples with *Equation 2.2*

$$Abs = \varepsilon c l \qquad\qquad Equation\ 2.1$$

$$Abs = \log_{10}\left(\frac{I_0}{I}\right) \qquad\qquad Equation\ 2.2$$

There are a number of factors which can cause experimental deviations from the Beer-Lambert law and it is usual to calibrate the instrument with a series of solutions of known concentration (c), to obtain the experimental calibration curve.[132]

Limitations- The use of an air-acetylene flame limits the range of CRMs which can be quantified by AAS. Some metals form refractory oxides within the temperature range of the flame so determination of their concentrations in solution is not possible. Where this is the case, ICP-OES and ICP-MS, which use a higher temperature argon plasma in place of an air-acetylene flame, have been used to quantify CRMs in samples. This was necessary for determination of Rh, Nd and Y.

Analysis - Methods of sample preparation used are indicated in *Table 2.1*. Digestions were carried out by boiling samples in acid solutions for 3 hours, or until total dissolution of samples was achieved, while maintaining a sample mass/acid volume ratio of 40 g/ml.[22, 133] 3 sub-samples were taken for analysis and 3 repeat readings were obtained for each solution. All measurements were carried out using an air-acetylene flame and Perkin Elmer Lumina Hollow Cathode Lamps (HCLs). Au, Pt and Zn analyses used single element HCLs, and Co and Cu analysis was conducted with a Co-Cr-Cu-Fe-Mn-Ni multi-element HCL. Specific parameters for the analysis of individual elements are given in *Table 2.2.* All analyses were conducted by calibration with solutions of known concentrations with the exception of Pt analyses which were conducted using the method of multiple standard additions.[134]

Table 2.1 Samples analysed by AAS, relevant sections of the thesis, elements analysed and sample preparation procedures.

Sample	Section	Element	Sample preparation
Magnetron ferrite core	*4.3.3*	Co	Digest whole sample in 1:1 HCl
Magnetron magnet	*4.3.3*	Co	Digest 1 g sample in 1:1 HCl
Li-ion battery cells (numerous types)	*4.3.3*	Co	Cut open cells and digest electrodes in 1:1 HNO_3
Contacts from PCBs (numerous samples)	*4.3.3*	Au, Cu	Digest whole samples in 1:1 aqua regia (3:1 HCl/HNO_3)
Waste thermocouple filaments	*5.3.2*	Pt	Digest in 1:1 aqua regia (3:1 HCl/HNO_3 v/v)
Chloroplatinic acid	*5.3.2*	Pt	Dissolve in 5% HCl
~5 mM chloroplatinic acid in IPA	*5.3.3*	Pt	Dilute 1/5 with IPA
Ta-capacitor powders with Zn as an internal standard	*Appendix A*	Zn	Digest 0.1 g sub-samples of powder in 1:1 HCl (3 sub-samples analysed per sample).

Table 2.2 *Parameters for Analysis of individual elements by AAS*

Element	λ (nm)	Slit (mm)	Flow Rate (L/min) Air	Acetylene	Integration time (s)	Read delay (s)	Replicates
Au	242.80	2.7/1.35	12.0	2.15	3	5	3
Co	240.73	1.8/1.35	10.0	2.50	3	5	3
Cu	324.75	2.7/0.8	10.0	2.50	3	5	3
Pt	265.95	2.7/1.05	10.0	2.50	3	5	3
Zn	213.86	2.7/1.8	10.00	2.50	3	5	3

2.2.2   *Inductively coupled plasma – optical emission spectroscopy (ICP-OES)*

Analyses of Rh and Pt in synthesised and purchased chloroplatinic acid samples reported in *section 5.3.2* were conducted by ICP-OES.

Theory - ICP-OES can determine concentrations of multiple elements concurrently, with detection limits in the sub-ppb range, making it an ideal technique for quantification of metals in WEEE. Leachates from sample digestions (produced in the same way as for AAS) are nebulised and then vaporised in an argon plasma. Atoms/ions within the plasma vapour are excited and emit photons of characteristic wavelengths. (*Figure 2.2*).
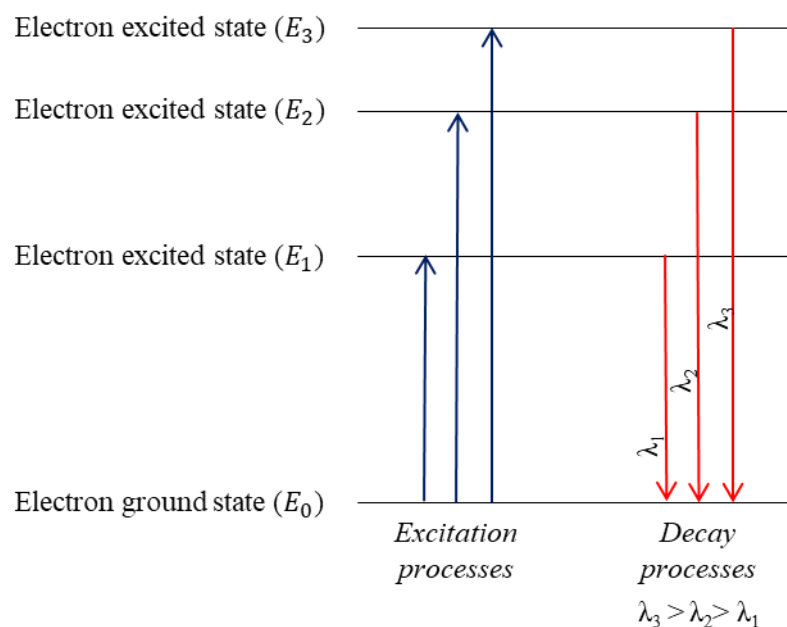
Figure 2.2 *Electronic decay processes resulting in emission lines*

The spectrometer optics separate the sample emission into its different spectral components enabling element identification by emission wavelength and quantification by emission

intensity. High plasma temperatures (6000-8000 K) prevent problems associated with formation of refractory oxides and low excitation efficiencies. The technique is suitable for analysis of elements at lower concentration than is possible with AAS employing an air-acetylene flame.[132]

Analysis - Analyses of Rh and Pt in of chloroplatinic acid samples reported in *Chapter 4* were performed by Dr Simon Curling, Bangor University Biocomposites Centre commercial analysis service – BC Materials, using an Agilent Varian 710 ES ICP-OES instrument with an axial torch, Varian SPS 3 autosampler, ICP expert II software, and the following operational conditions: plasma flow 15 l/min, nebuliser pressure 240 kPa, sample uptake delay 30 s, rinse time 10 s, dry argon as carrier gas. Quantitative analysis was conducted at 3 wavelengths for platinum (203.646 nm, 214.424 nm, 265.945 nm -1st to 3rd order spectra) with 3 replicates at each wavelength. Results for platinum are taken as the mean result from three wavelengths. Analysis of Rh was conducted at a single wavelength only (343.488 nm – first order spectrum) as poor calibration of 2nd and 3rd order spectra were obtained, probably due to interference from other elements present. Analyses were performed in duplicate for each sample. Samples were prepared by dissolution and dilution of chloroplatinic acid with 10% HCl.

2.2.3 *Inductively coupled plasma – mass spectrometry (ICP-MS)*

Quantitative analysis of Nd and Y in samples reported in *Section 4.3.2* was conducted by ICP-MS.

Theory - ICP-MS is suitable for simultaneous qualitative and quantitative determination of up to 70 elements, and uses an inductively coupled plasma as an ion source. The technique differs from ICP-OES in the use of a mass spectrometer as detector which increases the sensitivity of the technique to give detection limits in the sub parts per trillion range. Samples are introduced via a nebulizer into the ICP which acts as both atomiser and ioniser. Ions from the plasma are then passed into a mass analyser where they are separated according to their mass to charge ratio (*m/z*) by a quadrupole mass spectrometer.

Analysis - Analyses were conducted by ChemTest (Newmarket), an external analytical service. Analyses were conducted using a Perkin Elmer Elan 6100 ICP-MS instrument and Elan instrument control software (version 3.3). A plasma flow rate of 0.92 L/min; argon carrier gas; sample uptake delay of 40 s; read delay of 20 s; and rinse time of 15 s were used. Samples for analysis were prepared using the methods given in *Table 2.3*. Triplicate analyses on each sample were conducted and the result taken as the mean.

Table 2.3 *Samples analysed by ICP-MS, relevant sections of the thesis, elements analysed and sample preparation procedures*

Sample	Section	Element	Sample preparation
LCD display CCFL	*4.3.2*	Y	Digest phosphor in 1:1 HCl
MLCCs from PCBs	*4.3.2*	Y	Digest whole component in 1:1 HCl
HDD magnets	*4.3.3*	Nd	Digest whole sample in 1:1 HCl
Mobile phone speaker magnets	*4.3.3*	Nd	Digest whole sample in 1: HCl

2.2.4 X-ray fluorescence spectroscopy (XRF)

XRF is a non-destructive method for elemental analysis using the characteristic energies of X-rays emitted from an element following bombardment with high energy X-rays. XRF was used to identify the CRMs in WEEE samples discussed in *Section 4.3.2*. XRF was also used to establish alloy composition of waste thermocouple filaments in *Section 5.4.1*.

Theory - When atoms at the surface of a sample are bombarded with X-rays, these are absorbed resulting in ejection of an inner shell electron (K or L shell) leaving a 'hole' i.e. a vacant inner orbital, causing the atoms to enter an excited state (***Figure 2.3***). Atoms then relax when an electron from a higher energy orbital falls in energy to fill the vacant inner orbital, emitted X-rays as it does so. The energy of these emitted X-rays is characteristic of particular elements, so detection of emitted X-rays allows characterisation of elements present in samples. Excitation may result in loss of electrons from K, L or M shells (depending on the species). Electronic transitions into the K shell result in a K X-ray emission, transitions into the L shell result in L X-ray emissions and so on.[135]

Excitation processes   *Relaxation processes*
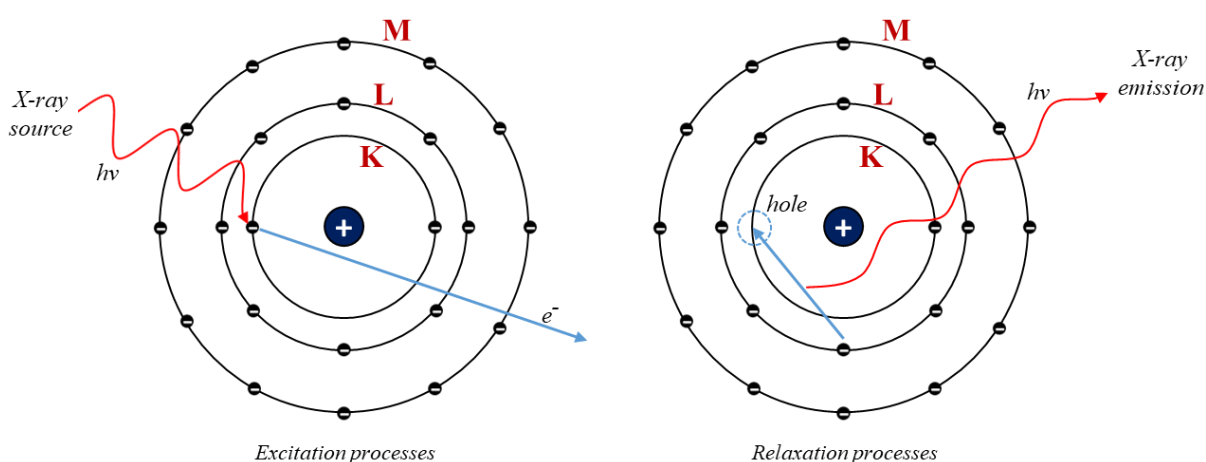
Figure 2.3 *The processes involved in X-ray fluorescence(adapted from Fifield).[135]*

Analysis - All analyses were conducted with a Fischer Instrumentation Fischerscope XDAL-FD system and Fischer WinFTM software. Manufacturer recommended setting for detection of trace metals were used, i.e. a 50 keV x-ray beam with Al primary filter. A beam with circular cross-section with varying diameter between 0.3 and 1.0 mm was used. Beam diameter was selected as appropriate for the size of component being analysed, and to focus analysis on particular portions of components. Elements present were identified by emission signals indicated at the characteristic energies given in *Table 2.4*. Appropriate scan times were established as part of the instrument evaluation (*Appendix A*). A scan time of 55 s was used to measure filament alloy compositions reported in *section 5.3.1*.

Table 2.4 Positions of emission peaks in XRF analysis

Element	Nature of electronic transitions	Emission energy (keV)	Element	Nature of electronic transitions	Emission energy (keV)
Ag	Kα_1	22.16	Pd	Kα_1	21.18
	Kβ_1	24.94		Kβ_1	23.82
Au	Lα_1	9.71	Pt	Lα_1	9.42
	Lβ_1	11.44		Lβ_1	11.07
Co	Kα_1	6.93	Rh	Kα_1	20.22
	Kβ_1	7.65		Kβ_1	22.72
Ga	Kα_1	9.25	Ru	Kα_1	19.28
	Kβ_1	10.27		Kβ_1	21.67
Ge	Kα_1	9.89	Nd	Kα_1	16.62
	Kβ_1	10.98		Kβ_1	18.63
In	Kα_1	24.21	Sb	Kα_1	26.36
	Kβ_1	22.28		Kβ_1	29.73
Mg	Kα_1	1.25	Ta	Lα_1	8.15
	Kβ_1	1.30		Lβ_1	9.34
Nb	Kα_1	16.62	W	Lα_1	8.40
	Kβ_1	18.63		Lβ_1	9.67
Nd	Lα_1	5.23	Y	Kα_1	14.60
	Lβ_1	5.72		Kβ_1	16.74

2.2.5   Scanning electron microscopy (SEM) & SEM/energy dispersive X-ray spectroscopy (SEM/EDS)

Scanning electron microscopy was used to measure diameters of filaments isolated from waste thermocouples and to investigate the platinum particles deposited on the FTO glass as DSSC counter electrode catalysts. SEM/EDS was used for the direct non-destructive analysis of waste thermocouple filaments (*Chapter 5*).

Theory

SEM - SEM is an electron probe method which provides high resolution images of samples by firing a focussed beam of electrons at their surface. Under vacuum, an electron beam is generated by thermionic emission from a tungsten filament in an electron gun and focussed through a series of condenser lenses and apertures into a very small diameter. This is directed at a sample mounted on a stage in a specimen chamber. Rastering of the electron beam across the sample surface using deflection coils results in backscattering and generation of secondary electrons by the sample, which are drawn to a detector by a positive charge. Backscattered electrons result from elastic collisions between incident electrons and electrons or nuclei in atoms of samples, and secondary electrons are created by inelastic collisions with sample electrons. Detection of these electrons reveals surface structure information, topographical contrasts and atomic number contrasts of samples.

SEM/EDS – Bombardment of samples with electrons also results in the generation of X-ray emissions from samples. This occurs in an analogous way to the process of X-ray fluorescence depicted in *Figure 2.3* except that it is the incident electrons which excite the atoms rather than an X-ray beam.

Analysis - Analysis of waste thermocouple filaments was conducted with a Hitachi TM3000 table top microscope running BrukerQuantax 70 software for EDS analysis. A 15 kV beam was used. SEM imaging of platinized counter-electrodes was carried out by Dr James Douglas, Department of Materials Science, Oxford University, at 5 kV using a 30 micron aperture, Secondary Electron (SE2) detectors and InLens detectors on a Zeiss Nvision instrument using a Gemini SEM column.

2.2.6 *Optical microscopy*

Visual inspection of thermocouple filaments was conducted with a Hampshire Micro:Wessex WSL1 long arm stereo microscope (*Chapter 5*).

2.2.7 *Electrical impedance spectroscopy (EIS)*

EIS is used to characterise the electrochemical performance of dye-sensitised solar cell (DSSC) platinum catalysts produced in *Chapter 5*. The technique reveals kinetic information about electrochemical processes occurring at the surface of the catalyst, and has been use to analyse symmetrical 'dummy cells' composed of pairs of platinized electrodes created from chloroplatinic acid samples to determine charge transfer resistances (R_{CT}), double-layer capacitances (C_{dl}) and exchange current densities (j_0) at the electrolyte|catalyst interface of electrodes. An overview of the application of EIS in analysis of DSSCs is given by Bisquert & Fabregat-Santeago.[136]

Theory - The impedance of an electrochemical system is a measure of its ability to resist the flow of current. When a sinusoidal AC potential (*E*) with maximum amplitude E_0 is applied to an 'ideal resistor', a sinusoidal current response (*I*) in phase with *E* results, regardless of the frequency of the applied potential (*ω*) (*Figure 2.6*). Real world electrochemical systems have more complex resistive behaviour described by impedance (Z) which is analogous to resistance but varies with *ω*. Studying the impedance of electrochemical cells with EIS reveals kinetic information about the individual chemical processes. To do this, small AC potentials (1-10 mV) are applied to cells. This result in a pseudo-linear current response i.e. with the same *ω* as *E*, but out of phase by an amount described by the phase angle (*θ*) (*Figure 2.4*). *E* can be expressed as a function of time using *Equation 2.3* in which E_t is the potential at time *t*, E_0 is the amplitude and *ω* is the radial frequency. The current response (I_t) is described by *Equation 2.4*. By measuring the sinusoidal wave form of *I* in response to *E*, *θ* can be measured and *Z* can be calculated using *Equation 2.5* which expresses impedance in terms of its magnitude (Z_0). Using Euler's relationship (*Equation 2.6*, with *j*=√-1) it is possible to express *Z* as a complex number using *Equation 2.7* in terms of the real (*Z'*) or restive, and the imaginary (*Z''*) or capacitive component, of impedance.
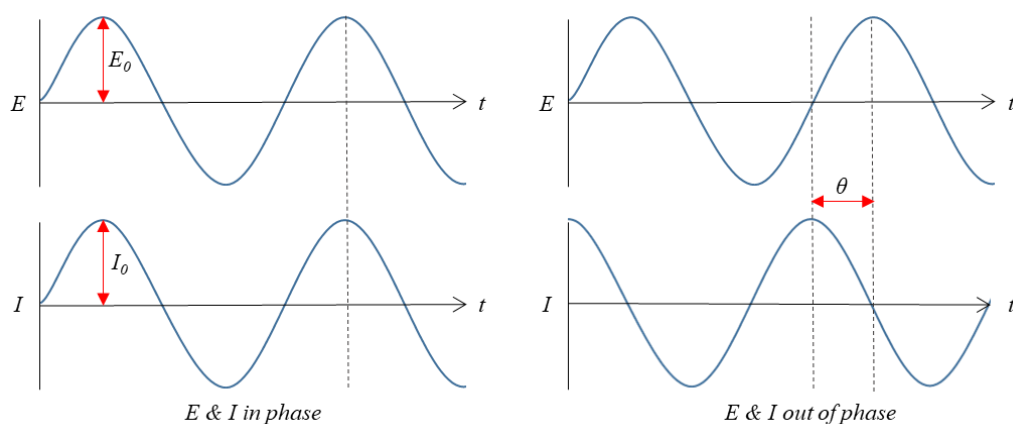
Figure 2.4 *Sinusoidal wave forms of applied AC potential (E) and current response (I) in phase with one another (left); and out of phase by the phase shift angle, θ (right)*

$$E_t = E_0 \sin \omega t \qquad \text{Equation 2.3}$$

$$I_t = I_0 \sin(\omega t + \theta) \qquad \text{Equation 2.4}$$

$$Z = \frac{E_t}{I_t} = Z_0 \frac{\sin \omega t}{\sin(\omega t + \theta)} \qquad \text{Equation 2.5}$$

$$e^{(j\theta)} = \cos \theta + j \sin \theta \qquad \text{Equation 2.6}$$

$$Z(\omega) = \frac{E}{I} = Z_0 e^{(j\theta)} = Z_0(\cos \theta + j \sin \theta) \qquad \text{Equation 2.7}$$

Impedance is measured over a range of frequencies, typically 100,000-0.1 Hz. The results of $Z(\omega)$ are related to the real (Z') and imaginary (Z'') components of impedance by (*Equation 2.8*), where $|Z|$ is the magnitude of impedance, related to Z' and Z'' by *Equation 2.9,* and θ by *Equation 2.10.*

$$Z(\omega) = Z' + jZ'' = (|Z|\cos\theta) + j(|Z|\sin\theta) \qquad \text{\textit{Equation 2.8}}$$

$$|Z| = \sqrt{Z'^2 + Z''^2} \qquad \text{\textit{Equation 2.9}}$$

$$\theta = \tan^{-1}\left(\frac{Z''}{Z'}\right) \qquad \text{\textit{Equation 2.10}}$$

The results of impedance at each frequency are generally represented on a Nyquist plot of the real (i.e the resistance) and imaginary (i.e. the capacitance) components of impedance (*Figure 2.5*). $|Z|$ can be represented as a vector on this plot, which forms an angle, arg Z with the Z' axis. R is the value of impedance when $\omega=0$, and C is calculated using $\omega_{max}=1/RC$ when arg $Z=45°$.[137]
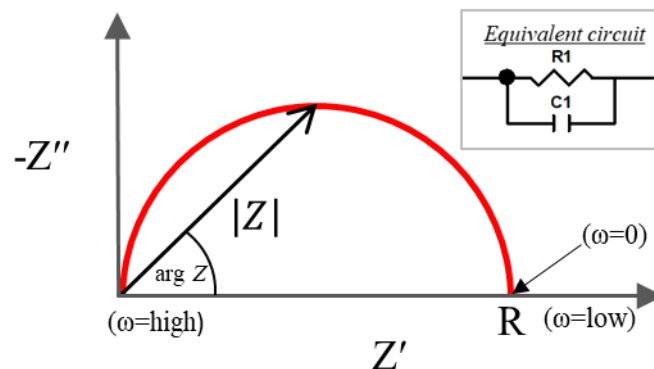
Figure 2.5 *Example Nyquist plot, test frequency, ω is varied from high to low frequency, each frequency leads to an extra point on the curve, where the curve crosses the x-axis the impedance is resistance only, vector indicates the magnitude of impedance, $|Z|$. The simple circuit is composed of an ideal resistor in parallel with an ideal capacitor.*

EIS data is interpreted by data-fitting an equivalent circuit model.R is the value of impedance when $\omega=0$, and C is calculated using $\omega_{max}=1/RC$ when arg $Z=45°$.[137] Common electrical circuit elements such as those shown in *Table 2.5* are combined to create a theoretical circuit which is representative of the physical electrochemistry of the system under study.

Table 2.5 *Equivalent circuit elements, their current-voltage relationships, impedances and phase shift properties*

Circuit element	Symbol	I vs E relationship	Impedance	Phase shift effect
Resistor	$\sim\!\!\wedge\!\!\wedge\!\!\sim$	$E = IR$	Z	$\theta=0°$
Inductor	$\sim\!\!\text{ccc}\!\!\sim$	$E = L\dfrac{dI}{dt}$	$Z = j\omega L$	$\theta=-90°$
Capacitor	$\dashv\vdash$	$I = C\dfrac{dE}{dt}$	$Z = \dfrac{1}{j\omega C}$	$\theta=90°$

For electrochemical systems such as DSSCs, complex combination of multiple components are used to build up equivalent circuits, e.g. diffusion of electrolyte species to sites of reaction at electrode surfaces results in impedance which is represented by a Warburg element. Electrochemical processes at counter-electrodes have been studied with EIS, by creating 'dummy cells' from pairs of counter electrodes.[138-142] The equivalent circuit model proposed for a cell created from a pair of platinized counter electrodes filled with electrolyte is a Randles circuit with a short Warburg element in which *Rs* is the electrolyte solution resistance of the electrolyte; *Cdl* is the double layer capacitance at the electrode│electrolyte interface; *Rct* is the charge transfer resistance at electrolyte│platinized counter electrode interface; and *Ws1* is a short Warburg diffusion (*Figure 2.6*). By fitting the data with this equivalent circuit, it is possible to extract value of *Rct* and *Cdl*.
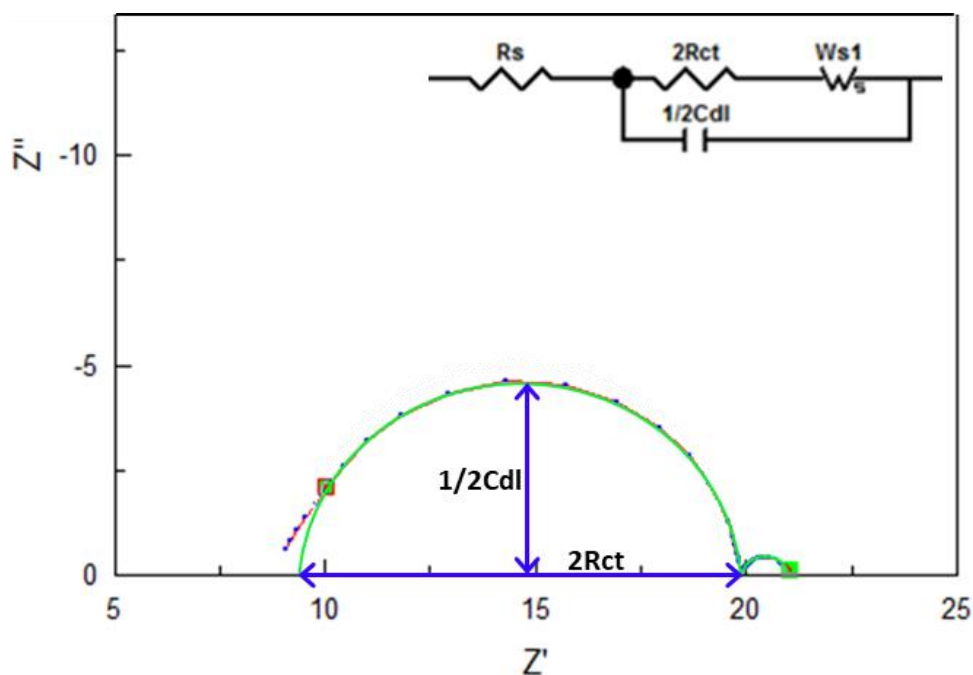
Figure 2.6 *Equivalent circuit fit for 'dummy cell' EIS data using a Randles circuit with short Warburg element (Ws1), showing Rct and Cdl*

Analysis - Impedance spectra of dummy cells were measured using a GAMRY Reference 600 Potentiostat at open circuit voltage. An AC voltage of 10 mV$_{rms}$ was applied over the frequency range 150,000 – 0.1 Hz. Charge transfer resistance (R_{CT}) values were measured from Nyquist plots of impedance spectra fitted to a Randles equivalent circuit with a short Warburg element (*Figure 2.6*) using Z-view software. Each curve was first modelled individually to give an estimate of the values. These values were put into the full model and constrained with only one free variable at a time. Once all the variables had been allowed to move freely the constraints were lifted one at a time until the whole model was free, except for the Ws-P parameter of the Warburg element which was fixed at 0.5 to give a finite Warburg to reflect the finite diffusion within the 25 μm distance between electrodes in cells. R_{ct} values are obtained as half of the real component of impedance for the 'dummy cells'.

2.3 Chemicals & Standards

Acids - HCl (31.5–33.0%) and HNO$_3$ (69–72%) were CertiFied AR (analytical reagent) grade, and were purchased from Fisher Chemicals and used as received.

Solvents, substrates and electrolyte materials – (*Chapter 5*): NSG TEC7 FTO glass (100 mm x 100 mm x 2.3 mm, 7 Ω/sq); isopropyl alcohol (IPA) (≥99.7%); 1-methyl-3-propylimidazolium iodide (98%); benzimidazole (98%); iodine (99.8% trace metal basis); and guanidinium thiocyanate (99%) were purchased from Sigma-Aldrich. 3-methoxypropionitrile (98%) was obtained from Acros Organics. All materials were used as received.

Standard solutions - All elemental standard solution used for atomic spectroscopy, ICP-OES and ICP-MS were TraceCERT® single element solutions (1000 mg/L) purchased from Sigma-Aldrich and used as received.

Elemental standards - (*Chapter 4 & Appendix A* - Evaluation of Fischerscope XDAL The metal foils and their sources are indicated in *Table 2.6*. Chloroplatinic acid hydrate (≥99.9% trace metal basis) was purchased from Sigma Aldrich, and 99.998% platinum wire was purchased from Johnson Matthey. All were used as received.

Table 2.6 *Metal foils used as standards for XRF evaluation*

Metal foil	Source
Co foil, Thickness: 0.125 mm, Purity: 99.9%, Coil width: 250 mm, Temper: Annealed, 100x100 mm	Goodfellow
Ge Sheet, Thickness: 0.5 mm, Purity:99.999%, Condition: Single crystal, Oriented:(111), Electrical type: N-Type	Goodfellow
Mg foil, Thickness:0.25 mm, Purity:99.9%, Temper: As rolled, 25x25 mm	Goodfellow
Ta foil, Thickness:0.04 mm, Purity:99.9%, Temper: Annealed, coil, 0.1 m	Goodfellow
Pd foil, Thickness:0.1 mm, Purity:99.95%, Temper: As rolled, 25x25 mm	Goodfellow
Pt foil, Thickness: 0.025 mm, Purity: 99.95%, Temper: As rolled	Goodfellow
Y foil, Thickness:0.125 mm, Purity:99.9%, Temper: As rolled, 25x25 mm	Goodfellow
Stainless Steel - AISI 302 Foil, Thickness:0.1 mm, Coil width:300mm, Temper: Hard, 50x50 mm	Goodfellow
Ag foil, Thickness:1.0 mm, Purity:99.95+%, Temper: As rolled, 25x25 mm	Goodfellow
Au foil, Thickness:0.025 mm, Purity:99.95%, Temper: As rolled, coil, 0.05 m	Goodfellow
In foil, thickness 0.5 mm, 99.999% trace metals basis	Aldrich
Nb foil, thickness 0.025 mm, 99.8% trace metals basis	Aldrich
W Foil, foil, thickness 0.05 mm, ≥99.9% trace metals basis	Aldrich
Al foil, 0.1 mm laboratory reagent, 250 g	Fisher

2.4   Statistics and errors

Reported values are the mean of three replicate measurements unless stated otherwise. Error estimates are given as the standard error on the mean (sem). Confidence intervals given in *Figures 3.10-3.13* in *Chapter 3* were calculated by Dr Ingrid Hallin, Dept of Environmental Science, Plymouth University.[143]

3 Temporal Trends in Precious Metal Content of WEEE - Implications for Future Recycling Potential[144]

Chapter summary

Effective and responsible recycling of WEEE is an essential component of any solution to the 'global WEEE problem'. Best-practice recycling is however costly, requiring manual pre-processing and responsible disposal of the plethora of toxic materials found in WEEE items, and incurring significant logistics costs when materials are transported between processing sites, often in different countries. For recycling to remain economically viable, it is essential that recycling potential of WEEE is sustained i.e. "that potential e-waste recycling revenues exceed costs of collection, transportation and processing".[145] Recoverable quantities of precious metals and copper must therefore remain sufficiently high to permit sufficient value to be derived from recycling of items to finance these operations.

To evaluate future recycling potential of WEEE, quantities of WEEE items generated in the future, their composition, recyclability and future costs of recycling must be considered. It is the purpose of the work presented in this chapter to shed light on the issue at hand and predict future recycling potential of high grade WEEE. Historical trends in PM and copper content of PC DRAM modules, originally placed on the market (POM) over the period 1991-2008 are evaluated. Observed temporal trends in PM and copper content of RAM modules are then applied to other high grade WEEE items to project temporal changes in PCB composition of items, which are considered in conjunction with projections of future waste arisings in Europe to estimate the recoverable value from PCBs in the future waste stream.

Previous results on the chemical analysis of PC RAM modules placed on the market between ~1991 and 2008 obtained by the author during his MRes research have been examined in detail and used to provide an assessment of the past temporal trends of PM and copper content of RAM. This assessment has then been used to provide projections of future trends in PM and Cu content in RAM, PCs and WEEE of computing EEE generally.

Total value of precious metals and copper in modules ranged from USD 33,000-54,000/tonne, with an average value across samples of USD 43,700/tonne. Gold and silver content of modules has remained reasonably constant over time, while palladium content has decreased by ~80% due to: miniaturisation of the Multilayer Ceramic Capacitors (MLCCs) in which it is mainly found; reductions in thickness of MLCC internal electrodes; and reductions in Pd

content of the electrode alloy. Copper content ranges from 1.8-5.1 g/module with a temporal increase observed in DIMMs of ~0.23 g/year. Linear extrapolation of this trend suggests an increase in copper content of DRAM modules by 75% by 2025. The increase in copper is thought to be as a result of increasing number of tracks on DRAM PCBs to support increasing functionality. It is likely that this trend will continue until 2020 despite the potential to reach saturation as additional layers can be added to multi-layered PCBs to support enhanced functionality once individual layers are saturated. Gold represents 85-95% of potentially recoverable value in modules, so changes in the content of the other metals has had little impact on the recycling value of PC RAM modules or recycling viability.

Limitations to the accuracy of projections of future recycling potential of items suffer from the limited accuracy introduced by use of static compositional data of current devices. This highlights a potential problem for any legislative or waste management measures implemented based upon recycling potential projections which use a static current composition for items. Should any significant changes in the concentration of the key PM metals Ag and Au, in PCBs of items occur as a result of design alterations, materials substitution, or 'thrifting' in manufacturing, recycling potential of items and the future viability of WEEE recycling may be compromised. This demonstrates the value of studying historical trends in the composition of items for more accurate projections of future recycling potential.

3.1 Background

3.1.1 Criticality of precious metals and copper

The strategic importance of recovering PMs and copper has been well explored; PGMs have been highlighted in the EU14[100] and EU20[53] critical materials reports and recovery of silver and gold has been shown by the Resource Efficiency Knowledge Transfer Network (KTN) to be of key importance to the UK economy with gold being the most unsecure of 69 metals assessed.[146] Schneider *et al.* have shown that PGMs have high economic resource scarcity potential (ESP) and that gold and silver have high abiotic depletion potentials (ADP).[147] Nasser *et al.* have shown copper, silver and gold score highly in criticality assessment.[148] The UK Resource Security Action Plan also identifies gold, silver and copper as unsecure or at risk.[149]

Global demand for gold in 2015 was 4,124 tonnes, approximately 20% lower than the record demand of 5,087 tonnes reached in 2013. Supply from secondary sources currently accounts for 28% of global production. EEE accounts for 6% of global gold demand.[150] Gold is predominantly used in EEE for contacts and in ICs.[69]

Silver demand reached a record high of 36,406 tonnes in 2015, with supply from secondary sources accounting for 12% of global supply. EEE is the major consuming industry accounting for 21% of global demand, exceeding supply from secondary sources.[151] Major applications of silver in EEE include: contacts; multilayer ceramic capacitors (MLCCs); thick film chip resistors; and more recently lead-free solders on circuit boards.[69] The photovoltaics industry also consumes a significant proportion of Ag for use in bus bars of solar cells.[152]

Global palladium demand in 2015 was 294 tonnes, only 0.5 tonnes below record demand set in 2014. Supply from secondary sources is sufficient to meet 20% of global demand. EEE accounts for 13% of global demand[153] with the major use being manufacture of MLCCs[69].

In 2015, 21.8 million tonnes of copper were produced globally with 16% supplied from secondary sources.[154] The electronics sector is the largest consumer of copper accounting for ~39% of global demand.[155] Major applications for copper in EEE include cables, wires, connectors, contacts and conductive tracks such as those on PCBs.[69]

The large proportions of these metals consumed by the EEE industry, and the significance that secondary production has in meeting global demand, emphasises the importance of efficient recovery from WEEE to offsets demand for primary resources. The economic driving force for WEEE recycling has been recovery of material value, >95% of which has been attributable to PMs and copper, with >80% attributable to gold alone.[30] Were it not for the presence of sufficiently valuable quantities of PMs in items, recovery of other metals found in PCBs would not be possible. The presence of the PMs grants economic viability to the recovery of certain CRMs which otherwise would be uneconomical.[156]

3.1.2 WEEE as a resource

WEEE is a secondary resource and a reserve of speciality metals[118] i.e.

> "a concentration or occurrence of material of intrinsic economic interest in or on the Earth's crust in such form, quality and quantity that there are reasonable prospects for eventual economic extraction".[157]

Useful analogies between primary and secondary resources have been made by others when assessing the potential of scrap materials as metal sources.[34, 64, 158] When assessing primary resources, a cut-off grade (COG) is established, below which it is not economically feasible to mine. It is possible to establish similar recycling COGs based upon levels of PMs and copper in WEEE items. These will vary between particular recycling processes and depend upon: total quantities of items available for recycling (governed by number of items placed on the market - POM; and lifespan of items); collection efficiency; recovery efficiencies of target materials; costs of recycling (including costs of labour, plant, energy, transport, and compliance with

regulation); and value of recovered materials.[124] Some WEEE items contain gold in concentrations ~200 times greater than in typical gold ores, e.g. gold can be 0.04 wt% (400 g/t) of a mobile phone, 200 times greater than typical gold ore – 1-3 g/t, and 14 times higher than the highest known grade deposit – 28 g/t (Tau Tona, RSA).[159] The cost of recycling an item and the ability to effectively recover precious metals is also significantly influenced by product design.

Concerns have been raised over the future viability of WEEE recycling due to component miniaturisation and substitution of expensive/rare materials in EEE in conjunction with ever rising recycling costs.[87, 128] Data on temporal trends in precious metal (PM) and copper content is important in order to verify these concerns and inform projections of future recycling potential, which is important knowledge for planning future recycling infrastructure and process development. For example, the PM content of mobile phones which have relatively high PM content, has been shown to increase over time as more functions have been added.[34] This paints a positive picture of likely future recycling potential of such devices.[159] It has however been suggested that the converse is true for computing technology, which would reduce recycling potential of such items in the future. Little data is available on temporal trends in value of computing technologies, however manufacturing trends may result in a major barrier to recycling as computing equipment currently accounts for a significant proportion of the derivable value in WEEE.[159]

It is the purpose of the work presented in this chapter to contribute to such data through the analysis of PM and copper content of PC DRAM modules placed on the market (POM) over the period 1991-2008. To gain a full understanding of the future viability of recycling, let us first examine the outlook for the individual stages of the recycling process chain and how this may affect viable recycling in the future.

3.1.3 The recycling process
Pre-processing - Automated processes involving shredding of items with PCBs inside cause PMs to be dispersed and lost through unintended co-separation with bulk materials fractions.[18, 106, 146] Material flow analysis (MFA) studies have shown bottom-line recovery efficiencies of gold and palladium from ICT equipment to be as low as 25% when such processes are employed. Manual isolation of PCBs achieves the highest bottom-line recovery rates (~95% for gold).[116] Manual pre-processing is costly, with high COGs in comparison to automated pre-processing, but efficient bottom-line recovery of PMs from high grade items justifies the costs, which are greatly affected by product design (DfRR), and the resulting ease of disassembly.[156]

When items are difficult to disassemble due to poor design for End-of-Life (EoL), or when low recoverable value prohibits manual disassembly (i.e. item grade<COG), semi-automated approaches using coarse crushing to break open housings and hand picking of PCBs has given intermediate pre-processing recovery rates for PMs (~70% for gold) at lower cost than manual processes.[116] As a consequence of the concentration-yield function,[18] (*Section 1.4.2*) COGs for WEEE and PM recovery rates are inversely related to the degree of automation used in pre-processing. Therefore, bottom-line recovery efficiencies, COGs, and the viability of WEEE as a PM source, are all largely determined by pre-processing method.

Recovery - Modern pyrometallurgical and hydrometallurgical refineries achieve >95% recovery of gold and can recover numerous metals in addition to PMs and copper. Because of high refining efficiencies the recovery process is generally less significant than the method of pre-processing in determining the recycling potential of WEEE.[12, 78, 116]

3.1.4   Market values of metals

Metal recycling is highly dependent upon the vagaries of metal values as shown by the dramatic reduction in quantities of gold supplied from secondary sources in 2013 and 2014 (*Figure 3.1*), which mirrors annual reductions in the price of gold since 2012.[150] As metal prices fall, COGs for recycling rise as recoverable value from WEEE and the viability of PM recovery from WEEE is reduced. Since the result of the UK 'Brexit' vote, PM prices have risen dramatically as investors lose faith in falling stocks and hunt for safer investment in gold, silver and palladium. In July 2016, silver and gold values reached a two-year high and the value of palladium rose by 12%., good news for the viability of WEEE recycling.[160]
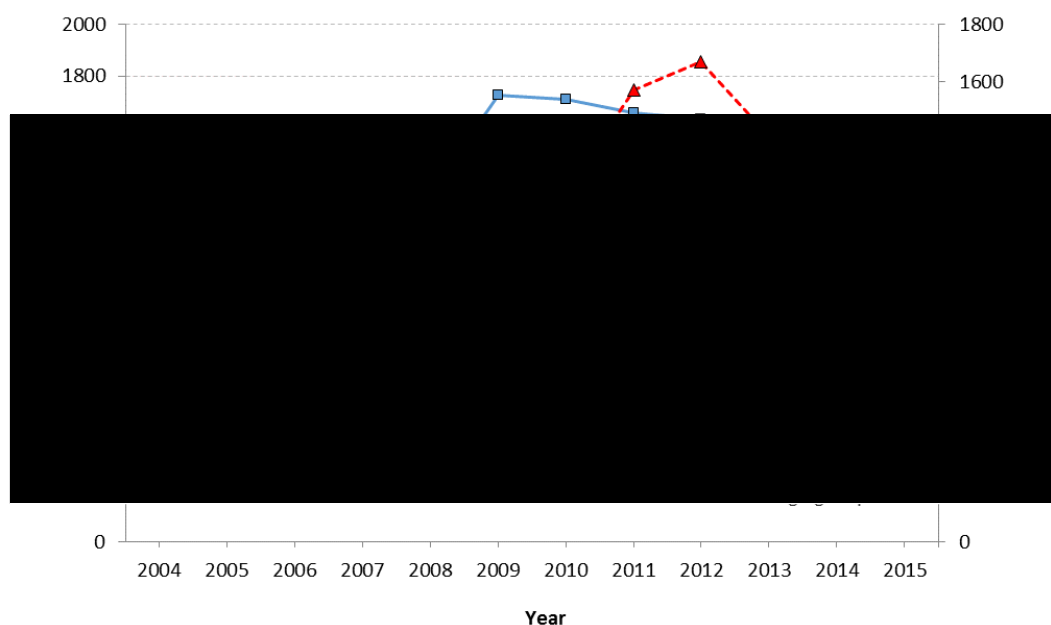
Figure 3.1 *Annual gold production from scrap & average gold price. Data from O'Connell et al.[150, 161]*

3.1.5   Waste management strategies

The recycling of circuit boards involves long and complex logistics systems. Take the UK as an example. WEEE is collected via numerous mechanisms including from consumers at household waste recycling centres (HWRCs), through distributor takeback schemes (DTSs), and from businesses by waste management and reverse logistics organizations. WEEE then finds its way to authorized approved treatment facilities (AATFs). Here PCBs are isolated from items and segregated according to grade. These are sold abroad to refiners operating pyrometallurgical and/or hydrometallurgical recovery processes such as Umicore and Boliden in Europe and Mitsubishi Metals in Asia.[67, 78] Often PCBs are sold to brokers acting as intermediaries, who amass sufficient quantities before shipping to refiners. To maintained economic viability of recycling, sufficient value generated from the sale of recovered metals must filter back through the value chain to finance costs incurred at each stage of recycling and during transport between them.

3.1.6   Outlook for waste management and viability of WEEE recycling

As global WEEE volumes increase, appropriate waste management will be crucial for mitigating environmental impacts, materials criticality and enhancing global resource-efficiency. The continued viability of WEEE recycling is crucial to global sustainability and management of the growing WEEE problem. This is determined to a large extend by the recycling potential of future WEEE i.e. *"that potential e-waste recycling revenues exceed costs of collection, transportation and processing".*[145] Grades of WEEE items must continue to remain above COGs for recycling also. Doubts over the future viability of WEEE recycling have been raised. Reductions in the value of precious metals present in WEEE and rising overheads for recycling raises COGs for recycling processes. This issue was highlighted as early as 2001.[87] Since 2013 costs of recycling have risen by 1.9% annually, a trend which is expected to continue until 2019.[162] The rising costs of electronics recycling via BATRRT has led to much WEEE being stockpiled, or exported to regions where recycling and recovery of PMs is conducted in a manner resulting in both low recovery yields and harm to the environment & human health. This has effectively reduced the size of the 'reserve' of metals present in WEEE, as a smaller proportion of WEEE arising (i.e. the total secondary resource) can be diverted to BATRRT processes. Additionally, the trend in the electronics industry towards miniaturisation and 'thrifting' has reduced quantities of PMs in items, affecting the grade of items and recycling revenues.[108, 163, 164]

Despite rising recycling costs and diminishing metal content in individual items, volumes of WEEE are increasing rapidly due to greater market penetration of electronics, technological innovation and decreasing product lifetimes. The size of the potential secondary resource is

therefore increasing and higher collection rates enabled by statutory recycling targets imposed by the growing global number of e-waste legislative instruments (*Section 1.4.2*) will effectively increase the quantity of WEEE made available for recycling. When larger quantities of WEEE are available, processing of lower grade materials becomes viable.[34] Resulting economies of scale compensate for reductions in grade of individual items to some extent, although uncertainty exists over how collection costs may scale with collection rate.[165] Recyclability, i.e. the probability of an item being recycled, taking into account the recycling difficulty of its material components in physical treatment and chemical recovery processes,[166] will also improve in the future as a result of superior product design for EoL[167-169] driven by the proliferation of EPR (particularly IPR), restrictions on hazardous substances, and proliferation of product eco-labels.[170] The expected effect of these factors will be lower recycling costs and greater recovery efficiencies of target metals.

Obtaining information related to future recycling potential of WEEE is essential for the development of legislation and new recycling capacity necessary to deal with ever growing volumes of WEEE.[171] This valuable information is acquired through 3 types of analyses: projections of mass flow of products over time; product lifespans; and material composition of items.[145, 172, 173] This enables quantities of WEEE items arising over time to be projected and the material content and potential recycling revenues to be established (i.e. the size of the potential metals reserve). Over 10 methods and models have been used to estimate WEEE generation in previous studies,[174] the method of choice depending primarily upon the availability and quality of data.[175] In addition to these considerations, components within items should also be investigated due to alterations to technologies over time.[40]

Zeng *et al.* projected the recycling potential of 'new' WEEE arising in China for the period 2010-2030 using the material flow analysis (MFA) and lifespan model of the Weibull function.[145] Based on previous projections of WEEE arising in Europe, Cucchiella *et al.* predicted the potential revenues from WEEE recycling in Europe in 2020.[172] The issue with such projections is that the compositional data of items applied to the mass flow projections are based on current and historical compositional data. Although these studies are robust, insufficient data on temporal changes in metal content of devices is available to allow changes in PM and copper content over time to be taken account of in projections. Both studies indicate a majority of the recoverable value from WEEE into the future will be from copper and PMs, however without data highlighting temporal trends in copper and PM content, it is difficult to take account of the potential effect of miniaturisation and 'thrifting' in manufacturing. It is the purpose of the work presented in this chapter to explore historical temporal changes in PM

and copper content of DRAM modules, and make projections for future recycling potential of PCBs based on observed trends in RAM.

Precious metals are predominantly found in PCBs of items which are constructed from common surface mount device (SMD) components. Dynamic RAM (DRAM) modules are essential PCB based components of PCs (*Figure 3.2*).[144] To investigate historical changes in PM and copper content of PC DRAM modules, samples have been gathered from Metech Recycling (UK) Ltd, dated, and analysed. DRAM is chosen for study as these devices are relatively simple PCBs, containing only a single type of each of those few SMDs which represent the main applications of PMs and copper in PCBs in general i.e. ICs, chip resistors, MLCCs, copper tracks, edge contacts, etc. Following chemical analysis of samples, this simplifies the task of rationalizing observable temporal trends in metal content in terms of changes to common PCB components over time. This task would be difficult for more complex PCBs such as motherboards and mobile phone PCBs with dozens of different kinds of SMD components. Historical temporal trends observed in DRAM, once rationalised against changes in PCB design, can then be used to make predictions on temporal changes in PM and copper content of items into the future.
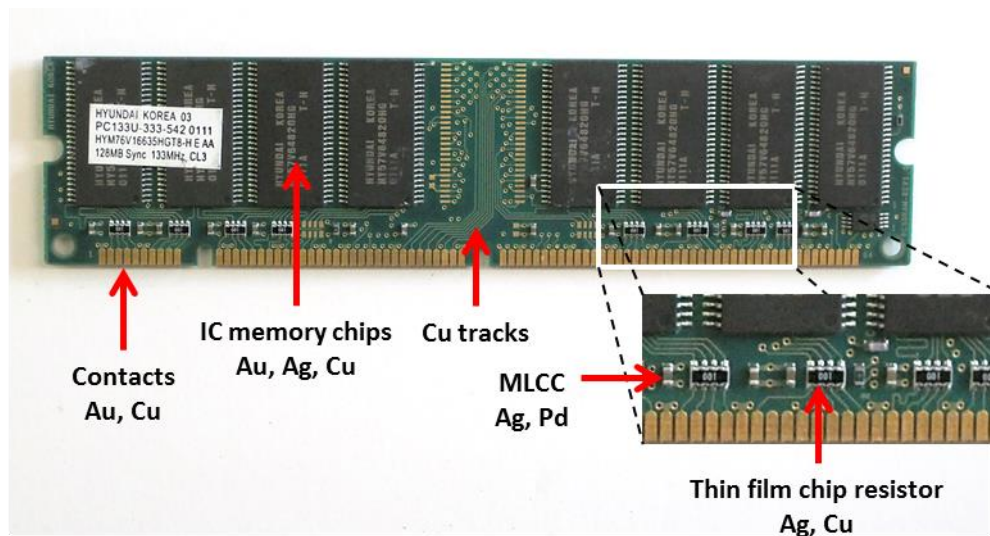
Figure 3.2 Anatomy of PC DRAM module and locations of precious metals and copper.[144]

This work represented the first published compositional data for DRAM modules and temporal data on PM and copper content in PCBs; and the first projections of future changes to PM and copper content of PCBs used with compositional data and product mass flow data to create a picture of future recycling potential which takes account of the potential future impact of

miniaturisation and 'thrifting' trends in manufacturing.[144] The value of inclusion of temporal trend data in projections of recycling potential is demonstrated.

3.2 Materials and methods

3.2.1 Evaluation of historic trends in composition and value of DRAM modules

A range of PC DRAM samples, covering memory sizes and RAM types from 4 MB FPM single in-line memory modules (SIMMs) through to 2 GB DDR3 dual in-line memory modules (DIMMs), were previously gathered from Metech Recycling (UK) Ltd., identified (*Table 3.1*) and analysed during the author's MRes project (*Table 3.2*).[22] Compositional data from this study is used to assess temporal trends in composition of DRAM modules. PCB dimensions of SIMM samples (**1**-**3**) are 108.5 x 26.0 mm while DIMM sample (**4**-**15**) PCBs are 133.5 x 31.5 mm. Sample masses range from 13.1-21.9 g with an average mass of 17.5 g.

Here in a continuation of that work the analytical data is re-examined and reanalysed in detail to extract data on temporal trends in composition and value. In order to create a new timeline of the samples, an investigation of historical data on the size of memory available in PCs POM, and the date of introduction of different RAM technologies was conducted.[176-178] .

Data on PM and copper content of samples were plotted against date of sample introduction based on the DRAM timeline. These plots were then analysed to investigate temporal trends in DRAM sample composition. To rationalise observed trends in Au content of samples, surface areas of edge contacts were compared. This comparison was conducted using images of the samples analysed, in which pairs of RAM modules for comparison were photographed side by side. Using Adobe Photoshop, the areas of the edge contacts in the images can be highlighted and the number of pixels in these areas counted using the pixel counting feature in the software. Comparison of the number of pixels within the areas of contacts in the images of each sample enables a comparison of their surface areas to be made.

Table 3.1 *DRAM modules analysed during author's MRes project.*[22]

Sample	Brand	Model	Memory type	Module type	Capacity (MB)	S
1	Samsung	KMM5361000G-7	FPM[b] DRAM	72-pin SIMM[g]	4	10
2	Micron Technology	MEMSIM016AAWW	EDO[c] DRAM	72-pin SIMM	8	10
3	Micron Technology	MT8D432M-6X	EDO DRAM	72-pin SIMM	16	10
4	Discovery	DISCOVERY S/N 1212772	SDR[d] SDRAM[e]	PC100 168-pin DIMM[h]	32	13
5	Samsung	KMM366S823CTS-GH	SDR SDRAM	PC100 168-pin DIMM	64	13
6	Hyundai	HYM76V16635HGT8-H E AA	SDR SDRAM	PC133 168-pin DIMM	128	13
7	Infineon	HYS64V16300GU-7.5-C2	SDR SDRAM	PC133 168-pin DIMM	128	13
8	Samsung	M368L1716ETM-CB0	DDR[f] SDRAM	PC2100 184-pin DIMM	128	13
9	Micron Technology	MT9VDDT3272LAG-265C4	DDR SDRAM	PC2100 184-pin DIMM	256	13
10	Kingston Technology	KTH-D530/512	DDR SDRAM	PC3200 184-pin DIMM	512	13
11	Hynix	HYMD512646PC8J-D3 AA-C	DDR SDRAM	PC3200 184-pin DIMM	1024	13
12	Promos Technologies	V916764K24QAFW-E4	DDR2 SDRAM	PC2-4200 240-pin DIMM	512	13
13	Micron Technology	MT8HTF12864AY-667G1	DDR2 SDRAM	PC2-5300 240-pin DIMM	1024	13
14	Kingston Technology	kvr800d2n5k2/2g	DDR2 SDRAM	PC2-6400 240-pin DIMM	2048	13
15	Samsung	M378B5673FHO-CF8	DDR3 SDRAM	PC3-8500 240-pin DIMM	2048	13

[a]IC: integrated circuits, [b]FPM: fast page mode, [c]EDO: extended data out, [d]SDR: single data rate, [e]SDRAM: synchronous DR... single in-line memory module, [h]DIMM: double inline memory module

.

Table 3.2 *Precious metal and copper content of PC DRAM samples 1-15[22] (errors given as ranges for triplicate analyses [a], and [...]*
and SIMMs

Sample	Contacts	No. of		Gold		Palladium		Silver	
		ICs	MLCCs	mass/mg	conc/ppm	mass/mg	conc/ppm	mass/mg	conc/[...]
1	Gold	12	12	20.8 (±0.5)	1,144 (±26)	3.43 (±0.03)	189 (±2)	133 (±5)	7,321
2	Tin	16	16	7.2 (±0.3)	327 (±12)	3.2 (±0.6)	150 (±30)	62 (±3)	2,841
3	Tin	8	8	3.8[b] (±0.3)	251[2](±17)	1.9[Ci] (±0.1)	124[Ci] (±8)	54 (±1)	3,567
4	Gold	4	15	10.5 (±0.2)	484 (±10)	1.49 (±0.03)	114 (±3)	7.4 (±0.3)	562 (±
5	Gold	8	39	17.8 (±0.1)	1,099 (±7)	2.1[Cii] (±0.2)	118[Cii] (±11)	24.0 (±0.7)	1,329
6	Gold	16	34	26.8 (±0.6)	1,319 (±27)	2.1 (±0.1)	103 (±5)	25 (±1)	1,251
7	Gold	8	16	17.5 (±0.4)	1,127 (±28)	1.6 (±0.1)	102 (±8)	13.5 (±0.5)	767 (±
8	Gold	8	49	20.8 (±0.3)	1,179 (±19)	1.69 (±0.08)	96 (±5)	14.5 (±0.7)	822 (±
9	Gold	8	49	18.2 (±0.5)	1,064 (±32)	1.0[Ciii] (±0.1)	57[Ciii] (±7)	124 (±5)	7,232
10	Gold	16	42	16.8 (±0.5)	786 (±22)	1.3 (±0.07)	59 (±3)	27.5 (±0.6)	1,290
11	Gold	16	39	23.4 (±0.7)	1,078 (±31)	1.0[Civ] (±0.2)	44[Civ] (±9)	33 (±1)	1,507
12	Gold	8	39	15.6 (±0.3)	980 (±19)	0.59 (±0.04)	37 (±2)	15.6 (±0.7)	979 (±
13	Gold	8	27	13.2 (±0.2)	968 (±17)	0.60 (±0.03)	44 (±2)	16.3 (±0.4)	1,195
14	Gold	16	47	18.0 (±0.6)	1,098 (±36)	0.399 (±0.004)	24.32 (±0.05)	20.5 (±0.2)	1,248
15	Gold	16	114	17.8 (±0.1)	1,083 (±7)	0.58 (±0.01)	35.7 (±0.4)	19.5 (±0.6)	1,208
Average composition		All samples (1-15)		16.5	932	1.5	86	39	2,208
		DIMMs (4-15)		18.0	1,022	1.2	70	28	1,616

[a]Sample to sample variation is generally 0.2-5.0% except where indicated. [b]Sample to sample variation is 6.6%. [C]Sample to sample variation is >5.0% [...]
limit of AAS instrument: [Ci]sample to sample variation of 19.2%; [Cii]sample to sample variation 9.1%; [Ciii]sample to sample variation of 11.9%; [Civ]sample [...]

3.2.2 Evaluation of recycling potential of DRAM

To evaluate recycling potential of metals in RAM, average compositions of RAM modules were calculated from data and compared with compiled compositional data on PC PCBs from available literature. The value of precious metals and copper, as well as the value fractions represented by each of these metals in samples was calculated using the following market values: Au: USD 1221.50/Oz (LBMA 19/2/16 AM); Ag: USD 15.37/Oz (LBMA 19/2/16); Pd: USD 513.00/Oz (LBMA 18/2/16 AM); Cu: USD 4575.00/tonne (LME 18/2/16 Cash buyer). To evaluate the significance of DRAM modules as a global source of PMs and copper, the total quantity of these metals available in waste DRAM generated in 2013 was calculated based on the previously calculated average composition of DRAM, and the quantity of waste DRAM modules arising in 2013. It was assumed that a minimum quantity of waste DRAM modules generated this year would be equivalent to the number of waste PCs arising that year. This was calculated using the WEEE directive assumption that WEEE arising is equivalent to the average of the number of items POM over the previous 3 years.[4] The value of metals in this quantity of DRAM was calculated. To provide a context to evaluate the significance of quantities of metals in DRAM, total quantities of gold, silver, palladium and copper in waste DRAM generated in 2013 are expressed as percentages of the global demand for these metals, demand from the EEE sector itself, and global supply from secondary sources that year.

3.2.3 Projections of future recycling potential.

Projections and confidence intervals for future quantities of metals in waste DRAM were obtained by linear regression analysis carried out in python in collaboration with Dr. Ingrid Hallin, Plymouth University.[179-181]

3.3 Results and discussion

3.3.1 Historic trends in composition and value of DRAM modules

A timeline of historic DRAM technologies POM based on dates of introduction of RAM technologies and memory sizes is shown in *Figure 3.3*. This was used to date analysed DRAM samples. Modules were assigned a date equal to the midpoint of the line representing their use over time. For example, sample **4** is a 32 MB PC100 SDRAM module. According to *Figure 3.3*, such modules were available in PCs for 2 years from the beginning of 1998 until the end of 1999. The sample was therefore assigned a date of 1999 ($\pm$1 year). Once dated, temporal variation in PM and copper content of modules was evaluated for temporal trends. As a means of comparison, *Table 3.3* compares average compositions of all RAM samples analysed (**1-15**) and average composition of DIMMs only (**4-15**) with literature values (dated where information was available) for precious metal and copper content, along with average

composition with per tonne values, and value fractions, for general PC PCBs, rather than just the memory modules described here.
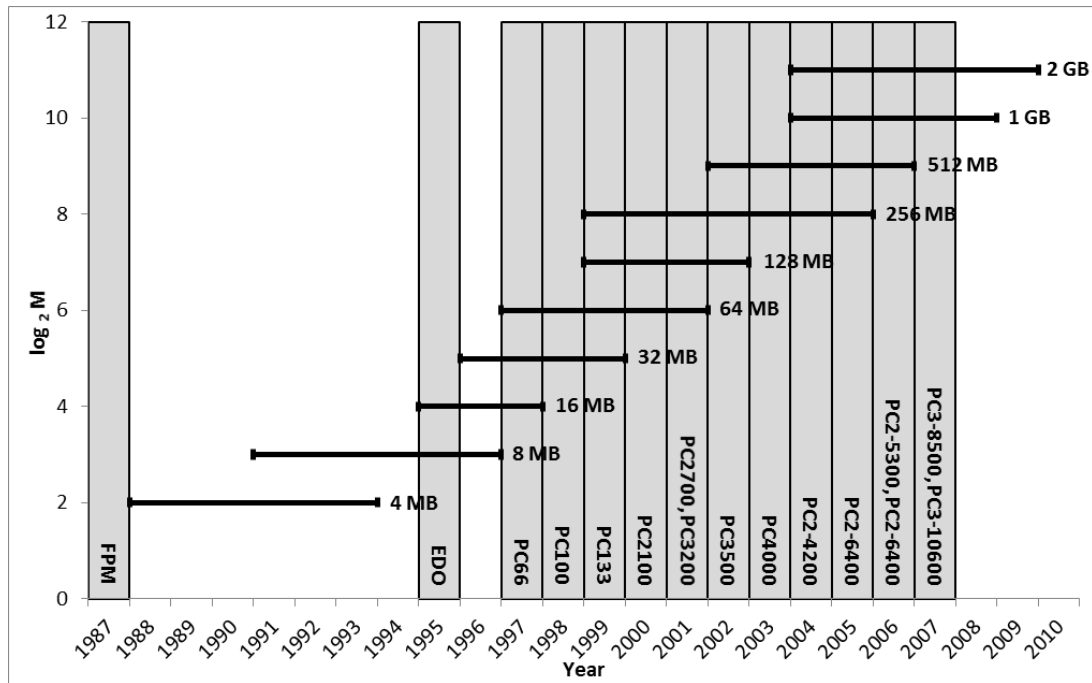
Figure 3.3. *Timeline of DRAM technologies in PCs POM. M is the Module Memory Capacity (MB); the vertical blocks (▭) show the year of introduction of RAM type (data from Mueller, 2011; Ögren et al.).[177, 178] The horizontal lines show the period when PCs POM were available with memory capacity M (data for from Polsson, 2013).[176]*

Table 3.3 *Literature values for precious metal and copper content of PC PCBs compared to calculated average composition of analysed DRAM samples. (Errors quoted are standard-errors of the mean)*

Source	Metal content (ppm)				Model year
	Au	**Ag**	**Pd**	**Cu**	
Average composition of DRAM (**1-15**)	932 (±61)	2,208 (±568)	86 (±12)	196x10³ (±18x10³)	1991-2008
Average composition of DIMM (**4-15**)	1,022 (±61)	1,789 (±517)	70 (±10)	200x10³ (±21x10³)	1999-2008
(Oguchi *et al.*, 2011)[34]	220	570	110	210×10³	Unavailable
	120	680	160	160×10³	Unavailable*
	270	760		260×10³	1985
	270	510		340×10³	1989
	450	590	150	300×10³	1994
	300	400		170×10³	1985
	130	230		200×10³	1989
	140			140×10³	1994
(Chancerel *et al.*, 2009)[106]	81	905			Unavailable
	250	1000	110		Unavailable
	230	1000	90		Unavailable
	156	775	99		Unavailable
	300	600			Unavailable
	600	700	100		Unavailable
(Tuncuk *et al.*, 2012)[12]	250	1000	110	200×10³	Unavailable
	86	694	309	185×10³	Unavailable
(Yamane *et al.*, 2012)[131]	1300	1600		202×10³	Analysis of 10lg sub samples sample from large batch of various models of PC PCB.
(Cui and Zhang, 2008)[78]	566	639	124	143×10³	Unavailable
	250	1000	110	200×10³	Unavailable

* average of 8 kinds of PCB

Gold - The gold content of the EDO SIMMs (**2** and **3**) is low (*Figure 3.4*) due to the use of tin rather than gold in edge contacts. The gold content of the other modules varies from 480-1320 ppm, a factor of 2.6. The average gold content of these modules is 18.2 mg/module (1030 ppm). This is a higher gold content than that for PC PCBs generally reported in the literature except by Yamane *et al.*, (Table 3.3), suggesting that RAM modules contain gold in higher concentrations than other PC PCBs such as mother boards and PCI cards.

Comparison of results for modules **2** and **3** with the rest of the samples shows that the bulk of gold in DRAM is found in the edge contacts. The results do not correlate with the number of ICs or edge contacts on modules. To the naked eye, it appears that the surface areas of edge contacts on SDR, DDR, DDR2 and DDR3 modules are very similar; and measurement of

contact surface areas of the DDR and DDR2 sample made from photographs (*Figure 3.5*) using Adobe Photoshop pixel counting function shows them to be within 2% of one another.
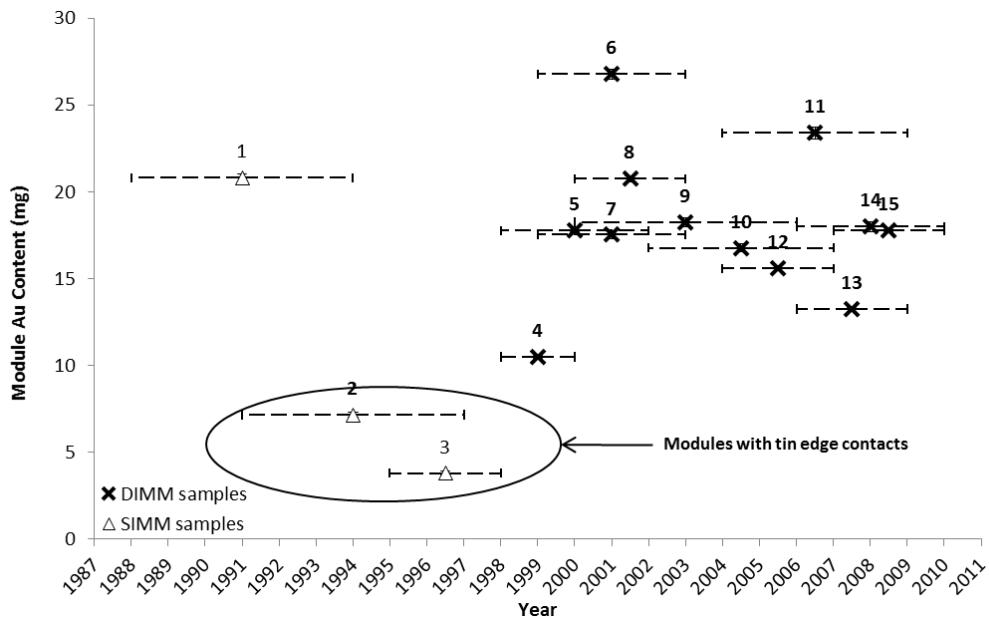
Figure 3.4 *Gold content of PC DRAM modules (dashed line represents best estimate of time period in which module was on the market (**Figure 3.3**); modules **2** and **3**, have tin rather than gold edge contacts*

Figure 3.5 Image used for comparison of contact surface areas of DDR (bottom) and DDR2 (top) DRAM DIMMs.

While gold content varies significantly from module to module, for those with gold edge contacts, no general trend over time is initially obvious. Manufacturers have opted to increase memory using the same module size, and with it roughly the same gold contact areas, rather than maintain memory capacity and reduce the module size. Variation in gold content in DIMMs may be explained by differences in thickness of the Au alloy layer of the contacts plated onto the module during manufacturing. This alloy is electroplated onto the module, and minor differences in the thickness of this layer resulting from variation in technical manufacturing skills, applied voltages, currents and duration of the plating process used in different manufacturing processes around the globe. For such a thin layer of alloy, minor changes to manufacturing parameters could result in the differences in gold content observed across samples.

Palladium - Palladium content per PCB varies significantly, ranging from ~3.5-0.5 mg/module, and shows a marked decrease over time (*Figure 3.6)*. The average palladium content (1.5 mg/module; 86 ppm) is somewhat lower than that generally reported in the literature for other PC PCB samples (90-309 ppm, *Table 3.3*). On these PCBs, Pd is principally found in the multi-layer ceramic capacitors (MLCCs), and while there is no correlation with the number of MLCCs per board (which has generally increased over time), the size of individual MLCCs has been reduced significantly over time. Capacitance improves with smaller units which results in a technical advantage from miniaturisation as well as cost savings for producers. The same is true for thinner layers of Pd in devices. This has enabled manufacturers to achieve additional cost savings by reducing the thickness of the internal electrode plates reducing Pd content further. In the early 1990s 100%Pd was favoured as the inner electrode material of MLCCs. Since then, AgPd alloys of decreasing Pd content have been developed. By 2004, MLCCs using 2%Pd alloy were in development. A minimum Pd content of the electrode alloy has now been reached as 100% silver alloys do not perform well due to technical and structural limitations.[182] Because of this, a similar decrease in palladium content over time will almost certainly be seen in other PC components and PCB based devices in which MLCCs have been used.
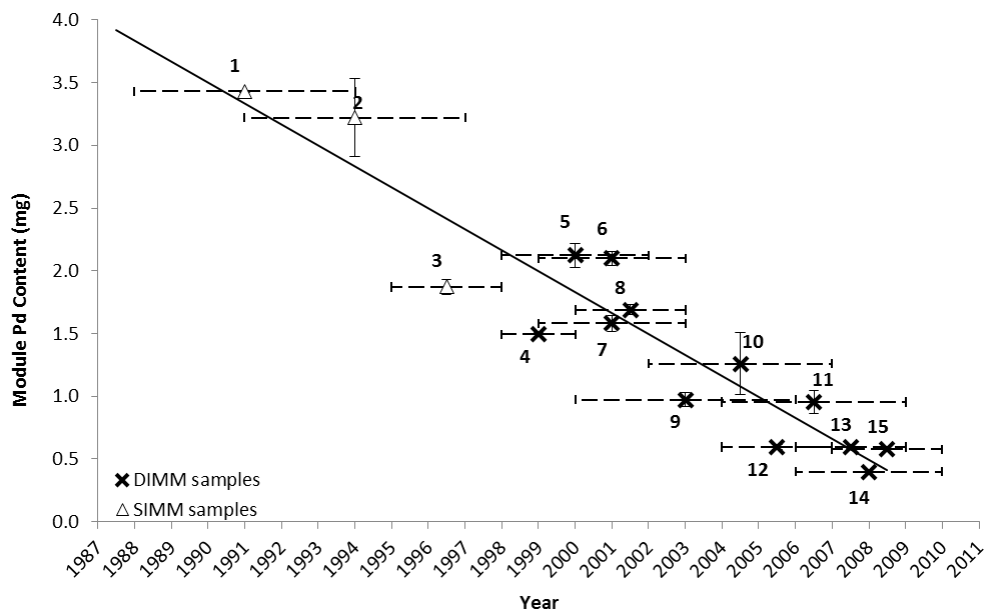
Figure 3.6 *Variation in palladium content of PC DRAM modules over time. The dashed line represents best estimate of period in which module was on the market (Figure 3.3); the solid line shows the temporal trend in Pd content.*

Platinum - No platinum was detected in any of the samples, which, using our detection limit of 60 μg/L for platinum in solution, puts the quantity of platinum in samples at <6 μg per module (<0.5 ppm). This is unsurprising since platinum is used in PC HDD platters rather than PCBs.

Silver - Silver content of modules varies quite widely from ~10-130 mg/module. In general SIMMs (samples **1-3**) contained significantly higher levels of silver (~50 – 130 mg) than DIMMs (typically <40 mg) (*Figure 3.7*) with the exception of the 256MB PC2100 DIMM (sample **9**), which has a very high silver content, a result confirmed by repeat analyses. SIMMs contain significantly higher concentrations of silver than any of the PC PCB samples reported in the literature (*Table 3.3*). Such modules however have not been utilised in PCs since the introduction of DIMMs (c. 1997) and are now infrequently found in the waste stream. With the exception of sample **9**, DIMMs contain relatively high levels of silver to PC PCBs reported by others (*Table 3.3*). Excluding sample **9**, the silver content of DIMMs is low, ~10-40 mg/module, with no observable trend over time.
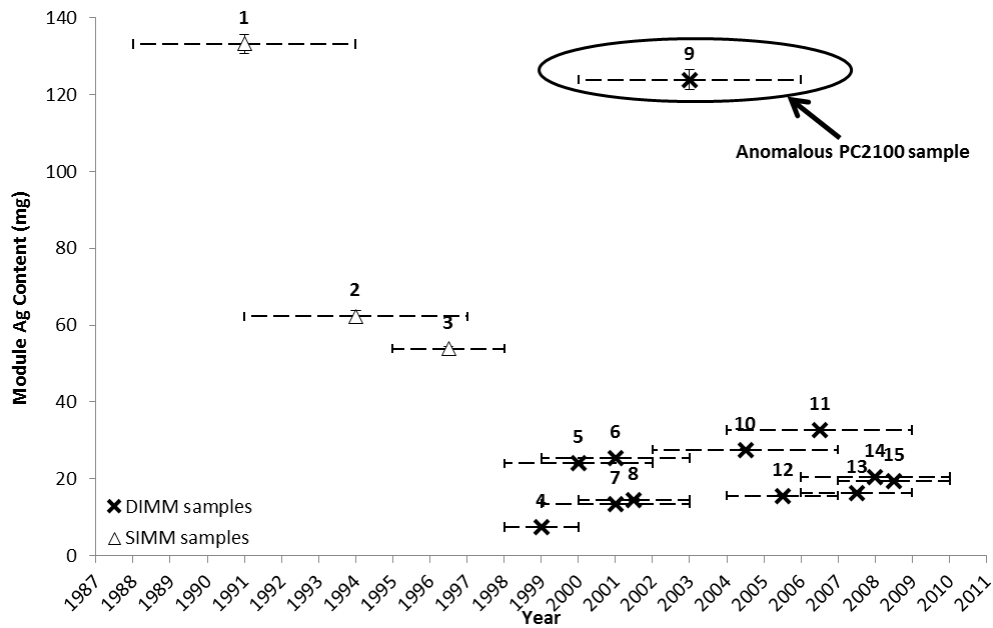
Figure 3.7 *Variation in silver content of PC DRAM samples over time (dashed line represents best estimate of time period in which module was on the market (Figure 3.3).*

Copper - Copper content ranges from 1.8-5.1 g/module (*Figure 3.8*). With an average copper content of ~ 200×10^3 ppm, samples exhibit comparable copper content to PC PCBs reported in the literature (*Table 3.4*). Taken as a whole, no general trend in copper content of RAM samples is seen. However, if we consider DIMMs alone (*Figure 3.8*) copper content has generally increased over the years.
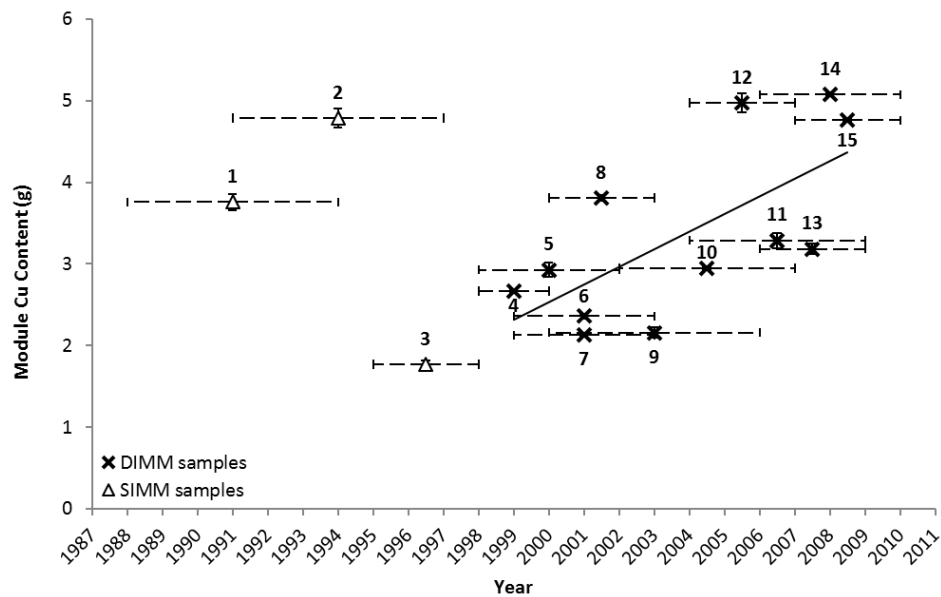
Figure 3.8 *Variation in Copper content of PC DIMM samples over time (dashed lines, represents best estimate of period in which module was on the market (Figure 3.4); solid line shows the temporal trend in copper content in DIMMs).*

Temporal trends in value of DRAM modules

Before discussing the trends in value of RAM modules it is necessary to identify the following two caveats: 1) our analyses do not cover every module used over the time period studied, and 2) we do not have data on the numbers of each individual module produced, or found in the waste stream, which would be necessary to provide a weighted average analysis.

While recognising these two factors following general comments on the trends in value of RAM modules in the waste stream can be made. The value of individual samples per module and per tonne, showing value contributions of PMs and copper, are given in *Figure 3.9*. Values range from USD 0.23/g to USD 1.11/g. The two lowest value modules are EDO samples with tin contacts. The more modern DIMM samples (**4-15**) vary in value by a factor of 2.4 from USD 0.46/g to USD 1.11/g, with an average value exhibited across all DIMM samples of USD 0.76/g. Gold represents the majority of inherent value in DRAM modules; 85-95% for the more modern DIMMs (**4-15**). Over the period represented by the samples there is a small increase in the value fraction of copper and a decrease in the value fraction of palladium. Over time, values and grades of modules have remained relatively stable since the introduction of DIMMs and the elimination of tin edge contacts from module designs. As SIMMs have not been included in PCs since 1997, they no longer represent a significant portion of DRAM in the waste stream. Therefore, the composition of waste DRAM modules generated today is more accurately represented by the average composition of DIMM samples (**4-15**).

The per tonne values of DRAM samples (*Figure 3.9b*) follow those for individual modules, and in general are significantly higher than those calculated from average compositional data for PC PCBs available in the literature (*Table 3.3*). Perhaps what is most important, in terms of the long-term recycling viability of DRAM modules, is that the per tonne values of the most recent module types analysed, DDR2 and DD3 DIMMs (**12-15**), appear stable.
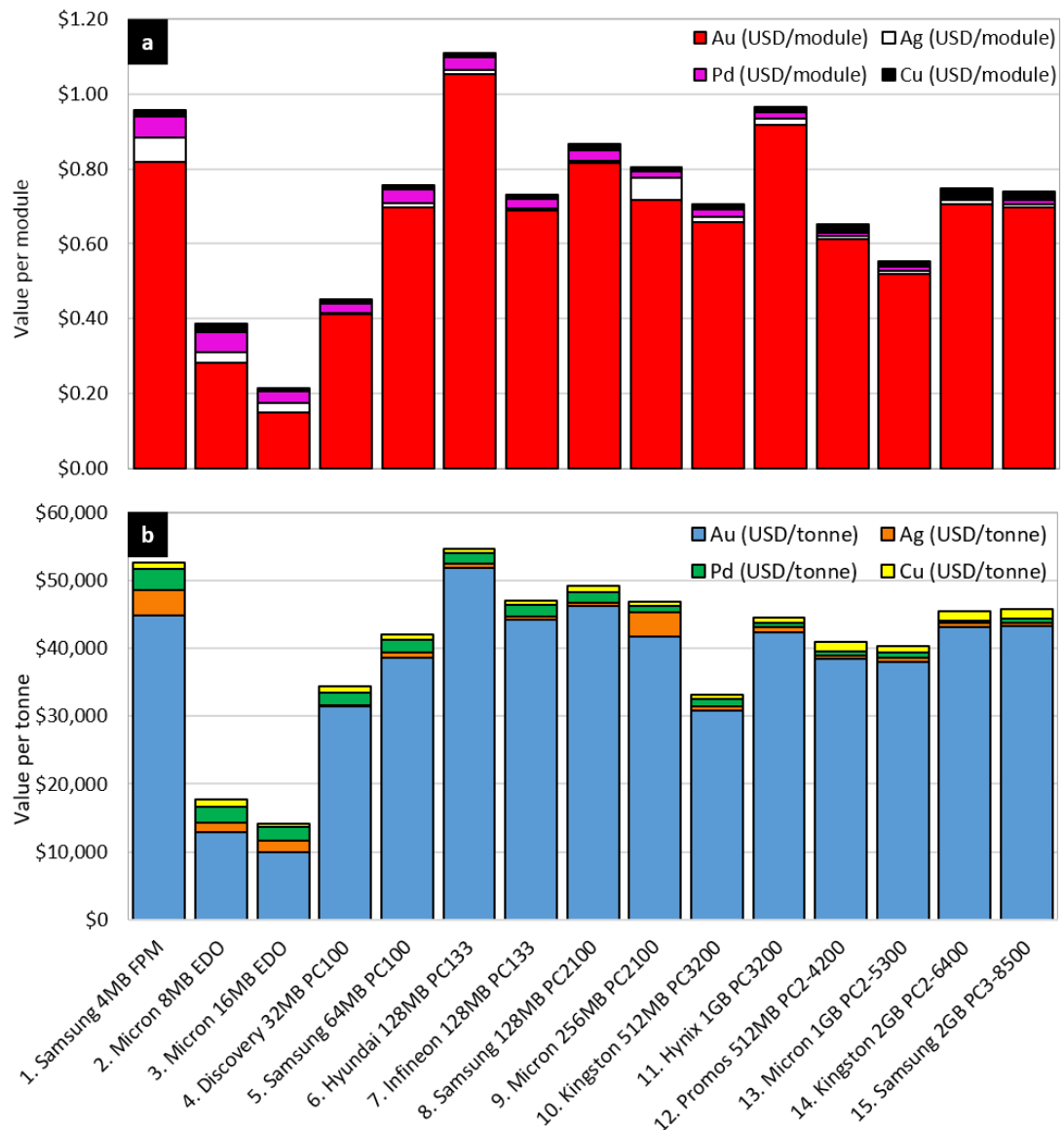
Figure 3.9 *Inherent value of DRAM samples, **a**) per module and **b**) per tonne, showing value contributions of PMs and copper.*

3.3.2 Recycling potential of DIMMs

As an indication of the potential contribution of DIMMs to global metal supply and demand (*Table 3.4*), minimum estimates of total potentially recoverable metals in DRAM in PCs POM in 2013 have been made assuming metal contents are given by the averages of those for samples **4-15** and that each PC POM contains a single RAM module. Assumptions made in the WEEE Directive[4] and annual PC sales data[183] suggest that 153.4 million waste PCs were generated globally in 2013.

Table 3.4 *Estimated quantities of precious metals and copper in globally generated waste DIMMs in PCs POM 2013, their values and proportions of global demand, demand from the EEE sector and global secondary production each represents (calculated from average metal contents of samples 4-15, data provided in O'Connell et al., Statista, 2015)* [150, 151, 153, 154, 183]

	Au	Ag	Pd	Cu	Total Value
DIMM average composition	18.0 mg	28.4 mg	1.2 mg	3.4 g	
Total metal available in DRAM of PCs sold in 2013 (tonnes)	2.46	3.90	0.16	459	
Market value of metals (million USD)	96.6	1.9	2.7	2.1	**103.4**
Value fraction	93.5%	1.8%	2.6%	2.0%	
As% of global demand	0.05%	0.34%	0.002%	0.002%	
As% of demand from EEE sector	0.83%	1.5%	0.012%	0.006%	
As% of global secondary production	0.19%	2.0%	0.009%	0.012%	

The actual number of DRAM modules POM is likely to be higher than the number in PCs POM, as modules which malfunction are replaced, and PCs are upgraded. Some PCs contain two modules when placed on the market, so data in *Table 3.4* are probably minimum values. It should also be noted, that the quantities presented represent the size of the theoretical 'reserve' of metals in waste arising, and not the quantities that will be available for recovery due to inefficiencies in the collection and pre-processing stages of recycling.

The estimated total value of metals in waste DRAM modules POM in PCs in 2013 was USD 103 million. 2.46 tonnes of gold was present, worth USD 97 million, 93.5% of total inherent value of the DRAMs. This is equivalent to 0.05% of global demand for gold, 0.8% of demand from the EEE sector and 0.2% of gold supplied from secondary sources that year. 3.9 tonnes of silver was present with a market value of USD 1.9 million and 1.8% of inherent value. This is equivalent to 0.3% of global demand, 1.5% of demand from the EEE sector and 0.19% of silver supplied from secondary sources. 0.16 tonnes of palladium were present with a market value of USD 2.7 million equal to 2.6% of inherent value. Palladium in DRAM is equivalent to 0.002% of global demand, 0.012% of demand from the EEE sector and 0.009% of palladium supplied from secondary sources that year. 459 tonnes, USD 2.1 million worth of copper were present in waste DRAM in PCs POM in 2013. This equates to 2% of inherent value, 0.002% of global demand, 0.006% of demand from the EEE sector and just 0.012% of copper supplied from secondary sources.

3.3.3   Outlook for future recycling potential

DRAM - *Figures 3.10-3.13* show projected gold, silver, copper and palladium content of DRAM modules to 2020 from a statistical analysis of DIMM data presented here, with 95%, 90% and 75% confidence limits shown as dashed lines. Gold content is projected to remain reasonably stable, while silver content will most likely remain roughly constant or even increase somewhat. Copper content is projected to increase by ~75%. Linear projection of Pd content in modules shows that Pd should have reached zero in ~2011 and predicts a negative Pd content by 2020. This is obviously not sensible, as Pd is still used in MLCCs of RAM modules and it is more likely that a minimum value is being approached. It has already been stated that Pd content in the alloy of the MLCC electrodes has already reached a minimum viable content of 2%. It is reasonable to assume that Pd content in individual MLCCs may continue to reduce until a minimum viable size of electrodes is reached, at which point Pd content of MLCCs will stabilise. If the number of MLCCs per module continues to rise as has been the case to date, then Pd content may begin to increase after this point in proportion to the number of MLCCs mounted on modules, at least until technological innovation results in replacement of Pd in MLCCs, or outright replacement of MLCCs in modules (and other PCBs).
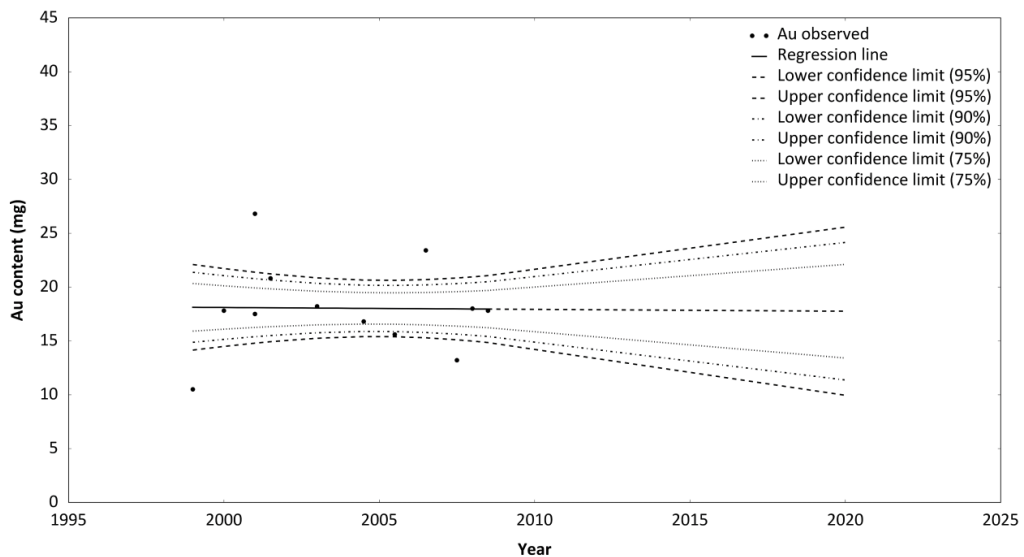
Figure 3.10 *Confidence intervals for projections of future quantities of gold in future waste DIMMs (produced in collaboration with I. Hallin)[144]*
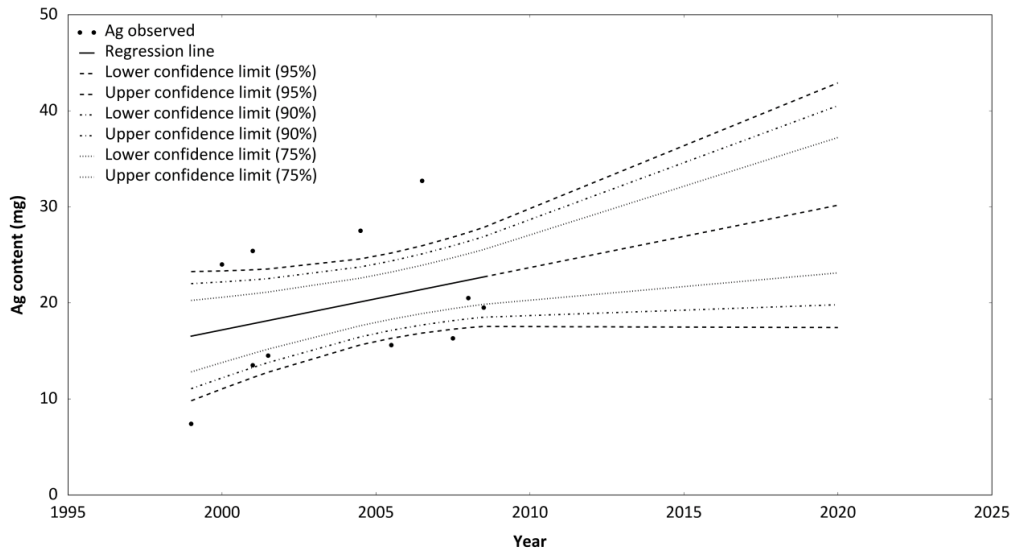
Figure 3.11 *Confidence intervals for projected quantities of silver in future waste DIMMs (produced in collaboration with I. Hallin)[144]*
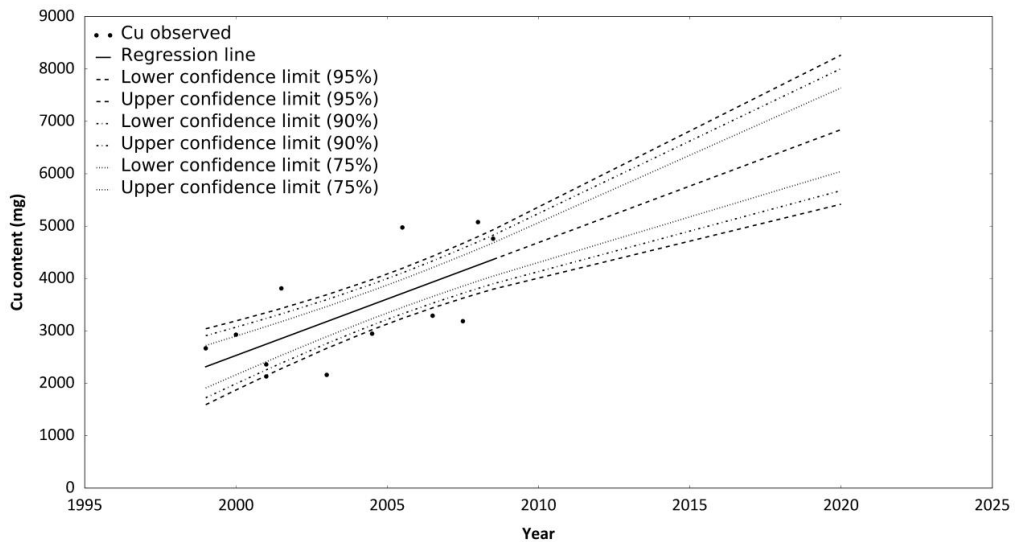
Figure 3.12 *Confidence intervals for projected quantities of copper in future waste DIMMs (produced in collaboration with I. Hallin)[144]*
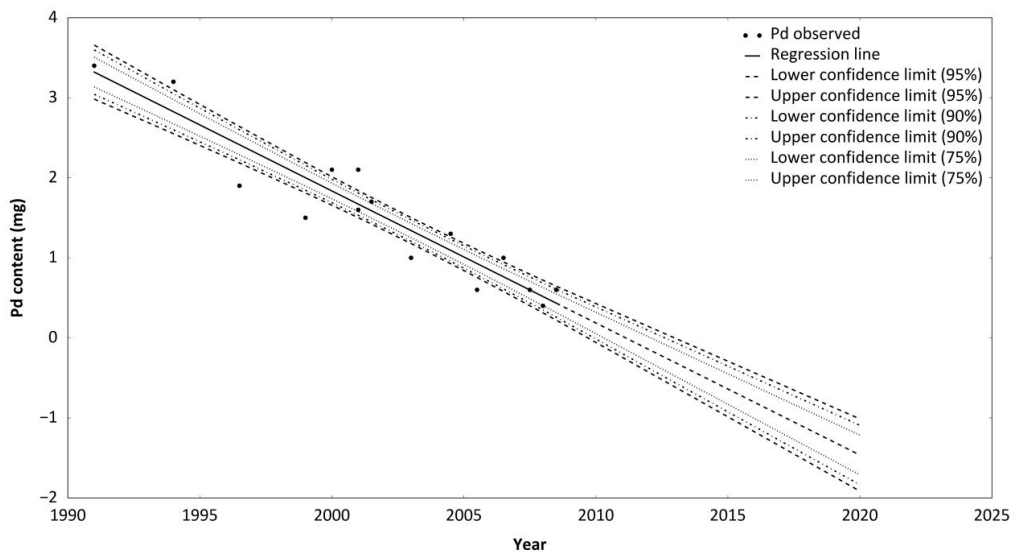
Figure 3.13 *Confidence intervals for projected quantities of palladium in future waste DIMMs (produced in collaboration with I. Hallin)[144]*

General WEEE - Global desktop PC sales are declining due to uptake of laptops, notebooks and tablets. Projections suggest a 28% reduction in global desktop PC sales over the next 5 years, from 133.9 million units in 2014 to 109.3 million units in 2019.[183] That said, PC sales in general are rising in the form of laptops and tablets.[173] This highlights the changing nature of the waste stream in general driven by technological innovation and changes in consumer demands. Projections of recycling potential and recovery potential (i.e. the total amount of potentially recoverable metals in items) of new items in the future as their volumes grow in the waste stream, such as the study by Cucchiella *et al*.[101] are important for issues previously discussed. The purpose of the Cucchiella study was to create a system through which the richest items in terms of material value for recovery could be targeted and therefore items in the study are ranked according to the inherent value of PMs and copper in waste items generated in 2020. This study applies available compositional data for numerous WEEE items available in the literature, to quantities of waste items generated in 2014 and a projection of generated waste in 2020 to calculate the potentially recoverable value from waste in 2020 and the growth in recoverable valuable materials in the future. To account for potential changes to composition a sensitivity analysis was performed in which the content of particular materials in items resulting in the majority of inherent value, was varied by 5%.

To highlight the impact that applying observable temporal trends in metal content to projections we have repeated the analysis for 2 different scenarios. *Scenario 1* is a base scenario and uses all data available in the previous study to quantify PMs and copper available in selected equipment types including a static composition of items; *Scenario 2* repeats the process but takes into account the temporal change in copper content observed in this study of RAM modules, applying a 75% increase in copper content in 2020 (*Table 3.5*). For consistency with the original study, average weekly market values for metals from Mar-Aug 2014 are used. Items selected for analysis have their copper and PM content concentrated in PCBs, as temporal data observed for RAM modules is indicative of temporal variations in PCB composition, not whole items which may contain additional copper as cables etc. In contrast to the original study, we have only included the values of PMs and copper in items, neglecting valuable bulk materials such as plastic and aluminium to highlight the impact on the value of copper and PMs in PCBs, which determine recycling potential of PCBs and represent a considerable fraction of recoverable value in items overall.

It can be seen by comparison of the scenario results that applying the increasing trend to copper results in a maximum of a 6% increase in projected potentially recoverable value for tablets. This is primarily due to the low proportion of recoverable value represented by copper in

comparison to gold in notebook computers and tablets, and silver in smart phones and cell phones. It is evident then, that any substitution of either of these metals over time through design change of items would result in a considerable mismatch between projections of recycling potential made based on static material content of PCBs in items, and the future reality.

Table 3.5 *Projections of future recycling potential of various WEEE items (based on data from Cucchiella et al., 2015).*[101]

Item	LCD notebooks	LED notebooks	Smart phones	Cell phones	Tablets	Avg value Mar-Aug 2014 (€/kg)
Metal						
Au (ppm)	0.22	0.22	0.038	0.024	.044	34,070
Ag (ppm)	0.25	0.25	0.244	1	.005	23,214
Pd (ppm)	0.04	0.04	0.015	0.009	.008	514
Cu (ppm)	135	135	14	26	27	5.2
Item weight (kg)	3.5	3.5	0.12	0.08	0.5	
Volume in 2014 (kt)	80	22	19	11.5	5.2	
Volume in 2020 (kt)	97	45	39	52	10	
2020 Scenario 1						
Au						
Content (t)	6.1	2.8	12.4	15.6	0.9	
Value (M€)	208	96	421	531	30	
Value fraction	56%	56%	19%	3%	93%	
Ag						
Content (t)	6.9	3.2	79	650	0.1	
Value (M€)	161	75	1841	15,089	2	
Value fraction	44%	44%	81%	97%	7%	
Pd						
Content (t)	1.1	0.5	4.9	5.85	0.16	
Value (M€)	0.6	0.3	3	3	0.08	
Value fraction	0.2%	0.2%	0.1%	0.02%	0.3%	
Cu						
Content (t)	3,741	1,736	4,550	16,900	540	
Value (M€)	19	9	24	88	2.81	
Value fraction	5%	5%	1%	0.6%	8%	
Total Value (M€)	389	180	2,288	15,711	35	
2020 Scenario 2						
Au						
Content (t)	6.1	2.8	12.4	15.6	0.9	
Value (M€)	208	96	421	531	30	
Value fraction	52%	52%	18%	3%	80%	
Ag						
Content (t)	6.9	3.2	79	650	0.1	
Value (M€)	161	75	1,841	15,089	2	
Value fraction	40%	40%	80%	96%	6%	
Pd						
Content (t)	1.1	0.5	4.9	5.85	0.16	
Value (M€)	0.6	0.3	3	3	0.08	
Value fraction	0.1%	0.1%	0.1%	0.02%	0.2%	
Cu						
Content (t)	6,548	3,037	7,963	29,575	945	
Value (M€)	34	16	41	154	5	
Value fraction	8%	8%	2%	1%	13%	
Total Value (M€)	**403**	**187**	**2,306**	**15,777**	**37**	
% increase	**4%**	**4%**	**1%**	**0.4%**	**6%**	

3.4   Conclusion

Elemental analysis of PC DRAM modules placed on the market over a period of approximately 17 years has shed light on temporal trends in PM and copper content of ICT PCBs with which to assess current and future recycling potential of PC DRAM modules, and PC PCBs in general.

DRAM is of a particularly high grade compared to other PC PCBs with an average composition for DIMMs of ~1,000 pm gold, ~70 ppm palladium, ~1,600 ppm silver and ~200×10^3 ppm (20 wt%) copper. The number of RAM modules in PCs POM in 2013 is ~153 million units which, based on the average composition determined for DIMMs, contained 2.5 tonnes of gold, 3.9 tonnes of silver, 160 kg of palladium and 459 tonnes of copper with a total market value of USD 103 million. Quantities of gold and silver in DRAM modules have been stable over the time period 2000- 2010. DIMMs show an increase in copper content over time, with a doubling of copper content of samples between 1999 and 2010. A decrease in the palladium content of modules at a rate of 5% per year is observed, which is attributable to miniaturisation of MLCCs over time. The palladium content of modules on the market in 2007 was only ~20% of that for modules on the market in 1993. It is likely that a minimum Pd content in MLCCs will be reached as Pd content of electrode alloys in these SMDs has reached a minimum, and there is likely to be a limit to how small these electrodes can be made in order to achieve sufficient capacitance for their function. It is probable that in the future the Pd content of modules (and other PCBs utilising MLCCs) will eventually begin to slowly rise again when additional MLCCs are incorporated to support advanced functionality.

In modern DIMMs, a general increase in copper content of 0.23g/module/year is observed over the period 1999-2008, which would result in an increase in copper content of ~75% if this trend were to continue until 2020. There is some question as to whether such a linear trend can continue, although as PCBs become more complex additional layers are incorporated into multilayer boards and this trend may enable an increasing trend in copper content to continue.

The value of the target metals in DRAM modules analysed ranges from USD 14,000- 55,000/tonne. Modern DIMMs, which represent the majority of RAM modules available in the waste stream today, vary in value by a factor of 1.65 over the range of USD 33,000- 55,000/tonne with an average value across samples of USD 44,000/tonne. The grade of DIMMs is higher than other PC PCBs reported, with the exception of results from Yamane *et al*. The major value fraction is consistently gold (>90% average for DIMMs).

Global sales of desktop PCs and therefore DRAM modules are diminishing as laptops and tablets gain further market share, and thus the total size of the 'reserve' of metals in PC DRAM modules is decreasing and therefore so is their recycling potential. Based on projections of global PC sales, it is likely that the annual number of waste DRAM modules produced will decrease in proportion with PC sales. Total quantities of gold and silver available in globally produced waste DRAM will decrease proportionally, it is likely that palladium content will be reduced significantly, but the amount of copper per DRAM module may well increase enough to compensate for the reduction in PCs sold so that the recoverable quantity of copper remains stable while the concentration of copper increases, which would enhance the viability of its recycling.

We have shown, by replication of projections of PMs and copper in notebooks, smart phones, cell phones and tablets made by Cucchiella *et al*.,[101] that incorporating temporal trends observed in DRAM modules into projections of recycling potential gives a variation of the total recoverable PM and copper value of ~0.4-6% for the items considered. Although this is a minor variation the high proportion of recoverable value in laptops and tablets as gold and silver, and silver in smart phones and cell phones, suggest that were temporal variations in these metals to occur in the future major discrepancies between recycling potential projections and the resulting future reality could be considerable, to the detriment of waste management operations and legislation based upon such projections.

We have found no temporal trends in PM content of DRAM which suggest that diminishing PM content in any one particular item will affect its recycling potential in the near future. However, shifts in consumption patterns of consumers away from current technologies to emerging technologies with lower PM content could have a detrimental effect on recycling potential of WEEE overall.

Finally, we note that the shift to cloud based software and data storage means that many of the current components of computers may no longer be necessary. Miniaturisation of computing devices, as has been seen in the shift from the use of conventional desktop PCs to the use of tablets for example, may result in modular components such as DIMMs, being eliminated. Such a shift in the design of devices would result in elimination of large gold contacts and significantly less recoverable value in devices, which would have a significant impact on recycling potential. It should be considered though that this shift to cloud based storage is accompanied by increased volumes of servers in data centres, which are still composed of modular components designed to be swapped out and replaced as necessary, and which generally represent higher grade material than PCs. Previous studies have shown that between

2008 and 2015 the amount of gold in German data centres would have increased by 61%, reflecting the increase in number of installed servers.[184] This may mean that the result of the shift to cloud computing simply results in a shift of where to recycle gold from.

4 Recovery of Critical Raw Materials from WEEE - Wales

Chapter summary

In this chapter, results of a trial conducted August 2012 – March 2013 on behalf of the Waste & Resources Action Programme (WRAP) entitled 'Critical Materials Recovery – Wales' (project code IMT002-012). The project aimed to investigate potential techniques for increasing the value generated gained from WEEE recycling in Wales through recovery of critical raw materials (CRMs), and to assess the suitability of adopting these techniques on an industrial scale at Metech Recycling (UK) Ltd. The trial was conducted at Metech and Swansea University, in partnership with Giraffe Innovations Ltd. These results formed the basis of the report 'Recovery of Critical Raw Materials (CRMs) – Wales.[185]

The first section of this chapter documents the work undertaken to collect WEEE samples form Metech Recycling for analysis, and to then evaluate the ability of available equipment to identify and quantify CRMs within samples. The second section reports CRMs identified within samples and their components. The final section outlines proposed methods to isolate CRM bearing components, and evaluates these methods in terms of cost-benefit and suitability for implementation at Metech to enhance value derived from CRMs in WEEE. Cost-benefit is only performed for processes which result in a material stream for which a downstream recovery process exists, so that an economic return on isolated materials can be generated. Barriers to recovery of CRMs in WEEE are discussed, along with recommendations for future actions to address these. These include a lack of available recovery infrastructure for CRMs from WEEE, and economic barriers resulting from the dissipative nature of applications of CRMs in EEE.

This work also forms a knowledge base for use by others seeking to develop advanced methods for CRM recovery from WEEE in the future, such as partners involved in ongoing trials under the current 'CRM Recovery' project.[186]

4.1 Introduction

Securing access to raw materials is a growing concern globally, and has become a priority for the European Union (EU) which imports nearly all of the non-energy raw materials it consumes.[100] Non-energy raw materials are linked to all industries and stages of supply chains, and in Europe it is estimated that 30 million jobs depend on these imports.[53] Green energy &

low-carbon technologies are crucial for mitigating climate change and improving/sustaining the environment. Scale of deployment of such technologies as photovoltaics (PV), wind turbines, energy efficient lighting and electric vehicles, may, however, be limited by access to CRMs. Technologies such as these, are vital for mitigating global climate change and currently account for 20% of global critical raw materials (CRMs) consumption. As clean energy technologies are deployed more widely in the future, their share of global consumption will grow.[20, 61, 187] The availability of raw materials is increasingly under pressure due to growing global demand and supply bottlenecks.

To address this, the EU Raw Materials Initiative identified a list of CRMs at EU level. A report was released in 2010 - 'Critical raw materials for the EU: Report of the ad-hoc working group on defining critical raw materials' which puts forward a concept of "criticality", where raw materials are labelled critical when the risks of supply shortage and the associated economic impacts of shortage are high.[100] Production of CRMs is concentrated within a small number of countries, many of which have resource hungry economies of their own. In 2010, >90% of rare earth metals (REMs) & Sb, and >75% of Ge and W was produced in China, 90% of Nb was produced in Brazil and 77% of Pt originated in South Africa. Today, this picture has altered little. In addition, many of the materials deemed critical, particularly the 'high-tech' metals such as In, are by-products of major metals production, and as such the market is not able to immediately respond to growing global demand by increasing supply. Rather the supply of these metals is highly dependent upon the markets and resulting supply of the major metals whose ores these minor metals are associated with (*see Figure 1.13*). It is also a lengthy process to bring new mines on-line, so rapid solutions to booms in demand for CRMs from primary sources do not exists.[188] Additionally, conservative policy affecting exports of CRMs such as export restrictions on REMs from China, and political instability in producer nations such as the ongoing conflict in DRC exacerbate CRM supply issues and heighten global resource-security concerns, pushing up market values.[100, 149]

In the EU report, 41 materials were assessed. [100] *Figure 4.1* shows these materials in terms of supply risk verses economic importance: The EU report concluded that the 14 raw materials falling within the top right cluster (known as the EU14) were considered "critical" due to their high relative economic importance and high relative supply risk. These CRMs are listed in *Table 4.1*. Since the initial report the EU14 list was revised in 2013 to give the EU20 list of CRMs, a further revision is due this year (2017) reflecting the fluid and time dependent nature of materials 'criticality'.
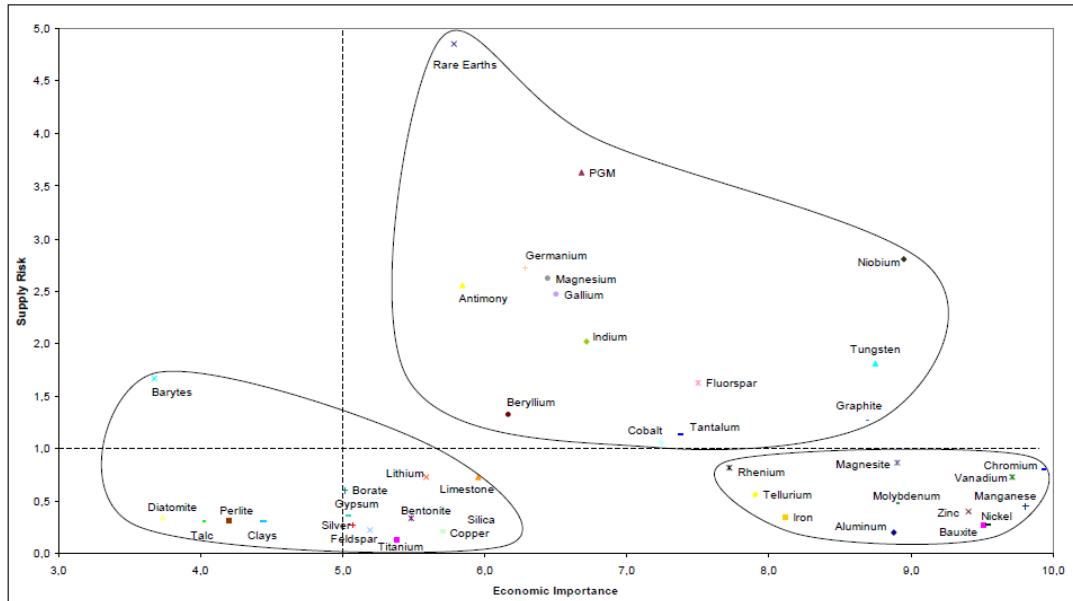
Figure 4.1 *Supply risk versus economic importance of 41 materials evaluated for the EU showing the EU14 CRMs[100]*

Table 4.1 *List of the EU14 Critical Raw Materials[100]*

Antimony	Beryllium	Cobalt	Fluorspar	Gallium	Germanium	Graphite
Indium	Magnesium	Niobium	Platinum Group Metals (PGMs)	Rare Earth Metals (REMs)	Tantalum	Tungsten

PGMs: Pt, Pd, Ru, Ir, Rh, Os; **REMs**: the lanthanide elements and yttrium (Y).

In addition to the EU14, future supply of all materials of economic importance, particularly those which are rare or 'high value', must be considered by the industries/sectors which rely upon them. Priorities applied in criticality assessment differ across sectors and so will the picture of materials criticality. Au & Ag are excluded from the EU14 despite the criticality of these metals to other sectors (see *Section 3.1.1*). This study includes Au and Ag as target CRMs with the EU14. It should be noted, the terms precious metals (PMs) and PGMs are generally used interchangeably. However, the EU14 definition of PGMs excludes Au and Ag. To distinguish these sets of metals, further discussion uses the EU14 PGMs definition, and PMs refers only to Au and Ag.

4.1.1 *Critical Raw Materials in EEE*

All strategically important materials mentioned so far are used extensively by the EEE sector (*Table 4.2*). For this reason, WEEE represents an important secondary reserve of CRMs.

Table 4.2 *Major Applications of Critical Raw Materials in the EEE sector*[51, 144, 189]

Critical Raw Materials (CRMs)	Major End Uses
Antimony (Sb)	SbO₃ flame retardants, hardener in Pb-acid battery electrodes; used as a decolourising & fining agent for glass e.g CRTs, cameras, photocopiers etc.
Beryllium (Be)	Used in EEE as Be-Cu alloys, widely used in telecoms & automotive sector
Cobalt (Co)	Mainly used in cathodes of Li-ion batteries, superalloys for jet engines & turbines; and SmCo permanent magnets
Fluorspar	Acid-grade fluorspar is a source of HF: a precursor in synthesis of almost all fluoro-chemicals, e.g fluorocarbons refrigerants replacing CFCs; used in IC & production
Gallium (Ga)	Major use in ICs, laser diodes, LEDs, photo-detectors, and PV solar cells
Germanium (Ge)	Used in fibre optics; IR optics; and semiconductors for EEE e.g. phones & PV
Graphite	Natural graphite is used in electrical arc lamp electrodes and batteries
Indium (In)	Indium-doped tin oxide (ITO) is a TCO used in electrodes of flat screens, IR detectors, high-speed transistor; and PV cells
Magnesium (Mg)	Used in laptop housing alloys
Niobium (Nb)	Used in the nuclear industry as Nb-Zr for fuel cells;. Nb-Ti-Sn alloy is used in magnetic coils of MRI equipment. Pure Nb metal used in cathodic protection systems for corrosion resistance
Tantalum (Ta)	Used in SMD Ta-capacitors, hearing aids & pacemakers
Tungsten (W)	Used for hard metals for cutting tools (tungsten-carbide); and heat resistant interconnect alloys in ICs
REMs	
Yttrium (Y)	Used in phosphors of CCFLs, CRTs and LEDs
Lanthanum (La)	Used in phosphors and electrodes of Li-ion battery electrodes (Li-.
Cerium (Ce)	Used in phosphors & batteries
Praseodymium (Pr)	Magnetic alloys and batteries
Neodymium (Nd)	NdFeB (NIB) magnets for HDDs, wind turbines, headphones and speakers; electrodes in NiMH batteries
Samarium (Sm)	Neodymium iron boron (NdFeB) magnets, cobalt magnets (SmCo), batteries
Europium (Eu)	Used in red phosphors
Gadolinium (Gd)	Used in phosphors & permanent magnets
Terbium (Tb)	Used in phosphors & permanent magnets
Dysprosium (Dy)	Used in alloy of NIB magnets
Erbium (Er)	Used in laser applications
PGMs	
Platinum (Pt)	HDD platters and thermocouple wire
Osmium (Os)	Used in Pt alloy for electrical contacts, light bulb filaments and medical implants
Iridium (Ir)	Spark plug tips, iridium crucibles to produce high-quality crystals for electronics
Ruthenium (Ru)	Hard disks, chip resistors, flat screen displays, plasma display panels
Rhodium (Rh)	LCD glass manufacturing, alloyed with Pt in thermocouple wire
Palladium (Pd)	SMDs, mainly MLCCs and hybrid ICs
Precious Metals	
Gold (Au)	ICs and contacts
Silver (Ag)	Used in numerous SMDs (ICs, chip resistors, MLCCs etc.) and Pb-free solder
Copper (Cu)	Present in almost all EEE components: connectors, contacts, PCB tracks, cables, transformers, turbines, electric motors etc.

In light of concerns over the future supply of CRMs, UK governments have highlighted increased recovery from wastes as a crucial strategy to enhance domestic CRM supply and mitigate issues of resource criticality. In 2012, in response to private sector concerns about the

availability of raw materials, Defra launched the 'Resource Security Action Plan' to help businesses profit from recovery of PMs, PGMs and other CRMs present in household WEEE, through better segregation and recovery.[149] The plan recognises the likely increase in demand for CRMs and calls for improvements to product design to support reuse and more efficient recycling of CRMs (DfRR), and substituting primary CRMs with secondary materials available within the economy.

According to the House of Commons report on 'Strategically Important Metals', the UK is recovering substantial quantities of Pt, Rh, Pd, and Au.[190] Research commissioned by WRAP has shown that the majority of UK treatment is primary treatment with little refining of metals from WEEE to their final pure states.[191] Rather, metal concentrates are produced and shipped for final refining in Europe, or the Far East. Low collection rates for WEEE prevent potentially recoverable CRMs from entering the recycling process chain. Mass based recovery rates of materials from WEEE which is collected and makes it way to recyclers are high, with >90% of materials recovered/re-used. However, this mass based rate of recovery accounts mainly for bulk metals, plastics and glass recovered from shredded materials produced by automated pre-processing. Such mass based reporting of recycling fails to highlight low recovery rates for CRMs which represent only a small mass fraction of the waste stream but a significant proportion of the embodied economic, environmental and strategic value of WEEE. Automated pre-processing in which products are shredded results in dispersion of CRMs throughout bulk material fractions, resulting in losses through unintended co-seperation.[62] The consequential detrimental effect of this dispersion on recovery rates of PMs in WEEE has been discussed (*Section 1.4.2*), and is applicable to recovery of CRMs from WEEE in general.

WRAP works with governments and business to deliver practical solutions which improve resource-efficiency. Management of WEEE is a key action area for WRAP who have launched numerous initiatives to improve the industrial ecology of the EEE sector (e.g. eSAP). WRAP is particularly focused on addressing the challenges of CRM recovery from WEEE, and for this reason, in 2012 commissioned the research reported in this chapter (IMT002-012: Recovery of Critical Raw Materials – Wales).[185] WRAP also leads the ongoing EULife pan-European 'CRM Recovery' project which aims to investigate the link between WEEE collection methods and CRM recovery rates, whilst investigating novel recovery processes which enhance CRM recovery.[186]

4.1.2   Trial Aims & Objectives

WRAP sought to work with the UK WEEE recycling industry to investigate opportunities in the treatment process to recover CRMs prior to the occurrence of dissipative losses, whilst

maximising the value generated for recycling businesses. The aim of the trial was to isolate components containing CRMs into fractions for downstream recovery during manual pre-processing, avoiding losses through shredding and in downstream recovery processes which do not target CRMs for recovery. This would increase their recovery rates from WEEE, thereby enhancing the value exploited from WEEE by recyclers.

WRAP commissioned Giraffe Innovations Ltd in partnership with Metech Recycling (UK) Ltd. who operated a manual pre-processing operation at their Approved Authorized Treatment Facility (AATF) in Hirwaun, South Wales. The trials were conducted by the author on behalf of Metech Recycling UK Ltd. who sponsored this EngD. As common with most AATFs, Metech already recovers PCBs which are sent for precious metals recovery (i.e. gold, palladium, silver, and copper are recovered). The aim of the trial was to develop and evaluate processes which could be implemented by Metech to improve CRM recovery rates and increase profitability of recycling operations. The findings of the trial were used as the basis of recommendations to enhance CRM recovery across the sector.[185]

4.2   Methodology

The stages undertaken during the trial were as follows. *Stage 1* - samples were selected and gathered from WEEE received by Metech for analysis & use in subsequent disassembly trials. *Stage 2* - available equipment for identification and quantification of CRMs within samples, and methods for doing so were evaluated. *Stage 3* - CRMs were then identified within samples. *Stage 4* - processes for disassembly of WEEE and generation of CRM bearing components as suitable material streams for downstream recovery were evaluated in terms of their suitability for implementation at Metech to enhance value derived from WEEE and CRM recovery rates.

4.2.1   Selection of Samples for analysis

WEEE items known to contain CRMs were selected based on: the proportion of the waste stream flowing through Metech each type of equipment represents; prior knowledge of likely composition based on the experience of Metech staff; and a review of available literature. These included items that had previously been problematic to recycle and extract value due to poor product DfRR, or high volume items from which the potential exists to recover regular quantities of CRMs. Replicate samples of WEEE items were collected (up to 12 samples of each item) to provide sufficient numbers for repeat analyses and to investigate a number of recycling methods on each.

4.2.2   *Evaluation of procedures for qualitative & quantitative determination of CRM content in WEEE*

For the purposes of the trial it was necessary to: identify CRMs within components; develop a library of these components to inform further processing; perform quantitative analyses to establish target materials content of downstream recovery processes. This information is necessary to establish likely financial returns for material fractions generated, for use in cost-benefit analysis (CBA) of proposed recycling processes to establish the economic viability of their implementation at Metech.

X-ray Fluorescence Spectroscopy (XRF)

In order to 'prospect' CRMs in samples, methodical analysis of sample components was necessary. An XRF spectrometer was used to detect CRMs in samples[*] This is a non-destructive technique which avoids the use of potentially hazardous chemical digestion procedures prior to sample analysis as required for alternative atomic spectroscopy techniques such as AAS or ICP-MS. The method was therefore thought to be suitable for use on-site at Metech by staff who have no formal training in practical chemistry. The instrument selected was the XDAL-FD system, leased from Fischer Instrumentation (GB) Ltd.

The instrument consists of: a movable stage on which whole PCBs are placed; a small X-ray beam (max diameter 1 mm) with variable cross-sectional area and shape; and a camera for imaging samples and targeting the x-ray beam. The instrument can determine which elements are present from characteristic energies of emitted x-rays from samples, automatically assigning peaks in the emission spectrum to elements. From the number of emitted x-ray photons detected for each element (i.e the area under the peak corresponding to a particular element, or counts per second -cps) the instrument can quantify the relative abundances of elements present in the scanned area of samples and report the relative mass percentage of each element present (rel.%), i.e. the sum of the relative masses of detected elements is 100% (*Figure 4.2*). Note that this is not the true weight percentage of elements in the sample since the mass of undetected material, such as light elements in plastics etc., is unknown.

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[*] for details of the instrument, its operational principles and experimental parameter used please see *Section 2.2.4*.
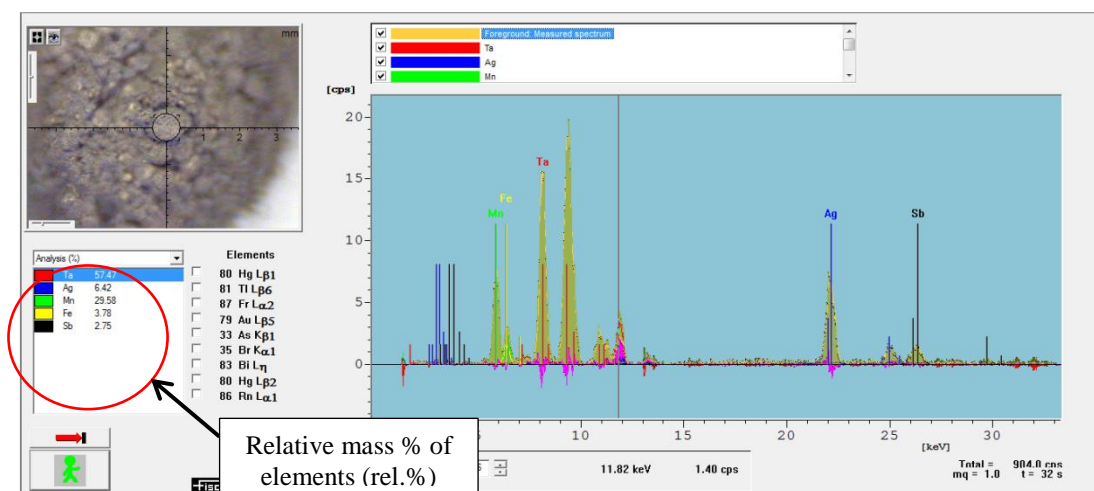
Figure 4.2 *Analysed x-ray emission spectrum of a powder sample and measured relative mass percentages of elements*

By moving the stage and customizing the beam, individual analyses of SMDs in place on PCB assemblies are possible. Spectra and images of components are also easily obtained with this technique. Although relatively simple in principle, using XRF for qualitative or quantitative analysis is complicated by 'matrix effects' i.e. the X-ray absorption profile of the sample and competitive absorption of both the excitation X-rays and emitted X-rays.[135] This is particularly problematic for non-homogeneous samples such as WEEE - especially layered structures where the top layer(s) can prevent penetration of X-rays deeper into the sample.

In light of this, it was necessary to evaluate the ability and limitations of the XDAL instrument in detection and quantification of CRMs in WEEE samples, and its suitability for use by Metech. The details of this assessment are given in Appendix A. For the purpose of the work described here the following points on instrument characteristics and performance are significant.

When attempting to detect CRMs in encapsulated components, matrix effects may necessitate grinding or cutting open of components to detect contained CRMs. Where such procedures were necessary to identify CRMs is indicated in the results section. Unless otherwise stated, CRMs were detected with surface scanning of components only. 16s scan times provide best outcome in terms of S/N ratio in spectra and time efficiency. Where elements detected represent only a few % of the overall composition of ground materials (as is the case for most CRMs present), instrument precision for determining these elements is ~10%, too high to base significant alterations to recycling operations upon. The XDAL instrument is an excellent rapid qualitative and/or semi-quantitative method for rapid identification of CRMs in samples. Much calibration and preliminary standardisation work would however be required before the

XDAL could be used as a reliable quantitative technique with comparable precision to other methods such as AAS, ICP-OES or ICP-MS. This is due to low precision resulting from poor homogeneity in ground samples and large particle sizes relative to beam diameter. Therefore, the XDAL is used to identify CRMs in samples only and where necessary quantitative analysis is conducted with AAS or ICP techniques.

4.2.3   Identification of Critical Materials in Samples
Sample disassembly and XRF identification of CRMs in samples

Disassembly was performed with standard tools, e.g. powered / manual screw drivers, snips, pliers, scalpels, and powered grinding & cutting tools. XRF was then used to identify CRMs in samples.

Generation of an image library of CRM bearing components

Following identification of CRMs in PCB components with the XDAL, a library of component images and spectra was compiled to support decision making on further processing. Once a component had been identified as containing target materials, its image was captured directly using the camera of the XDAL and saved with its corresponding x-ray emission spectrum. It was then possible to identify CRM bearing components in PCBs visually by reference to this library. Example images and spectra of components are presented throughout *section 4.3.2*.

From images of PCBs it was possible to assess: the presence of gold in contacts on PCB surfaces; the number of contacts; and the type and number of components present on the PCB. To verify accuracy of evaluation using the image library, an image of a PCB was taken and a colour coded overlay applied to the image indicating concentrations of target elements. The accuracy of the assessment, PCB components of the boards were methodically analysed and the results compared to the results from visual inspections.

4.2.4   Evaluation of Processes for Implementation
Assessment of disassembly and CRM concentration processes

Processes enabling more rapid disassembly may reduce process costs, which is essential for the recovery of small, low value quantities of CRMs from WEEE. Methods of sample disassembly, isolation and concentration of CRM bearing components as distinct material streams for downstream recovery were developed and evaluated. These included processes for disassembly of whole items and their sub-assemblies e.g. disassembly of mobile phones into PCBs, batteries, screens etc.; and isolation of components from sub-assemblies such as

removal of SMD components form PCBs with subsequent sieving to separate components by grade & CRM content.

Following disassembly and PCB isolation, components identified as CRM rich require isolation from whole PCBs in a cost-effective manner to generate material streams suitable for downstream recovery i.e. a CRM pre-concentration method. Several methods were evaluated. Supported by data in the compiled library of X-ray emission spectra and images of components, methods were trialled which enabled isolation of CRM bearing components from PCBs and separation of these components into distinct material streams in which particular CRMs are concentrated. This was an attempt to separate CRMs which are lost in current recovery processes (e.g. Ta capacitors) into material flows of their own for diversion to alternative recovery processes.

The methods trialled were also evaluated in terms of their suitability for scale-up and implementation at Metech Recycling considering aspects such as practicality and compatibility with current environmental permits. It should be noted that Metech's environmental licenses do not permit the use of any liquid based processes. For this reasons techniques involving the use of acids for digestion or flotation processes were excluded from the trial.

For each method, necessary information to perform a cost-benefit analysis (CBA) was captured including: time taken, energy required, costs of necessary equipment and consumables, processing capacity. Output fractions suitable to identified CRM recovery processes were analysed quantitatively to establish a 'value' based on likely returns from sale of materials to refineries. CBA was only performed for processes which generate output fractions for which suitable downstream recovery process for valorisation of these fractions could be identified.

<u>Disassembly & separation processes</u>
Manual Disassembly -Processes involved use of the following tools & equipment.

Precision power cordless screw driver - Used to remove small screws from all devices to disassemble samples into their component parts, particularly for disassembly of phones, MP3 players, cameras, LCD screens.

Snips - Used to cut around surface mounted PCB components to isolate them; to directly cut connections between PCBs and components; to remove surface mounted components from

TV power boards, cut sections of Mg-alloy casing away for analysis; and open SMD components for XRF analysis of internal CRMs.

Pliers - Used to pull relatively large SMD components & contacts from PCBs; and crush SMD components prior to XRF analysis of internal CRMs.

Scalpels (various thicknesses) - Used to cut SMDs from PCBs boards when components are connected by a series of thin contacts e.g. ICs; thicker scalpels were used to remove components soldered directly on to PCBs.

Flat head screw driver - Used to scrape low profile soldered SMDs from PCBs when they cannot easily be removed with scalpels.

Dremel multi-tool with grinding and cutting attachments - Used to cut open Li-ion batteries for XRF analysis of internal electrode materials; cut open/grind layers away from SMDs for XRF analysis of internal CRMs; cut open housings of WEEE samples for rapid disassembly as an alternative to unscrewing; and cut away precious metal rich regions of PCBs i.e. those with large regions of Au-alloy such as edge contacts.

Hammer - Used to break open the steel housing of magnetrons and break magnets for rapid isolation without full disassembly.

Scissors - Used to cut through plastic and foil to gain access to components during disassembly; and surface stripping SMDs from PCBs.

Standard Precision Screw driver kit – used to remove small screws from devices during disassembly process allowing isolation of specific components of WEEE samples.

Guillotine – Used to cut through PCB fibre-glass laminates of PCBs to isolate gold edge contacts. Method is only suitable for straight cuts and boards with thin, flexible substrates. Guillotine was also used to cut through plastic of LCD housings for rapid disassembly.

Wet Tile Cutter - A Rubi ND-200 Wet Saw / Electric Tile Cutter was used to isolate components from PCBs e.g. edge contacts as shown in *Figure 4.3*; used as an alternative to the guillotine for rapid disassembly of samples.

Figure 4.3 *Removing edge contacts from server boards with a Rubi ND-200 wet saw / electric tile ccutter*

Thermal Methods - Additional processes trialled to enhance the rate and cost-benefit of disassembly and component isolation processes included the following.

Cryo-cracking - Liquid nitrogen was used to embrittle plastic housings and casings of products **7-10** so they could be easily fractured for access to constituent components. Items were submerged in liquid nitrogen for 20 seconds, then removed and struck with a hammer to shatter and remove the casings to allow simple 'cherry picking' of internal CRM bearing components. An example of a Sony Walkman MP3 player following liquid nitrogen treatment and fracturing is shown in *Figure 4.4*. Cryo-cracking is widely used in plastics recycling.[192]

Figure 4.4 *Sony Walkman Following Liquid Nitrogen Treatment (left), cracked open to reveal internal CRM bearing components (right).*

De-soldering of PCBs (thermal methods) - Heating methods were investigated to soften solder attaching SMDs to PCBs, enabling their isolation. As thermal treatment of whole PCBs is a complex process, de-soldering methods could only be trialled on a small scale using the following methods.

Blow Torch - PCBs were clamped in place above a beaker and heated using a Dremel 2200 Versaflame blow torch to soften solder and SMDs were scraped from PCB surfaces using a scalpel, collecting in a beaker below.

Soldering Iron - A soldering iron was used to manually de-soldering individual SMDs.

Paint Stripping Gun - A 2kW paint stripping heat gun was used to soften solder in specific areas of PCB assemblies.

Solder Bath - Solder baths are commonly used for soldering PCB assemblies. A variety of boards were placed on the surface of molten solder in a small 500 W solder bath (*Figure 4.5*). This softened the solder allowing components to be scraped from PCB surfaces in bulk, or individually removed with tweezers.
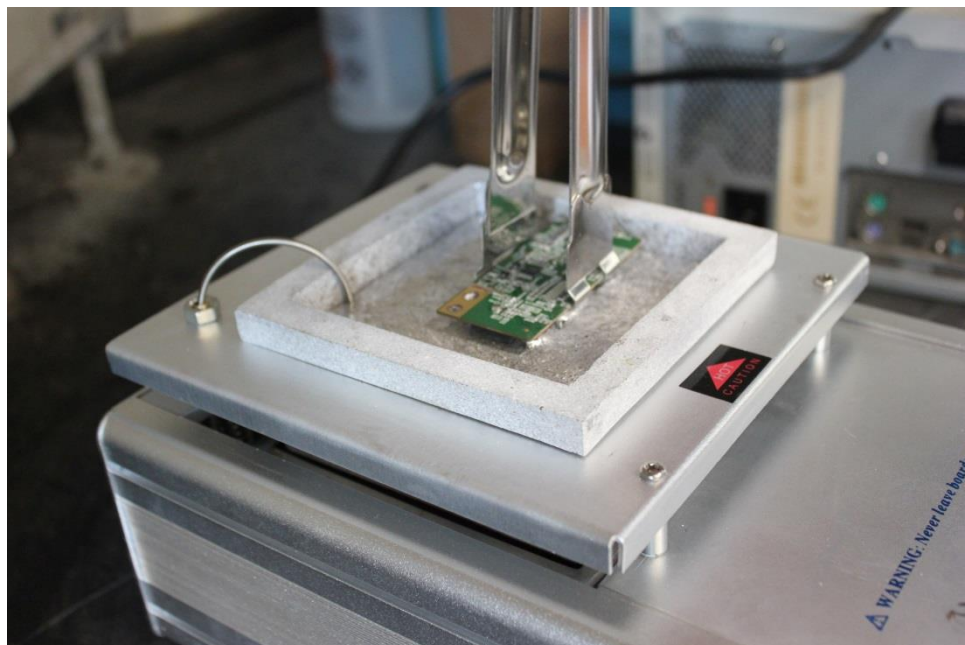
Figure 4.5 *PCB placed on to the surface of liquid solder in a small solder bath*

NIR oven - An Adphos NIR lab unit with 1 m heated length was used to heat boards and soften solder. A power setting of 70%, rates of travel through the heated length of between 5 m/min

and 7 m/min, and heating temperatures of 200-240°C used in an attempt to identify optimum conditions.

CRM concentration processes

Microwave Ashing - Dry ashing is the act of heating a material to a high temperature to volatilize or decompose organic components, in this case epoxy of PCBs, producing an ash containing inorganic components, in this case CRMs and target materials for recovery. Ashing was used to concentrate CRMs in isolated edge contacts. A microwave furnace which was used to ash samples at 800 °C for 30 minutes within fibre crucibles. Ashing was conducted by CEM using a CEM Phoenix microwave muffle furnace.

Sieving – SMDs were sieved using a range of mesh sizes, to segregate SMDs by size and investigate the suitability of the method to generate material streams in which particular CRMs are concentrated. SMDs isolated from PCBs were combined with virgin SMDs donated by Metech recycling to give an appropriate quantity with which to evaluate the sieving procedure. These were loaded into the top of the stack of sieves of various aperture sizes which was shaken for 60 s. Sieves with the following aperture sizes were used in a stack. 9.52 mm, 2.80 mm, 1.68 mm, 1.4 mm. SMDs and CRMs contained in each fraction were recorded.

Cost benefit analysis (CBA)

The second stage of the project was to assess the application of separation processes & concentration processes on an industrial scale through Cost Benefit Analysis (CBA). The value of material streams generated (Total Benefit – B) was compared to the total costs of its production from WEEE samples (Total costs – A).. Monetary values have been assigned to each cost and benefit identified using data on expenditure and revenues from sale of materials from Metech and other industrial sources, with any assumptions or estimations discussed below.

Total Costs (A) – Total costs are calculated from: operational overheads absorbed as an hourly labour rate incurred during processing provided by Metech Recycling (UK) Ltd., a full breakdown of which is given in *Table 4.3* (£15.838/hour at the time of the assessment (2013, based on operational costs in 2012); chemical purchase costs; costs of electricity consumed (£0.09546/kWh, taken directly from Metech's power bill at the time of the trial); refining & treatment charges for CRM materials fractions produced based on terms provided by BASF precious metals.

Table 4.3 *Overheads for Metech by percentage split*

Overheads	% Split
Transport Costs	5.45
Disposal Costs	0.32
Production Facility Rent/Rates	16.72
Salaries & Benefits-Production	28.99
Salaries & Benefits- Admin & Sales	27.95
Rent, Rates & Insurance	2.36
Heat & Lighting	1.54
Machinery Servicing & Repair	0.16
Premises Repair	0.20
Security System Maintenance & Rental	0.25
UK Business Expenses	1.01
UK Marketing Expenses	1.14
Postage	0.06
Telephone	0.95
Stationery & Books	0.32
Professional Fees	3.74
Equipment Hire	0.55
Repairs & Renewals Tools & Equipment	0.09
Computer Repairs & Maintenance	1.35
Cleaning	0.73
Bank Charges	0.55
Subscriptions & Site Waste Management	1.48
Clothing Costs	0.04
Refreshments	0.10
Miscellaneous Costs	1.50
Premises Expenses	0.06
Safety Equipment & Supplies	0.07
Production Expenses	1.54
Other Business Expenses	0.77
TOTAL	**100.00**

Total Benefits (B) - This is based on: the value of recovered component materials (from quotes received from refineries following submission of samples to them for assay and market values for metals at the time of the trial i.e. Au - £35.9652/g; Cu – £5.46/kg; Ag – £0.69495g; Pd – £14.3566/g), and; avoided refining charges and transport charges because of concentration enhancement of target materials in output fractions.

Cost Benefit (C) –is calculated as the difference in total costs and total benefits (*C=B-A*). CBA has been carried out on a number of combinations of separation techniques, each specific combination being suitable for a particular sample investigated. E.g. cryo-cracking to isolate PCBs of MP3 players, mobile phones and cameras, with solder bath treatment to isolate SMDs. This enabled identification of the most profitable processing options for samples.

Notes and Assumptions:

i) Times taken for processes are obtained from trials on single items and assumed to represent the average ability of Metech employees for a pace of work which can be maintained throughout the day. Cost-benefit analyses are therefore indicative of achievable benefits only, and a time in motion study on site would have to be conducted to verify profitability of proposed processes following scale up and implementation. It is assumed that while an item is being processed e.g. submerged in liquid nitrogen, or being ashed, employees are working on other stages of the processing.

ii) It is assumed no material is lost in any of the separation processes themselves.

iii) It is assumed that recovery rates for metals from ashed and unashed samples are equal and that all refining terms remain the same.

iv) The value of Ag, Au, Pd and Cu content in isolated fractions were obtained directly from BASF Metals Recycling (refinery) following assay of submitted samples, assuming a recovery rate of 98% for Au & Cu, 95% for Ag and 85% for Pd. Refiners only pay the supplier on recovered Au, Ag, Pd and Cu content, and no rebate is given for other materials present.

v) Treatment charges of £1.80/kg for material received, and refining charges of £475/kg for Pd, £200/kg Au, £25/kg for Ag are applied by refineries. No refining charge is applied for Cu. (terms supplied by BASF precious metals at the time of this study – Feb 2013).

vi) The financial benefits of separating components are based on production of 500 kg of components, which is the minimum quantity required for refining.

4.3   Results & Discussion

4.3.1   *Selection of Samples for analysis*

Table 4.4 lists samples used in the trial. Sample **1**-**6** & **11**-**16** are generated by Metech in existing manual disassembly operations. Samples **7**-**10** are whole products which are not currently disassembled by Metech because it is too expensive to do so. Samples (**11- 16**) were chosen to demonstrate and evaluate methods for isolation of CRM bearing components from PCBs.

Table 4.4 *Samples for analysis supplied by Metech Recycling (UK) Ltd*

#	Sample Item	No. of samples	Type
1	Sanyo domestic microwave magnetron	12	Component
2	Hard Disk Drives (assorted 3½ inch drives)	12	Component
3	TV Power boards (2 types)	6	Component
4	STB front panel PCBs (2 types)	12	Component
5	Sony Li-ion laptop batteries	11	Component
6	HP Laptop screens	12	Component
7	Mobile Phones (assorted)	12	Whole product
8	MP3 players solid state memory (assorted)	6	Whole product
9	RSA security anti-hacking dongle	12	Whole product
10	Digital Cameras (assorted)	12	Whole product
11	PCB from TV LCD	5	Component
12	Graphics card	5	Component
13	Server board	5	Component
14	Ethernet card	3	Component
15	Power board from Fridge	2	Component
16	Main PCB from TV	1	Component

4.3.2 *Identification of Critical Materials in Samples*

<u>Sanyo domestic microwave magnetron</u>

Ferrite cores from the filter box and ring magnets as shown in *Figures 4.6* were isolated from magnetron samples. Iron oxide and barium or strontium carbonate are used in manufacturing of hard ferrite magnets.[193] XRF of the ring magnets shows iron and strontium (*Figure 4.7*) to be present, with the XRF software indicating the presence of small amounts of critical Co. The Co $K\alpha_1$ peak (6.93 keV) are masked by the intense Fe $K\alpha_1$ and $K\beta_1$ peaks (6.40 and 7.06 keV respectively) and the presence of the Co $K\beta_1$ peak (7.65 keV) is not obvious due to its low intensity. XRF shows ferrite cores to be predominantly iron with some Zn and Cu and without the strontium carbonate ceramic (*Figure 4.8*). This probably means that its composed of Ni-Zn-Cu ferrite.[194] The presence of cobalt is once again automatically detected by the software, however the same issue with peak masking and low intensity is observed. The presence of Co in each sample was confirmed by AAS, and is discussed in *section 4.3.3*.
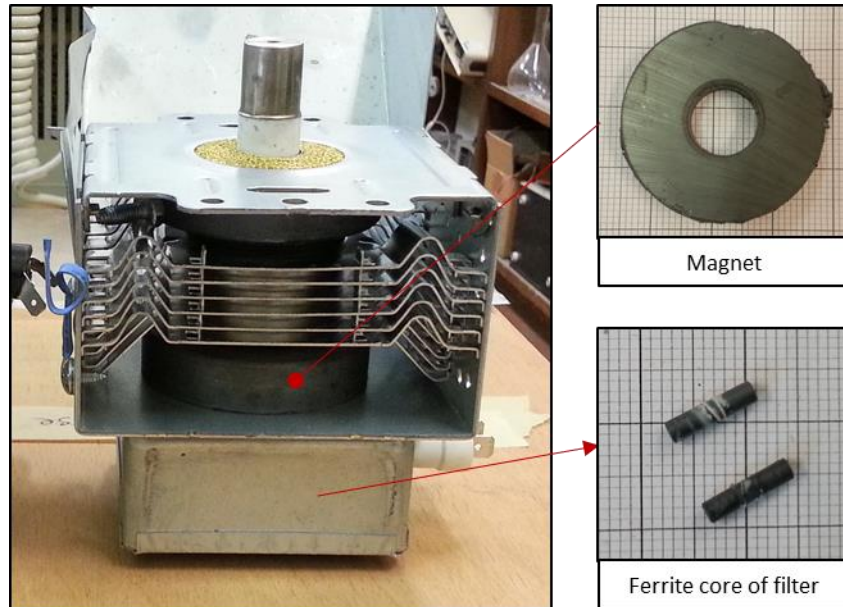
Figure 4.6 *Magnetrons (top left) and isolated magnets (top right) and ferrite cores of the filter (bottom right)*
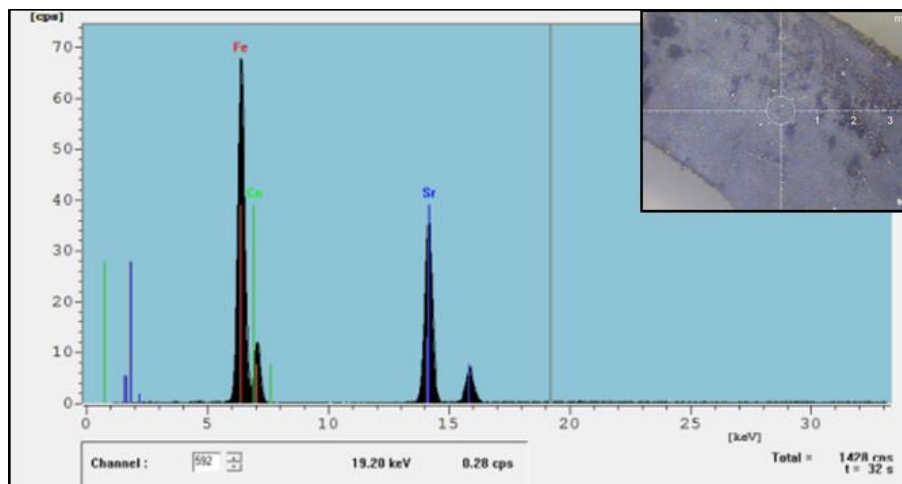
Figure 4.7 *XRF spectra of magnetron magnets indicating the presence of Co*
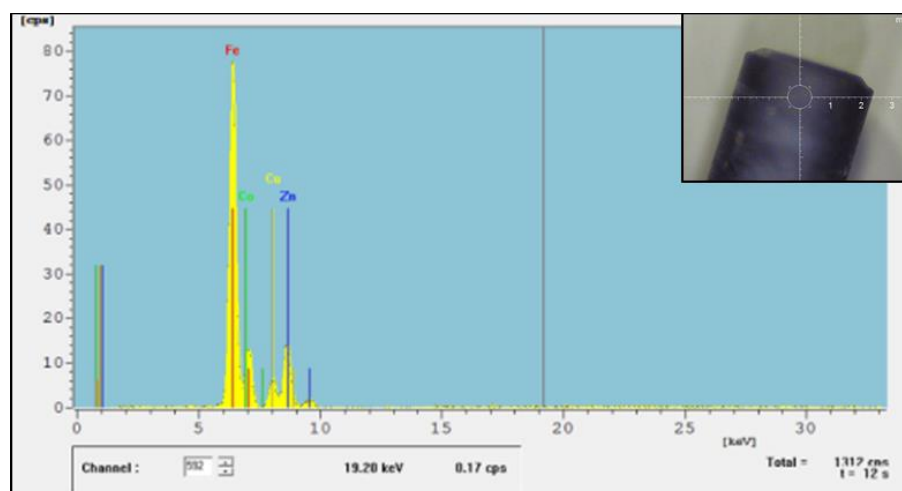
Figure 4.8 *XRF spectra of ferrite cores from the magnetron filters indicating the presence of Co*

Hard Disk Drives (HDDs, 3½ inch)

CRMs in hard disk drives (HDDs, *Figure 4.9*) are well known and a comprehensive investigation into the concentrations of CRMs in laptop HDDs (2½ inch drives) based on data available from manufacturers and recyclers was conducted by the Öko-Institut e.V.[19] The main CRM bearing components are the voice coil accelerator magnets and the PCB of the device. The most common alloy for HDD magnets is $Nd_2Fe_{14}B$ which are known as neodymium iron boron (NIB) magnets; dysprosium may also be present. The platters of the HDD are also reported to contain PGMs.[19]

Figure 4.9 *Typical hard disk drive (HDD)*

Platters - No Pt was detected by XRF in the platters of HDDs.

NIB magnets   Two NIB magnets are present in each HDD. XRF analysis of the magnets revealed the presence of Nd in the alloy, no Dy was detected (*Figure 4.10*).
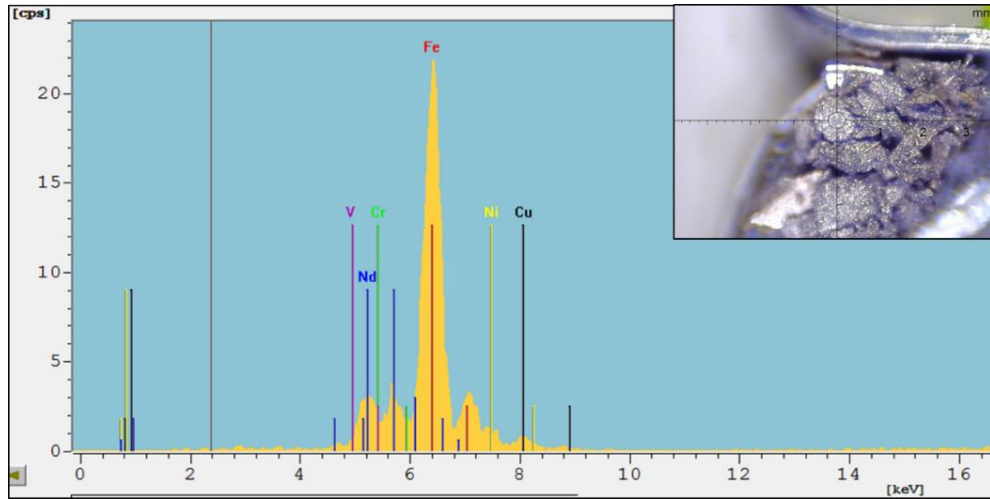
Figure 4.10 X-ray emission spectrum of NIB magnetic alloy showing the presence of Nd

Set top box front panel PCBs

The STB board is a PCB with a series of mounted blue and green LEDs. Both blue and green LEDs contain Ga and Ag (*Figures 4.11 & 4.12*), and green LEDs may also contain Au. Ga based semiconductors such as GaAs, GaP and GaAsP are used to create the LED itself. Ag may be used as wiring, or in the solder, and Au is possibly present as connecting wire. The high Br peak may be associated with the polymer cap possibly in a flame retardant.
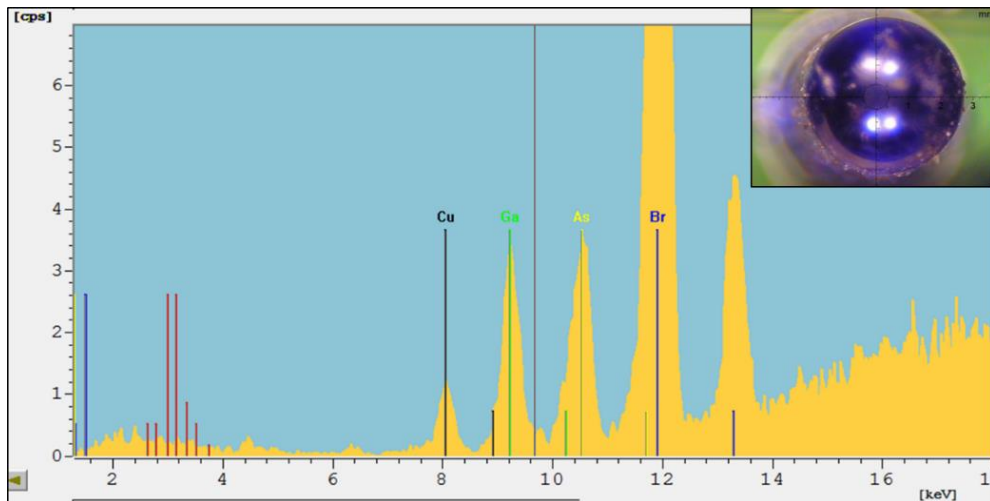
Figure 4.11. Blue LED containing Ga and Ag
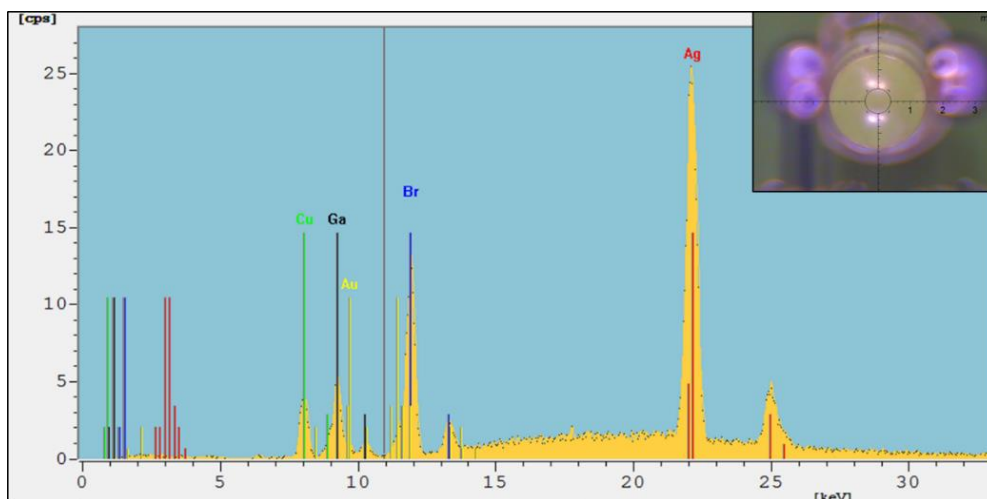
Figure 4.12. *Green LED containing Au, Ag and Ga*

Sony Li-Ion Laptop Batteries

Battery packs were disassembled to reveal 6 LIB cylinder cells and a PCB, all of which were found to contain CRMs (*Figure 4.13*). The PCB was constructed of typical components (LIBs and PCBs are discussed in subsequent sections on common components).

6 x LIB cylinder cells

PCB
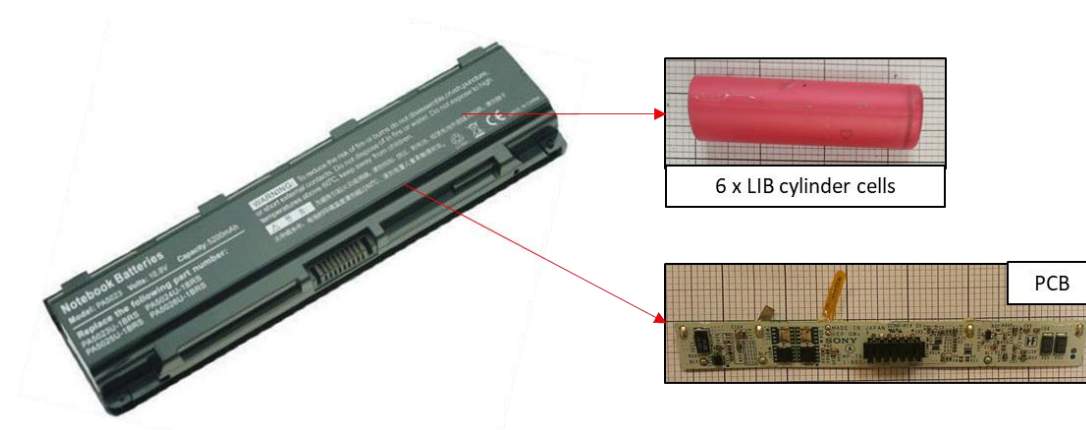
Figure 4.13 *Laptop Li-ion battery pack and isolated LIB cylinder cells and PCB.*

HP Laptop Screens

Prior to analysis, HP laptop LCD screens were disassembled into housing materials, major and minor PCBs and the LCD sandwich itself which was further disassembled to remove the cold cathode fluorescent lamp (CCFL) backlight. (*Figure 4.14*). XRF of components revealed the presence of Mg, Y, Nb, Sb, Ru, Ag and Au in the screens.
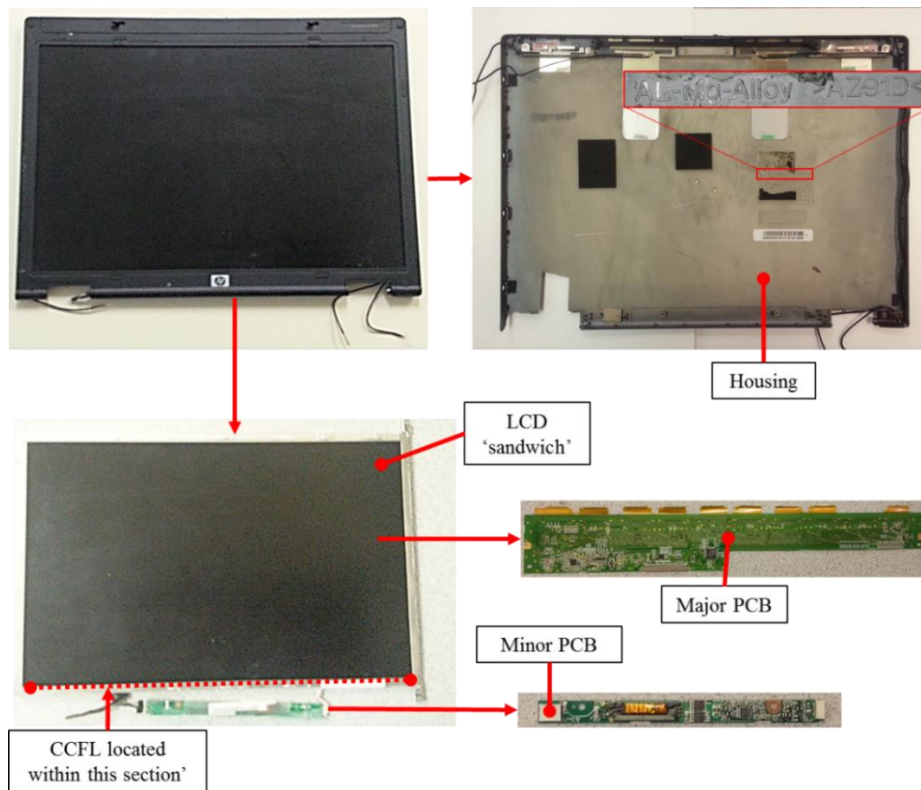
Figure 4.14 Disassembly of LCD Screen and isolation of housing, PCBs and LCD sandwich.

Cold Cathode Fluorescent Lamp (CCFL) - XRF analysis of the CCFL revealed the presence of Y in the phosphor (at 14.96 keV - *Figure 4.15*) and Hg in the terminals of the tube. ICP-MS analysis showed each CCFL contains 13mg of Y (equivalent to 1.7 wt% when wires are removed) probably present as the red phosphor $Y_2O_3:Eu^{3+}$.[99] No other CRMs were revealed during XRF analysis suggesting that, although known to be present, quantities of other REEs are below XRF detection limits and present in comparatively low quantities.[195]
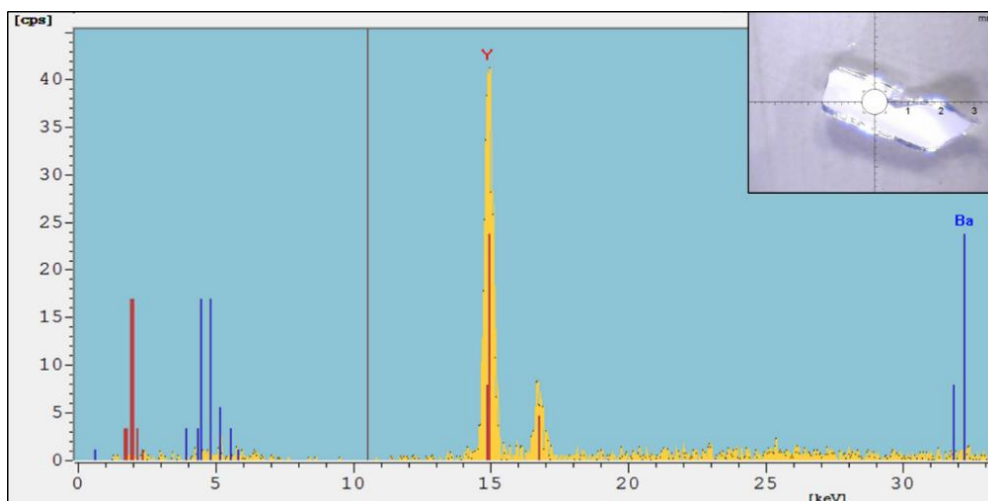
Figure 4.15 X-ray emission spectrum of CCFL phosphor containing yttrium.

LCD Housings - Housings were labelled as the anodised Mg-alloy AZ91D (*Figure 4.16*). This means that it should be composed of 90% Mg, 9% Al, and 1% Zn. Although the XRF is incapable of detecting the aluminium or magnesium, a single peak at 8.64 keV corresponding to Zn suggests that AZ91D is the likely alloy (*Figure 4.17*).

Figure 4.16 AZ91D Mg alloy laptop LCD screen housing
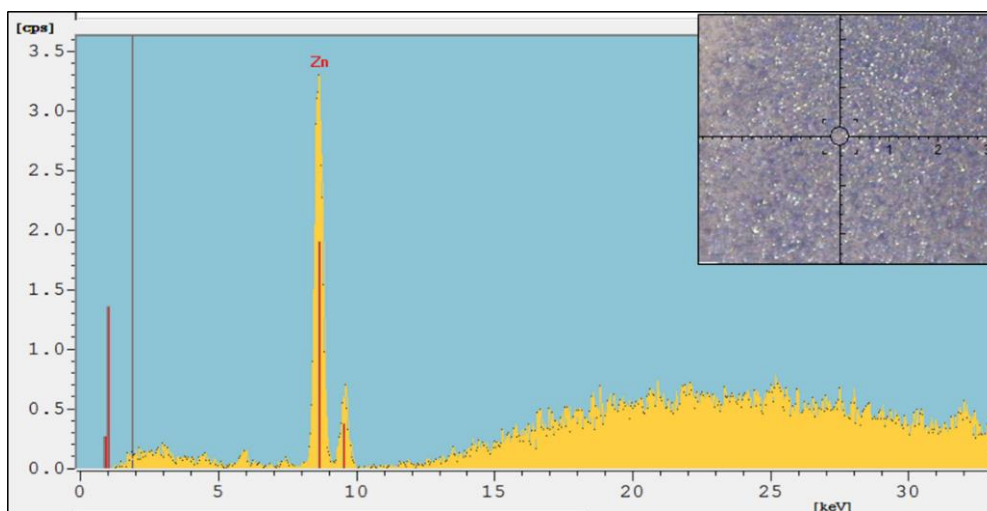
Figure 4.17 *X-ray emission Spectra of AZ91D Mg alloy laptop LCD screen housing showing the presence of Zn*

Screens - In is known to be present as ITO in screens with a major fraction of global In production consumed by display manufacturing. However, In was undetectable by XRF. The Öko-Institut e.V. have reported a figure of 39 mg of In on a 14-inch display.[19] In light of this and the fact that recovery of In from LCDs was not a commercially available process at the time of this study (2012-13) economic recovery of In from this dissipative application was, at the time, unlikely.

Mobile phones

Visual inspection of mobile phone samples selected for the trial revealed that they are constructed with common components. Taking a Nokia 6230i as a representative sample, the phone was disassembled to isolate its LIB, charging contacts, SD card, PCB, speaker magnet and screen (*Figure 4.18*).
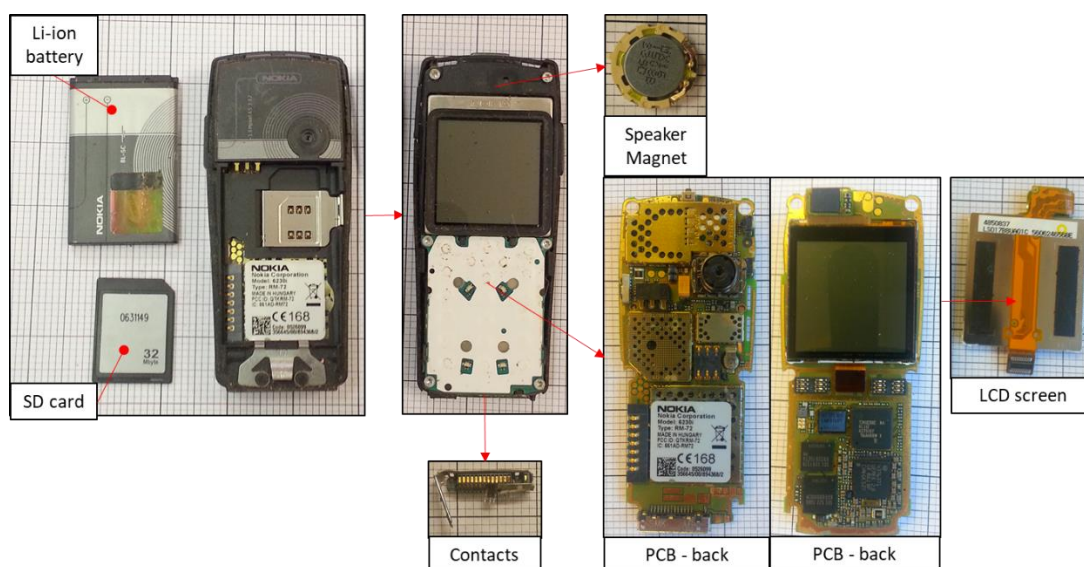
Figure 4.18 *Disassembly of Nokia 6230i mobile phone*

Screens – screens are attached to the PCBs through a connector which bears SMD components and Au contacts, common in PCBs (*Figure 4.19*). The nature of the contacts and components is discussed in the subsequent section about PCBs. Once again it was not possible to detect In on the screen with XRF.

Figure 4.19. *Connectors on screens of mobile phone and MP3 player*

Speaker Magnets – speaker magnets were cut open to access the magnetic alloy inside. XRF analysis revealed the presence of Nd (*Figure 4.20*).
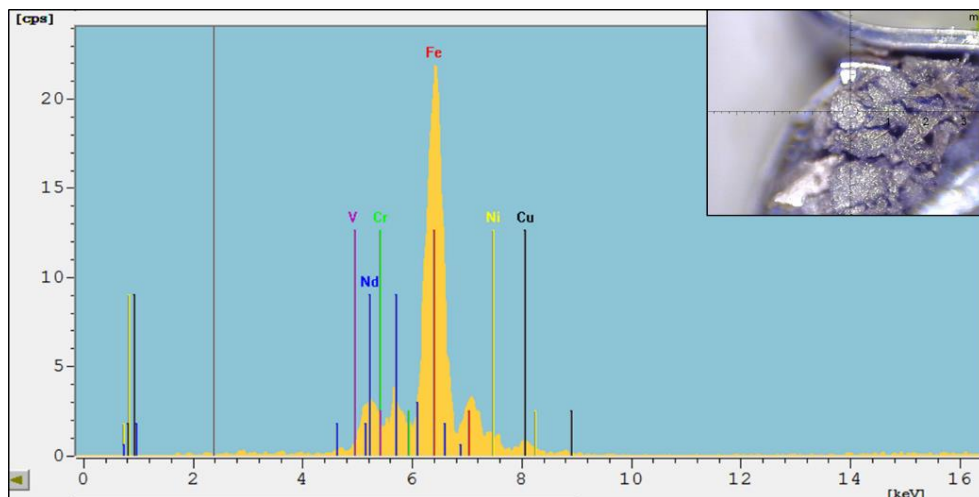
Figure 4.20 *X-ray emission spectrum of the magnetic alloy in mobile phone speaker magnets.*

Contacts – XRF analysis of gold contacts from the base of the phone reveals Au and Pd (*Figure 4.21*). Au is coated onto the surface of the Ni-Cu alloy of the contacts, and Pd is probably present in the Au-alloy used as the coating. Numerous sets of contacts were isolated from the phone, including several sets from the PCB and a set which contact the battery. XRF of battery contacts revealed Au but no Pd was detected. Contacts from the PCB are discussed later.
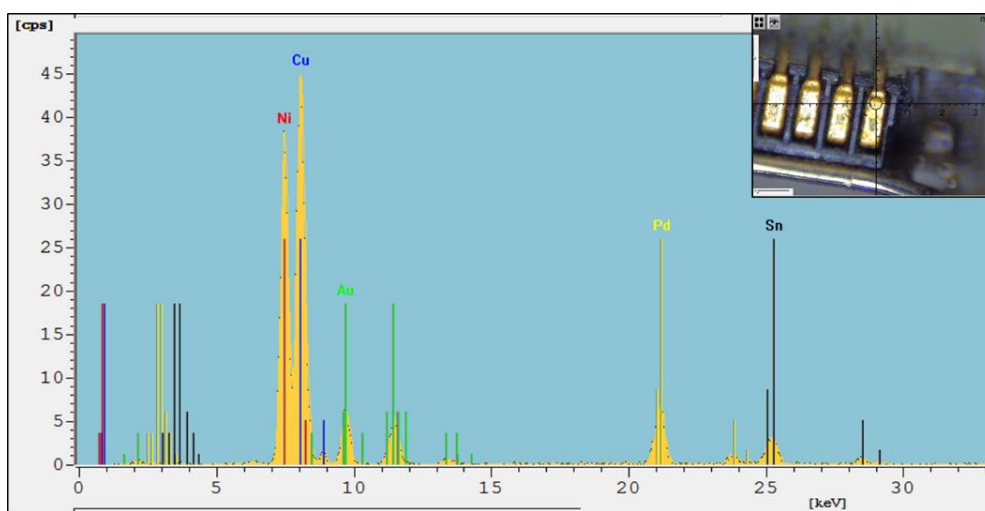
Figure 4.21 *X-ray emission spectrum of gold contacts of mobile phone sample*

SD Card - The SD card contacts contained Au (*Figure 4.22*). SD cards were disassembled in search of additional CRMs but Sb in the plastic of the SD card housing was the only additional CRM identified (*Figure 4.23*).
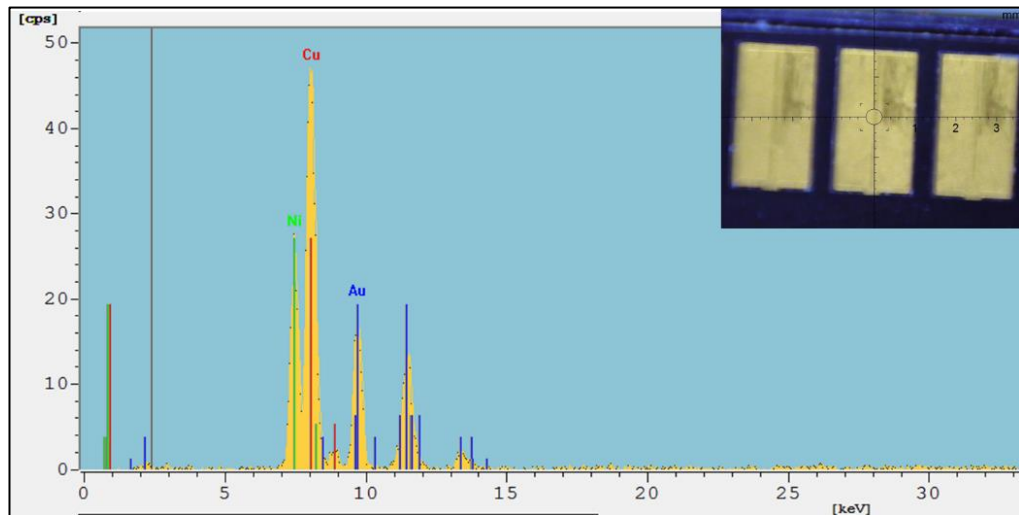
Figure 4.22 X-ray emission spectrum of SD card contacts
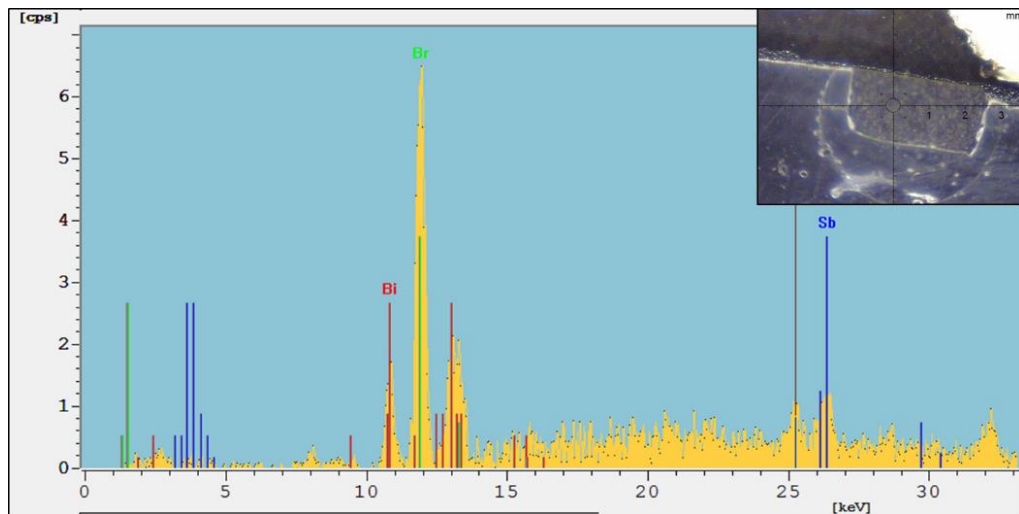
Figure 4.23 XRF spectrum of SD card plastic containing Sb

MP3 players solid state memory

A Sony NWZ-s639F was disassembled into its housing, two PCBs (a main PCB and minor PCB), its Li-ion battery and its LCD screen (*Figure 4.24*). Once again, In could not be identified in the screen by XRF, and CRM content of PCBs and batteries is discussed later.
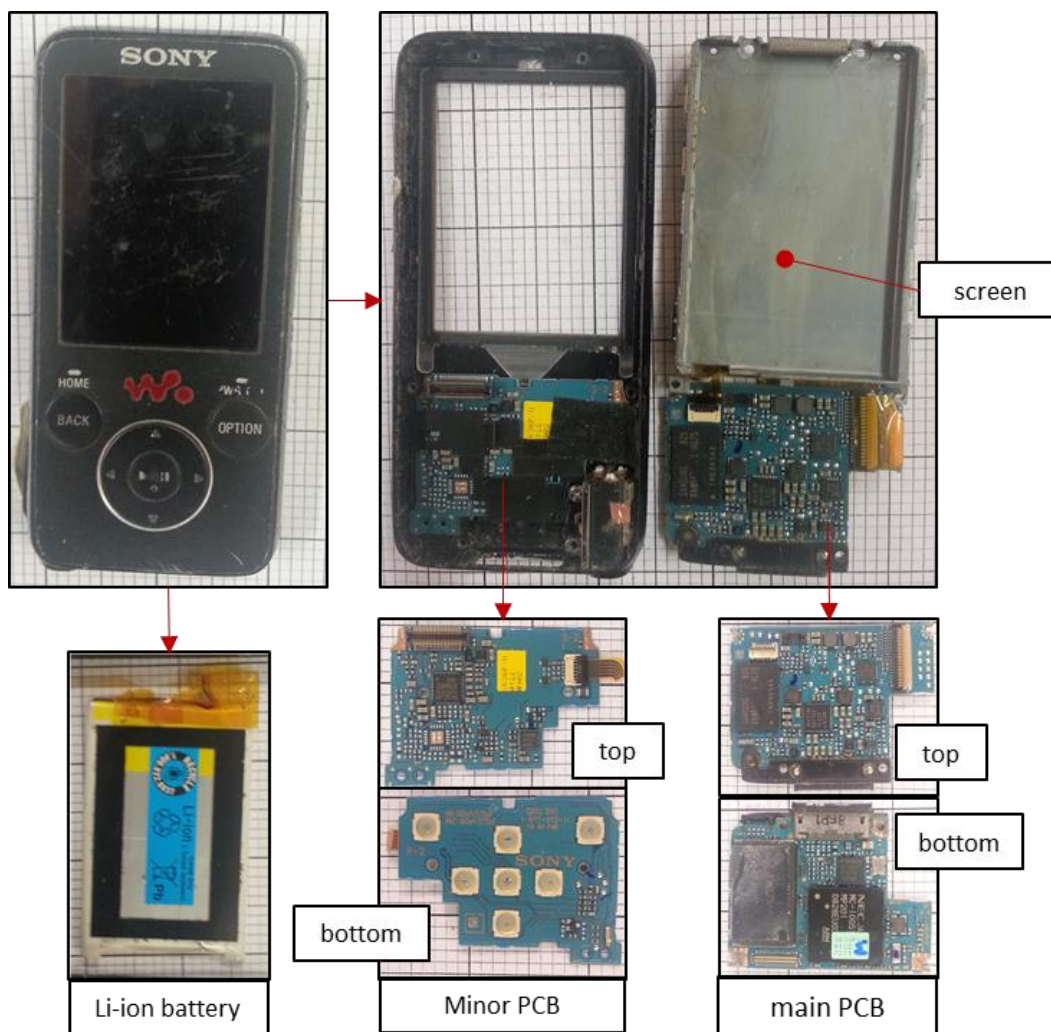
Figure 4.24 Disassembly of Sony NWZ-s639F digital media player into its component parts

RSA security anti-hacking dongle

Disassembly of the dongle was not possible as the housing was a sealed unit. To access the internal electronics a Dremel multi-tool with a cutting disk was used to cut through the hard plastic casing at its edges (*Figure 4.25*). Internal components including a primary lithium button cell, LCD display and PCB were found encapsulated within the transparent plastic resin. Poor design for end-of-life results in difficult, timely and costly disassembly of these devices. Isolating the encapsulated components is therefore economically unfeasible so samples were not analysed further.

The dongle provides a good example of poor design for end-of-life posing a barrier to recovery of any CRMs present. The Li-battery is a primary cell and so unlikely to contain any EU14 CRMs, however, Li has been highlighted as critical in numerous criticality assessments.[21] In addition, poor design prohibits depollution of the device prior to recycling by removal of the

battery. Shredding of the device with its battery in place, despite being environmentally detrimental and forbidden under the WEEE directive is therefore inevitable. This highlights the necessity of DfRR with careful consideration of end-of-life during product design.[120, 121, 123]
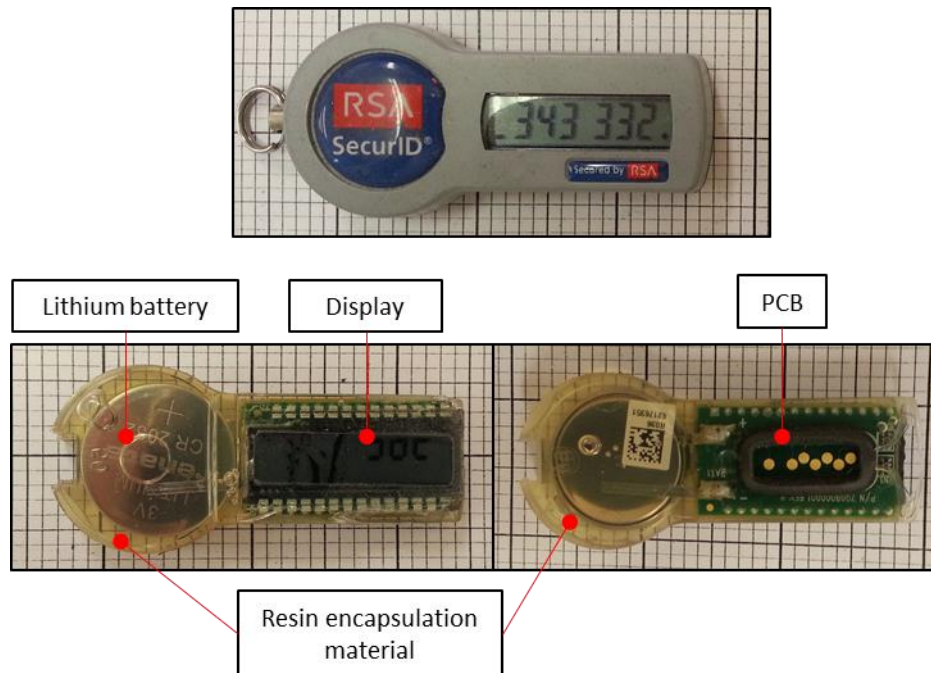
Figure 4.25 *RSA anti-hacking security dongle (top) with top vies (bottom left) and bottom view (bottom right) of its encapsulated internal components.*

Digital Cameras

A Sanyo Cybershot digital camera was selected as a representative example of cameras collected for the trial. It was disassembled into its component parts which include a PCB and Li-ion battery (*Figure 4.26*). No In was detected on the LCD screen.
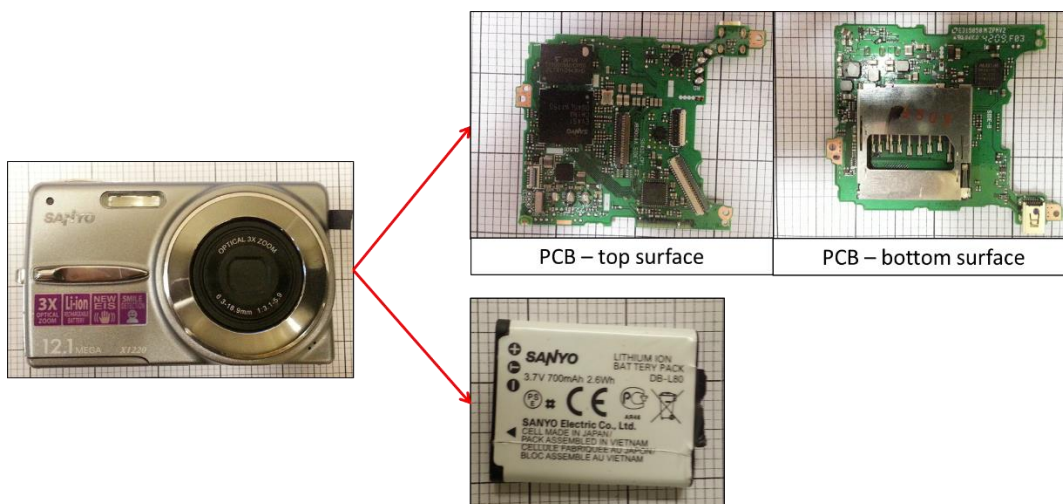
Figure 4.26. Sanyo Cybershot digital camera and its isolated PCB and Li-ion battery

Common components in devices

Li-ion battery cells

Lithium ion battery cells were isolated from laptop battery packs, cameras, MP3 players and mobile phones (*Figure 4.27*). Li-ion batteries cells are manufactured in cylinder or packet (pouch) forms, depending on the way in which electrodes of the cells are folded or rolled. Cell casings prevented x-ray penetrating so the batteries were cut open to expose the internal electrodes for XRF analysis which revealed the presence of Co (*Figure 4.28 4.29*). This is unsurprising as Co is used in cathodic materials of LIBs. Traditionally this has been lithium cobalt oxide ($LiCoO_2$), but newer cathode materials, e.g. ($LiCo_{1-(x+y)}Mn_xNi_yO_2$) contain less Co.[196, 197]
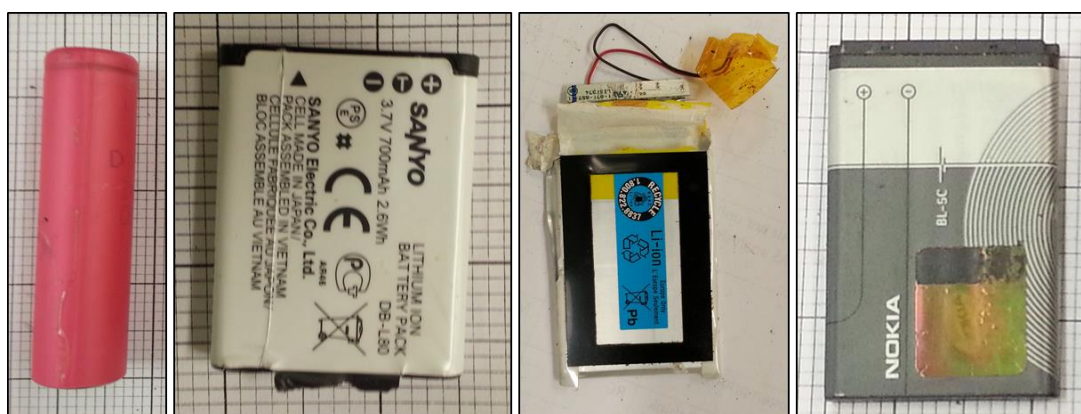
Figure 4.27 Example LIBs. From left to right, cylinder cells from laptop battery packs, and packet cells from cameras, MP3 players and mobile phones
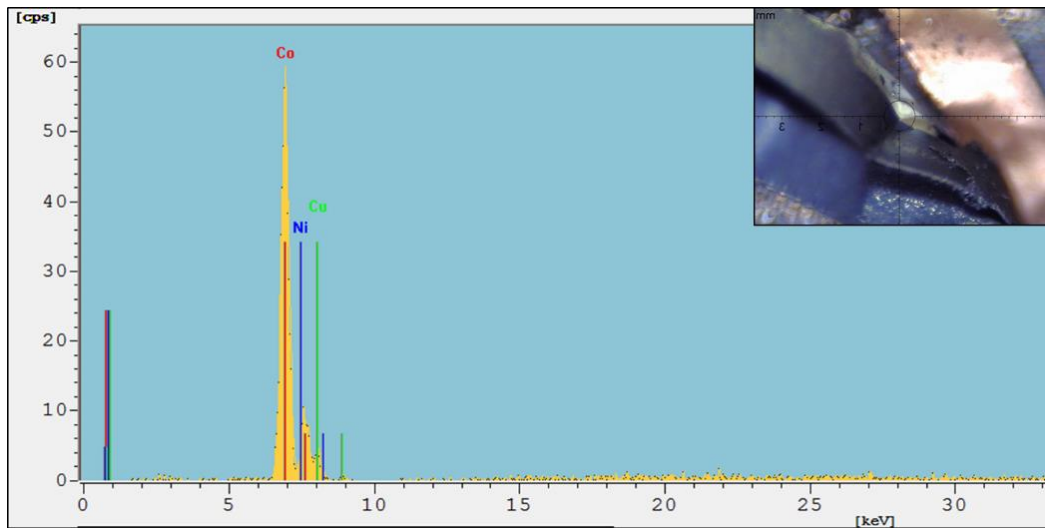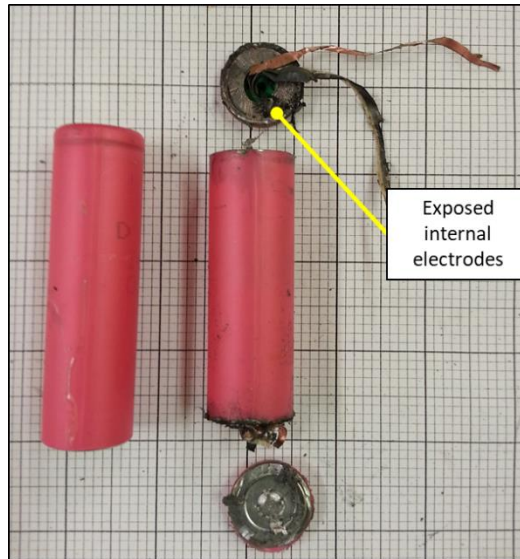
Figure 4.28 *Li-ion cylinder cells from laptop battery packs cut open to reveal internal electrodes (top) and x-ray emission spectra of electrode material (bottom)*
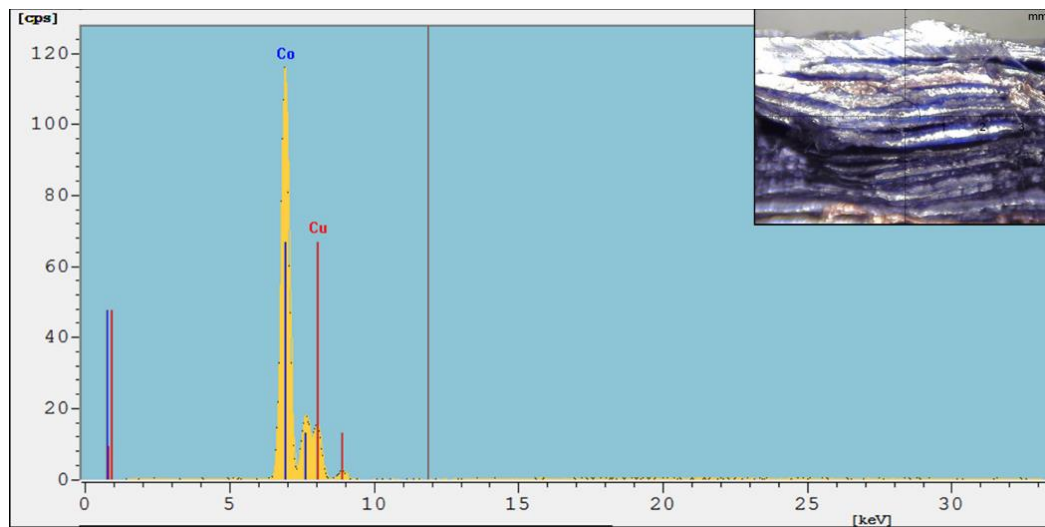
Figure 4.29 *X-ray emission spectrum of electrodes in Nokia 6230i mobile phone Li-ion battery*

Printed Circuit Boards (PCBs)

This section outlines the common components in which CRMs have been identified in PCBs. Samples discussed include PCBs from TVs, fridges, STBs, phones, digital media players, cameras, LCD screens and HDDs.

Contacts - Contacts are normally a Cu-alloy, coated with Au-alloy to provide corrosion protection.[198] Two main kinds of contacts were found: those coated directly onto PCBs such as the edge contacts on PC PCI cards (e.g. graphics cards – *Figure 4.30*); and those in connectors soldered to PCBs such as HDMI, VGA, and USB ports (*Figure 4.31*). The presence of gold was confirmed in by XRF in all contacts which appeared golden to the naked eye (*Figure 4.32*). On occasion, Pd was also found in combination with gold, suggesting Pd is used as an alloying element in the Au-alloy coating.
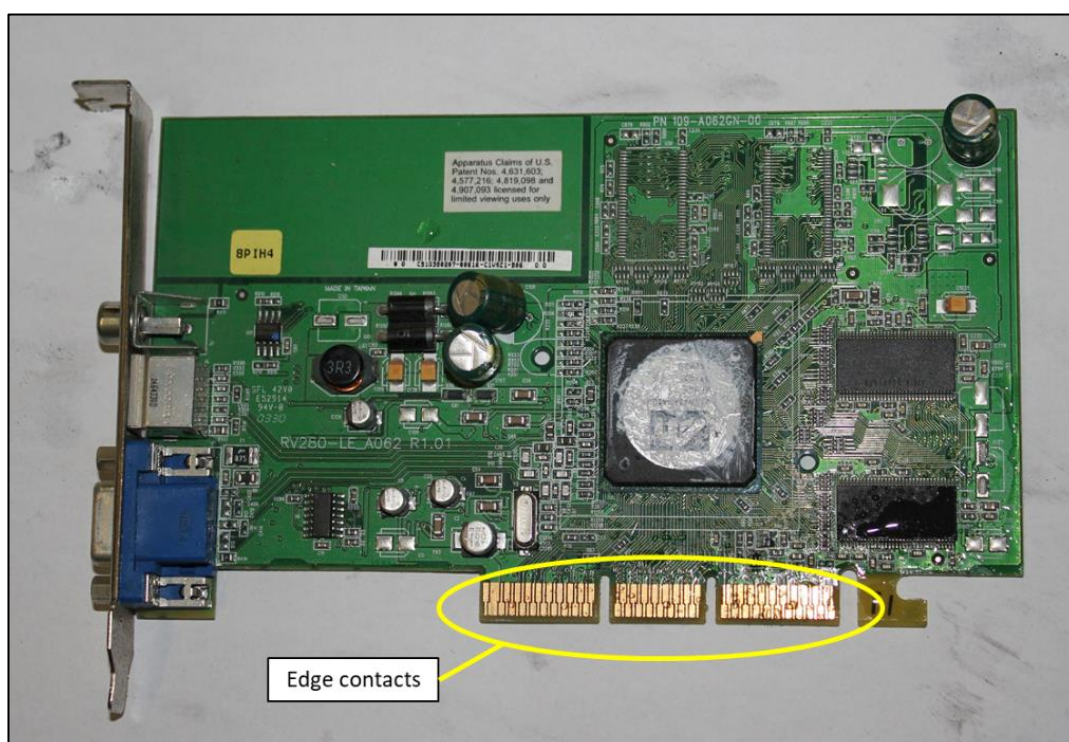
Figure 4.30 *Edge contacts on a PC graphics card*
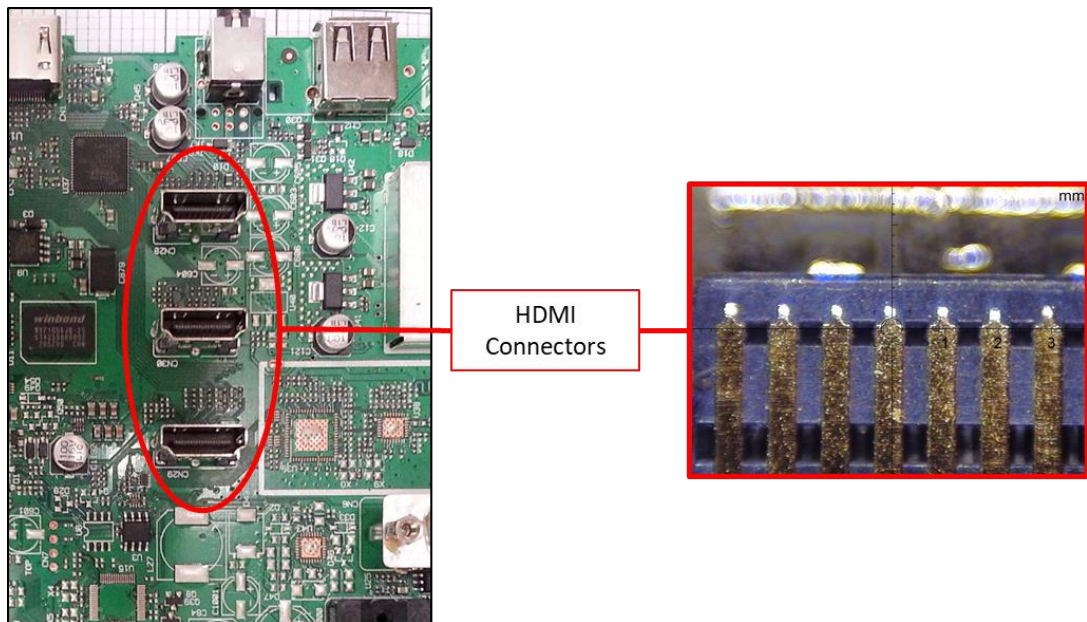
Figure 4.31 *HDMI connectors on a TV PCB (left) and the gold coated contacts within (right)*
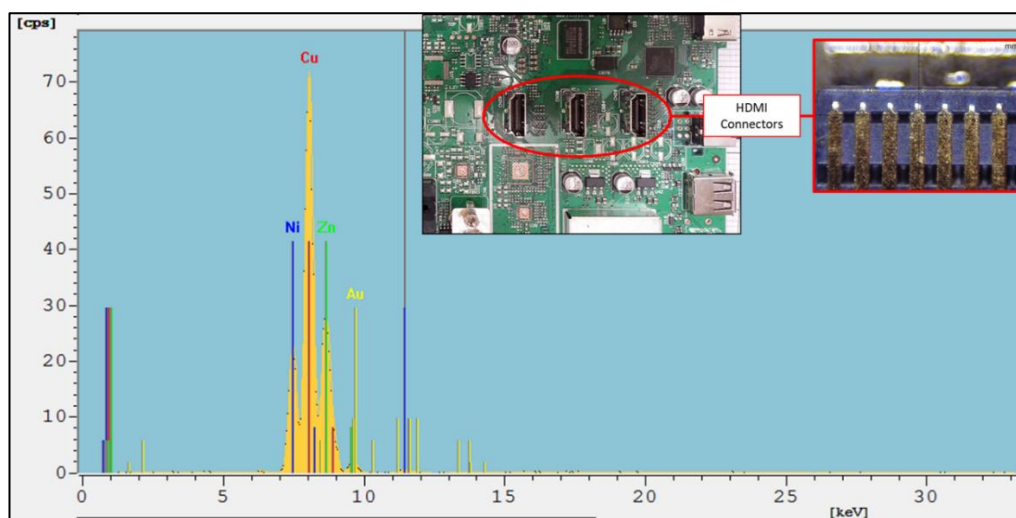
Figure 4.32 *HDMI ports on a TV PCB and their X-ray emission spectrum indicating the presence of gold (9.71 keV)*

Surface Gold **-** Many of the PCBs found in the samples had large areas on their surfaces coated with Au. This was prevalent in mobile phones and the PCBs from LCD screens (*Figure 4.33*). XRF analyses confirmed that the alloy was similar in composition to that used in PCB contacts PCBs, always containing Au, with a small quantity of Pd on occasion.
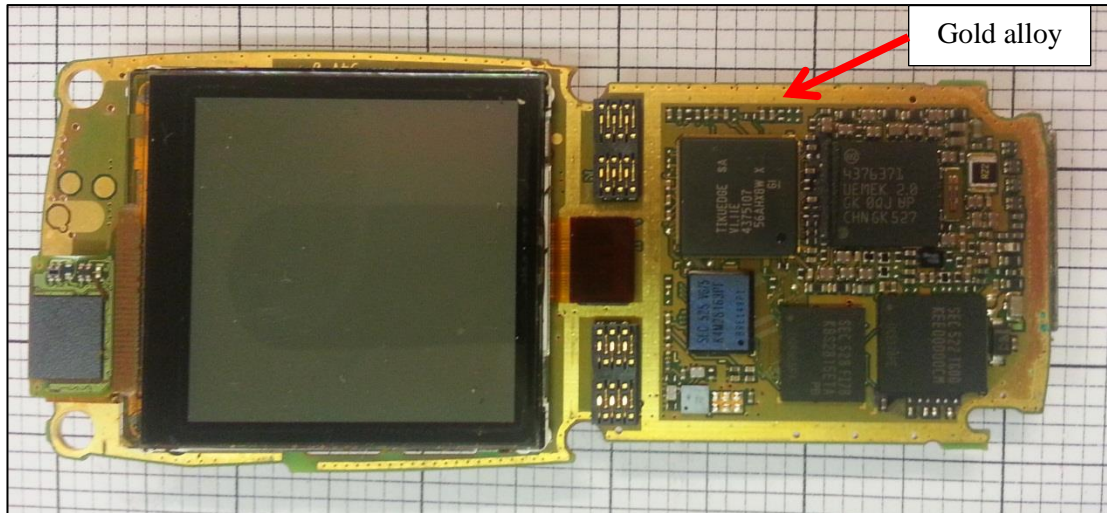
Figure 4.33 *Plated Au on the surface of mobile phone PCB*

Solder - All modern electronic devices use lead-free solder in compliance with the RoHS directive. These solders contain a Ag-Sn alloy, as shown in XRF spectra of PCBs from cameras, phones, TVs, LCDs and MP3 players (*Figure 4.34*).
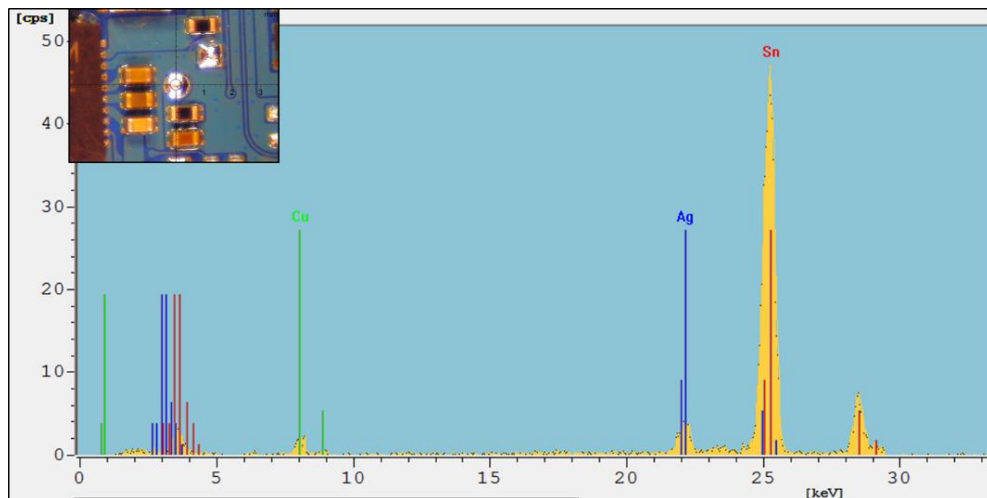
Figure 4.34 *X-ray emission spectrum of Pb free solder containing Ag on the PCB of a digital media player (MP3 player)*

Surface Mount Device (SMD)Components

Chip Resistors - The most commonly encountered SMDs were chip resistors (*Figure 4.35*) found in all PCBs analysed. These vary in size but are always black and frequently numbered on their surface. XRF analysis of chip resistors shows Ag, Ru and Sb with almost no exceptions, and Pd in approximately half of those analysed. Some of the larger resistors which less common also Co (*Figure 4.36).*
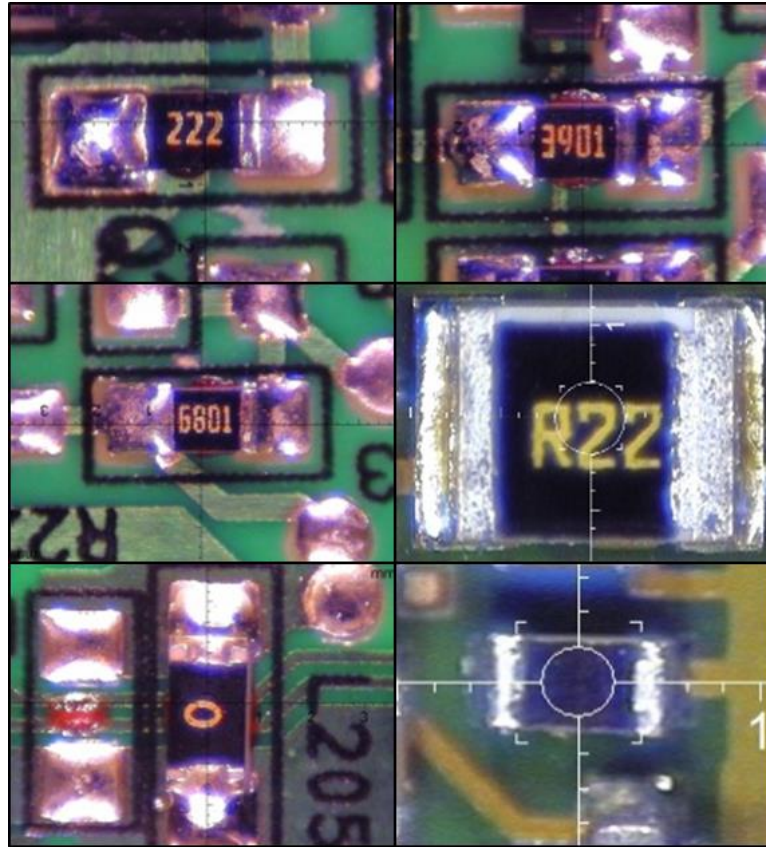
Figure 4.35 Examples of surface mount chip resistors
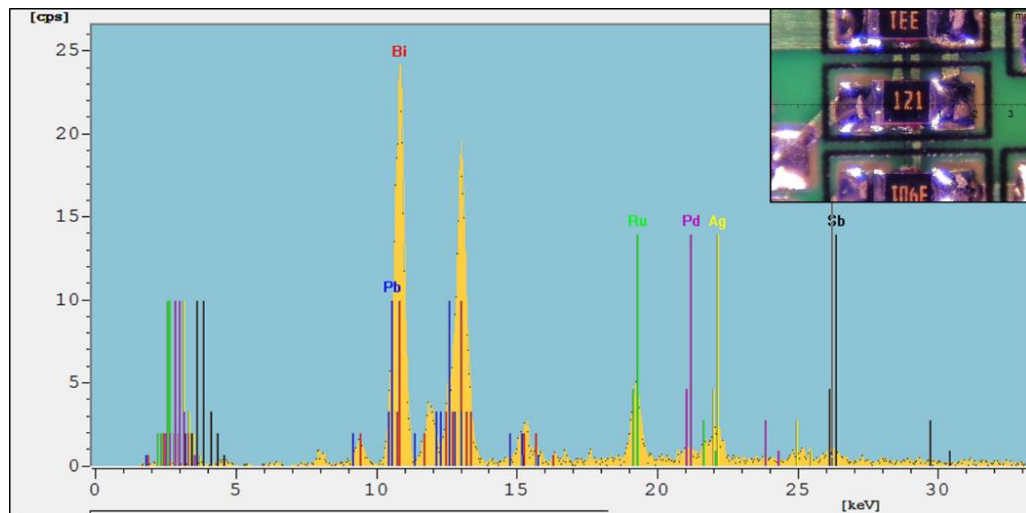
Figure 4.36 X-ray emission spectrum of a chip resistor SMD containing Ru, Pd, Ag & Sb

Integrated Circuits (ICs) - ICs were encountered in every PCB sample (*Figure 4.37*). XRF analysis revealed ICs to always contain Au & Ag (*Figure 4.38*), often Sb, and occasionally Pd. Surprisingly, no tungsten was identified even in ground samples, which is a known interconnect material used in ICs.
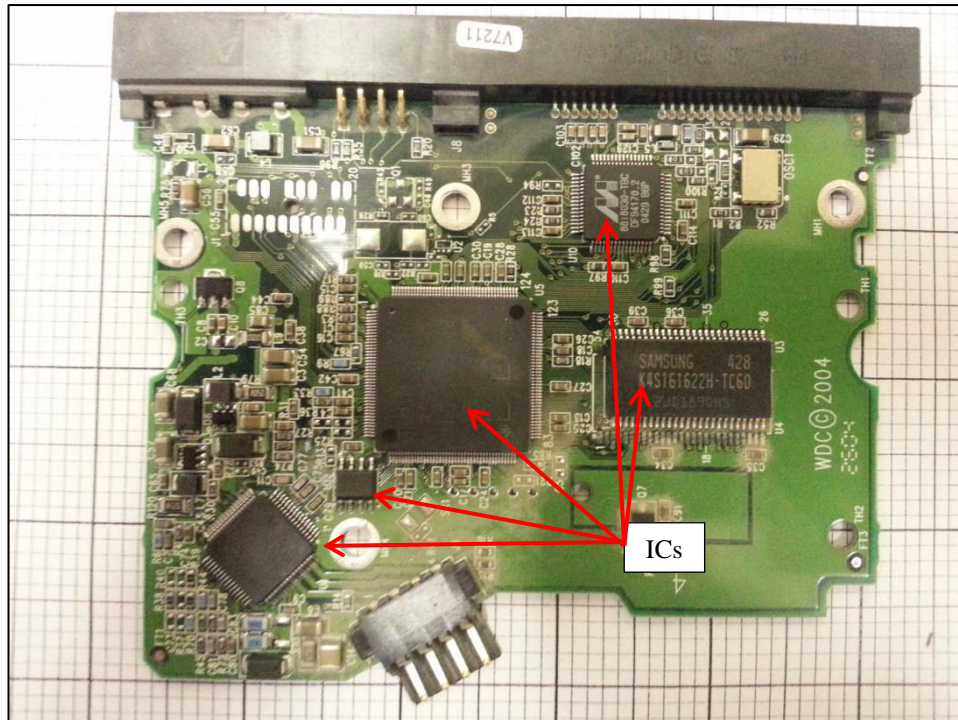
Figure 4.37 *ICs on HDD PCB*
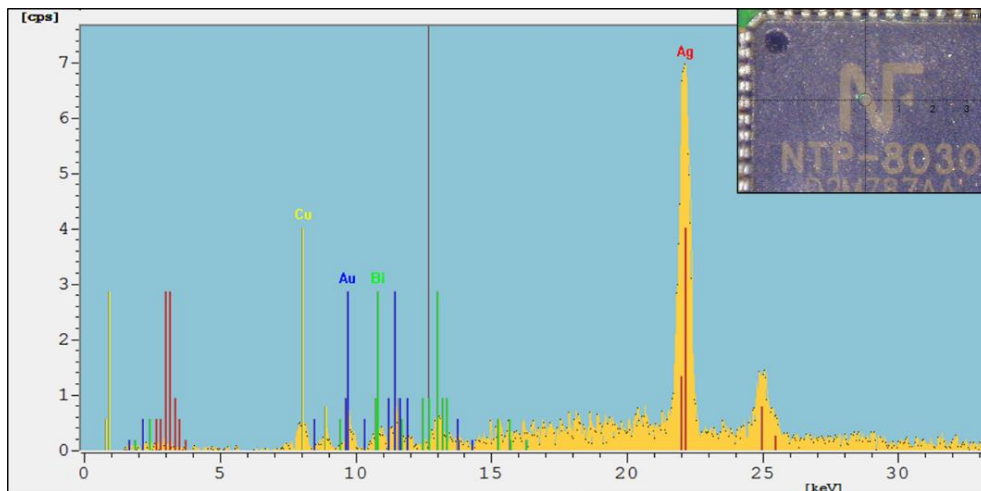
Figure 4.38 *X-ray emission spectrum of an IC showing the presence of Au & Ag*

Multi-layered Ceramic Capacitors (MLCCs) - These SMDs are very common on PCBs, occurring in a variety of sizes and colours, with varying CRM content. XRF surface scanning of MLCCs revealed that Y is present in brown coloured MLCCs (*Figure 4.39*). This is unsurprising as Y is used as an additive in $BaTiO_3$ to control formation of the appropriate 'core shell' microstructure for MLCCs.[199] *Table 4.5* shows the Y content of two sizes of typical capacitors determined by ICP-MS .
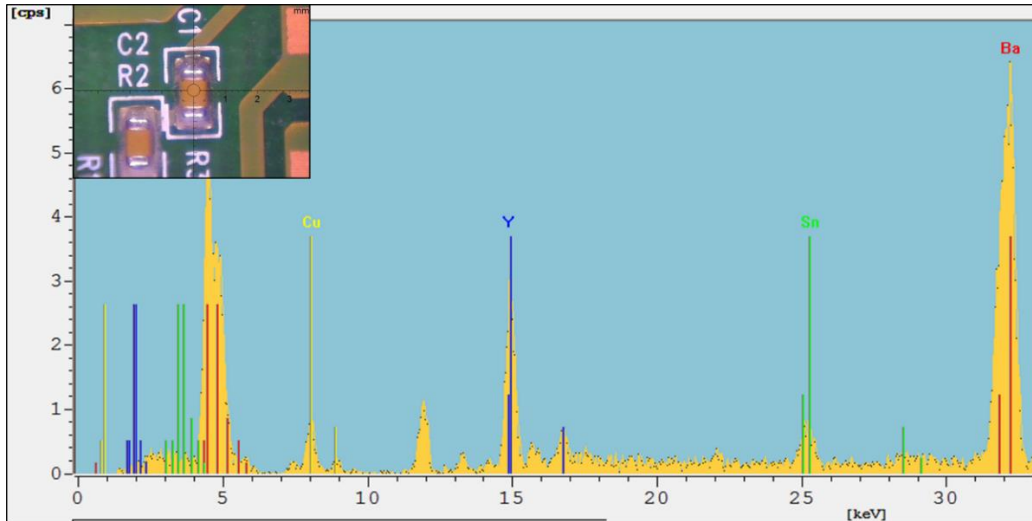
Figure 4.39 *Typical capacitors and XRF analysis showing presence of yttrium (Y)*

Table 4.5 *Yttrium content in capacitors*

Size	Y content (wt%)
0.55 x 0.25mm	0.3 %
0.90 x 0.60mm	0.8 %

Less frequently encountered, but prevalent in highly miniaturised electronics such as mobile phones and MP3 players were Nb containing MLCCs. Nb too has been used as an additive to $BaTiO_3$ to control microstructure formation.[199] Examples of CRM found with Nb in MLCCs include: purple and blue MLCCs found to contain Pd (*Figure 4.40*); gold-coloured MLCCs containing Ag (*Figure 4.41*); and red MLCCs containing Pd (*Figure 4.42*). Off-white coloured SMDs of two sizes (1.8 mm x 1.1 mm & 0.9 mm x 0.6 mm) containing Ir were also found (*Figure 4.43*)
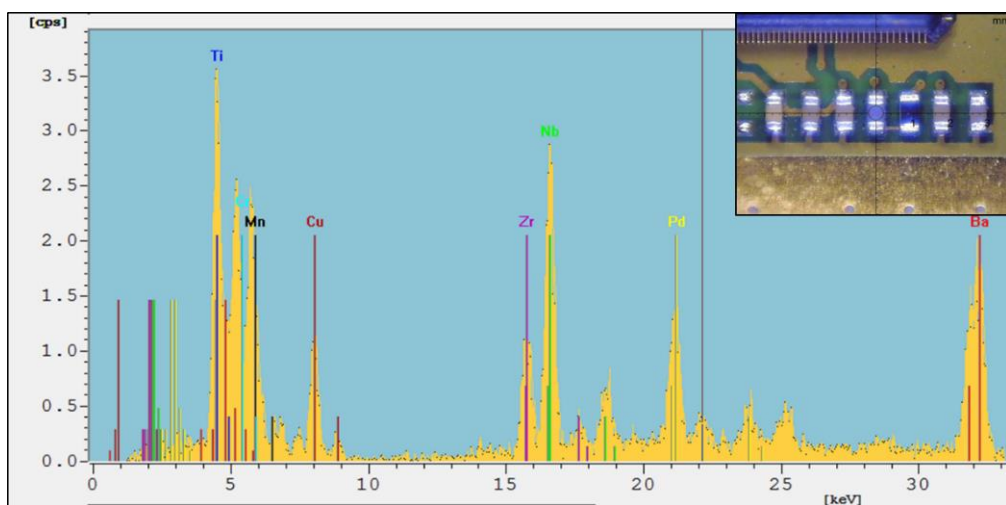
Figure 4.40 *X-ray emission spectra of typical blue MLCC indicating the presence of Pd.*
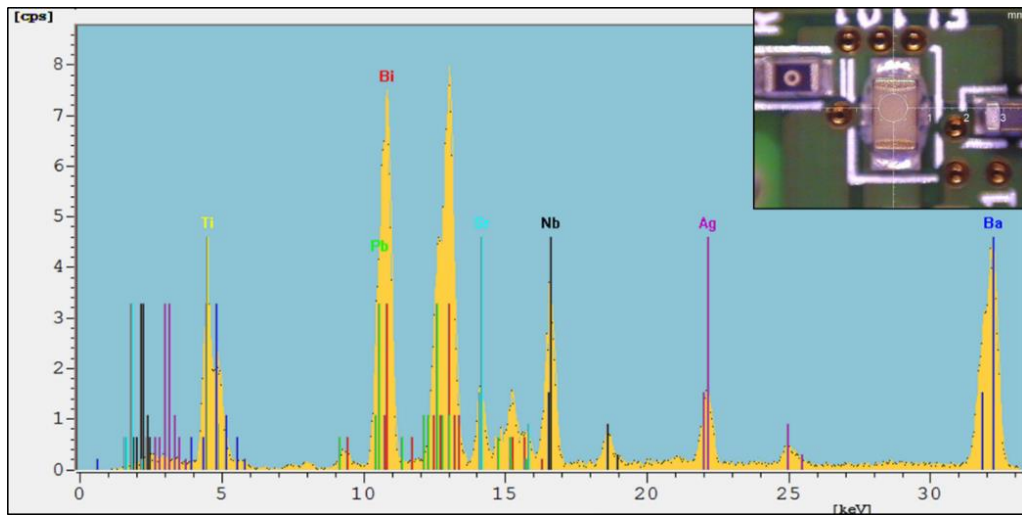
Figure 4.41 MLCC containing Nb & Ag
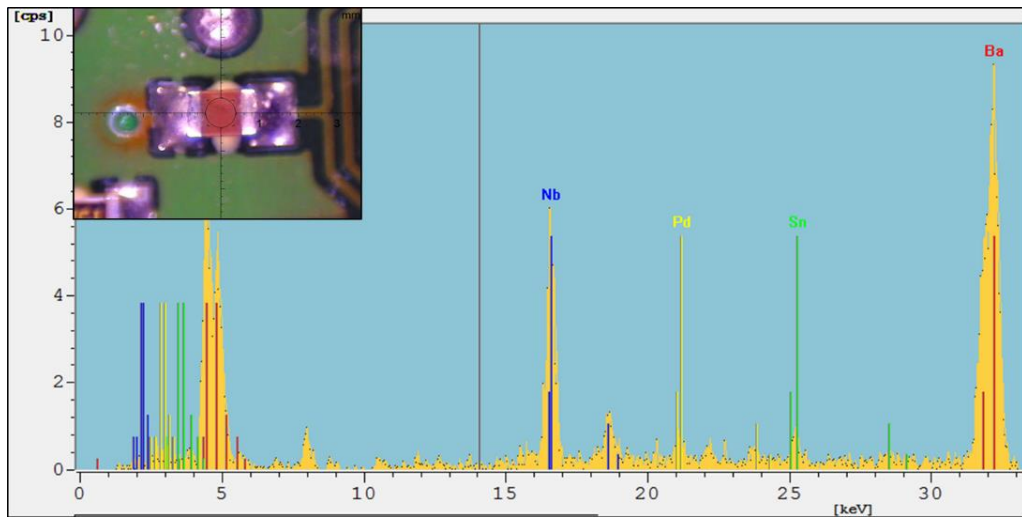
Figure 4.42 Red MLCC containing Nb & Pd
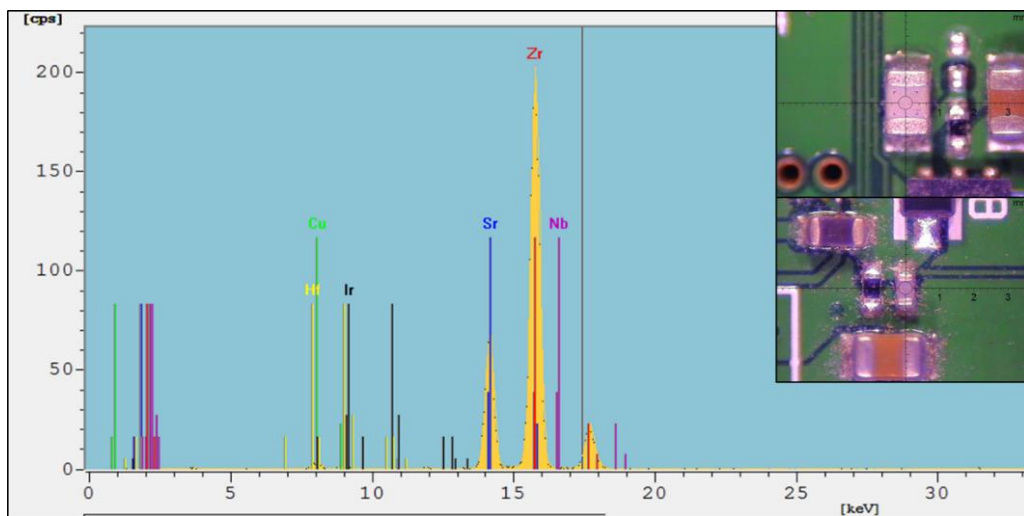
Figure 4.43 Typical x-ray emission spectrum of large (top) and small (bottom) MLCCs containing iridium Nb & Ir

Transistors – Transistors are common in all PCBs. They generally appear in two forms: 3-pin small outline transistors, and standard small outline transistors. Standard small outline transistors were identified in PCBs of items such as HDDs and TVs, but were not present in highly miniaturised PCBs e.g. mobile phones, MP3 players etc. In these devices, smaller 3-pin transistors are common. Standard small outline transistors consistently contain Au, Ag and Sb (*Figure 4.44*). 3-pin small outline transistors of two varieties were identified in samples. Those most commonly found were black in colour and numbered on their surface, consistently found to contain Au, Ag and Sb (*Figure 4.45*), just as their larger counterparts. A second variety of 3-pin transistor were found various colours (pink, green & yellow) on server boards and found to contain Au, Ag, and Ga (*Figure 6.46*).
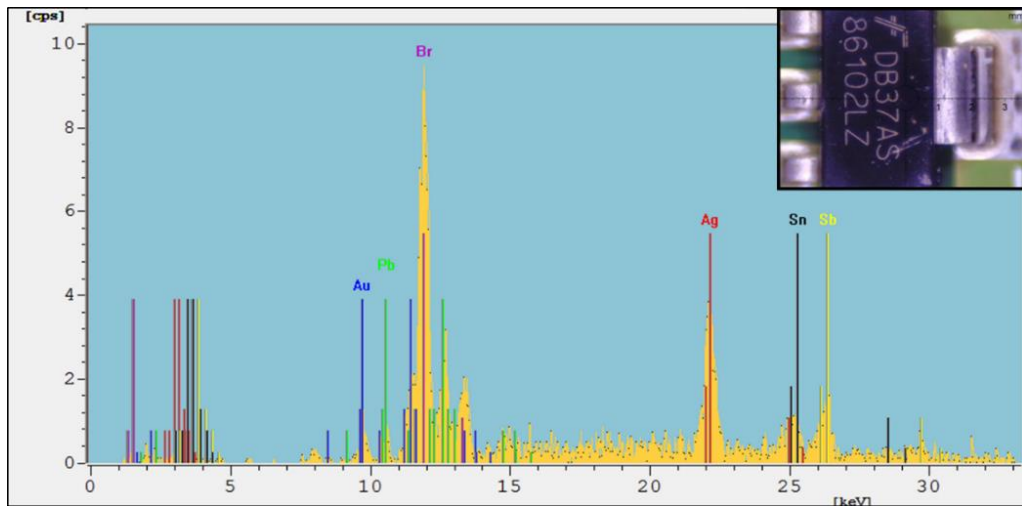
Figure 4.44 *X-ray emission spectrum of small outline transistor containing Au, Ag and Sb*
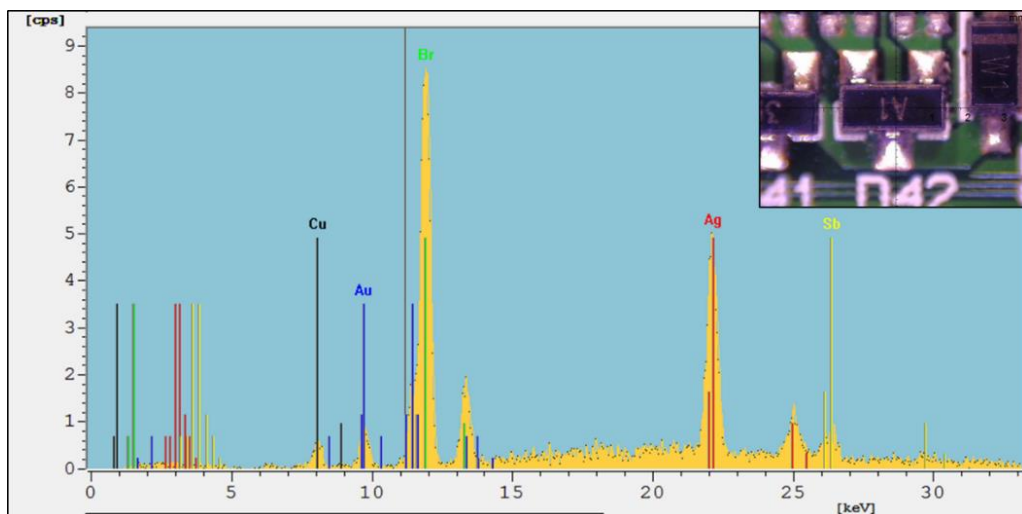
Figure 4.45 *Typical SMD transistor containing Au, Ag and Sb*
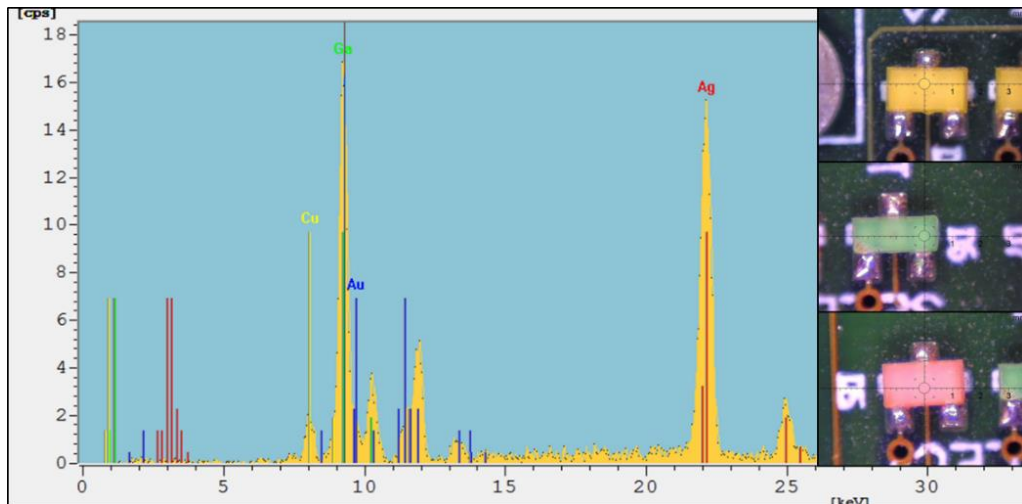
Figure 4.46 *X-ray emission spectrum of coloured 3-pin small outline transistors containing Au, Ag, and Ga, present on server board sample.*

Tantalum capacitors – Ta-capacitors occur frequently in miniaturised PCBs where high charge storage density is required, but not in TV & Laptop LCD PCBs, TV & Fridge power boards, and STB base boards. Where Ta-capacitors were present, they numbered 1-3 per PCB, with the exception of the server board sample which contained 15 of these SMDs. Ta-capacitors of difference sizes and capacitances are used. (*Figure 4.47*). To detect Ta in capacitors with XRF, the plastic of the encapsulation had first to be cut open *(Figure 4.48)*, or the whole device had to be ground into powder. The Ta containing capacitor is encapsulated within moulded plastic containing Sb (probably as SbO_3). Ag was also detected at the component terminals.
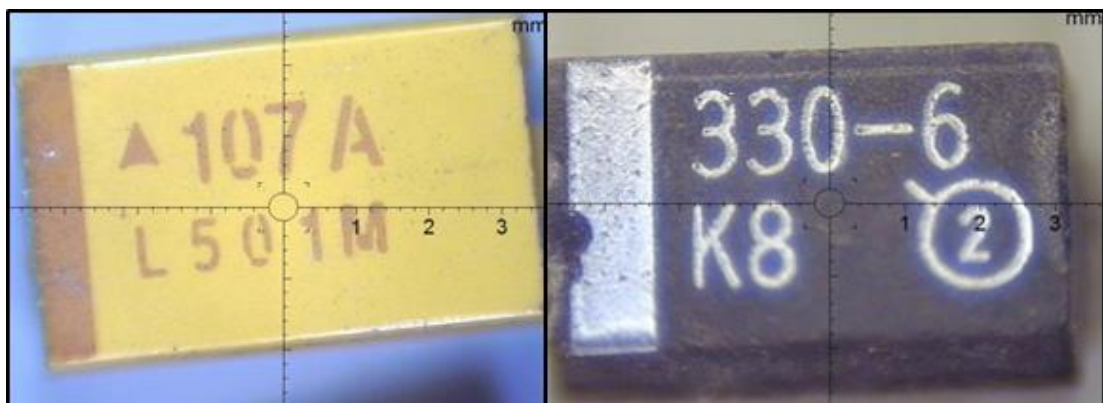
Figure 4.47 *Typical tantalum capacitor SMDs from samples*
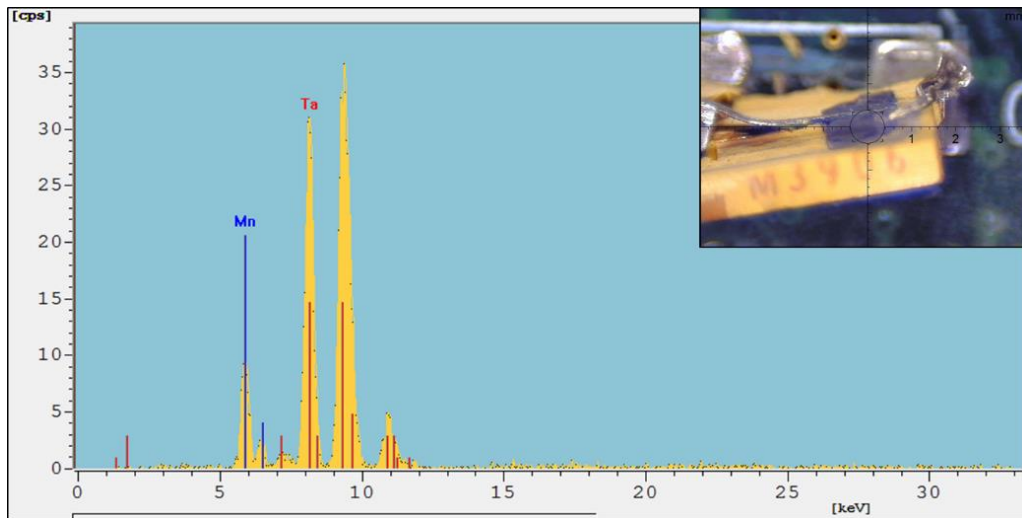
Figure 4.48 *X-ray mission spectrum of exposed Ta metal of typical Ta-capacitor SMD revealing the presence of and measured x-ray emission spectrum*

As described in *Appendix A*, Ta capacitors were used to evaluate the performance of the XRF instrument. A typical capacitor (107 A, *Figure 4.47*) was ground to powder with inclusion of a known quantity of Zn as an internal standard for quantitative analysis. The results shown that Ta makes up ~60 wt% of this capacitor (*Table 4.6)*.

Table 4.6 *Average CRM content of 100 µF 10V 107A Ta-capacitors*

Mass of capacitor (g)	Wt% Ta	Wt% Ag	Wt% Sb
0.2887	62(±9)	3(±1)	1.6(±0.5)

Chip Arrays - These are common to all PCBs examined with the exception of power boards.. XRF consistently confirmed the presence of Ag and either Ru, or Pd with Au (*Figure 4.49*).
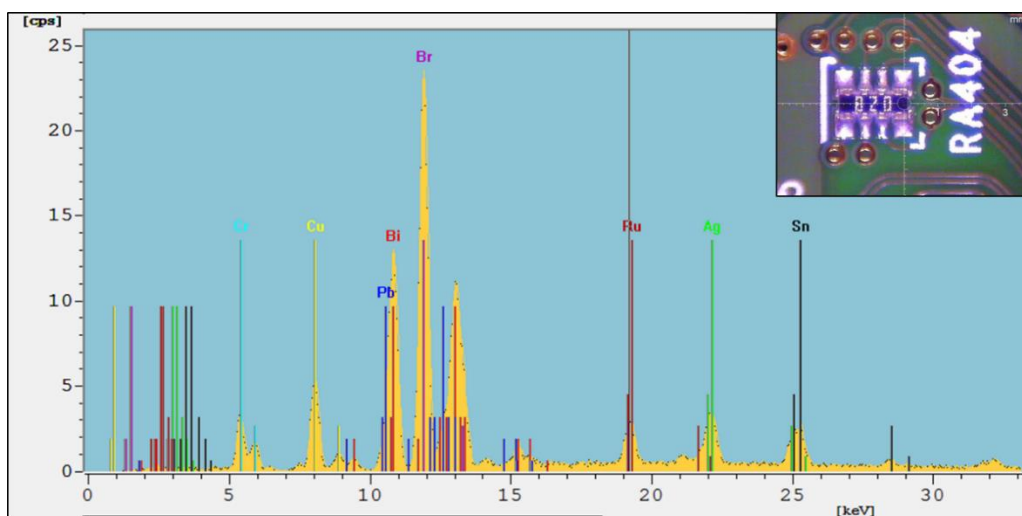
Figure 4.49 *X-ray emission spectrum of a typical chip array SMD containing Ag and Ru*

118

Inductors - These were mainly found on the PCBs of mobile phones, with infrequent occurrence on other miniaturised PCBs. Three different types were identified based on composition, distinguishable by colour (brown, grey and purple). Brown inductors contain Pd, Ag and Nb (*Figure 4.50*), there is Ag in grey inductors (*Figure 4.51*), and Ag and Co in purple inductors (Figure 4.52).
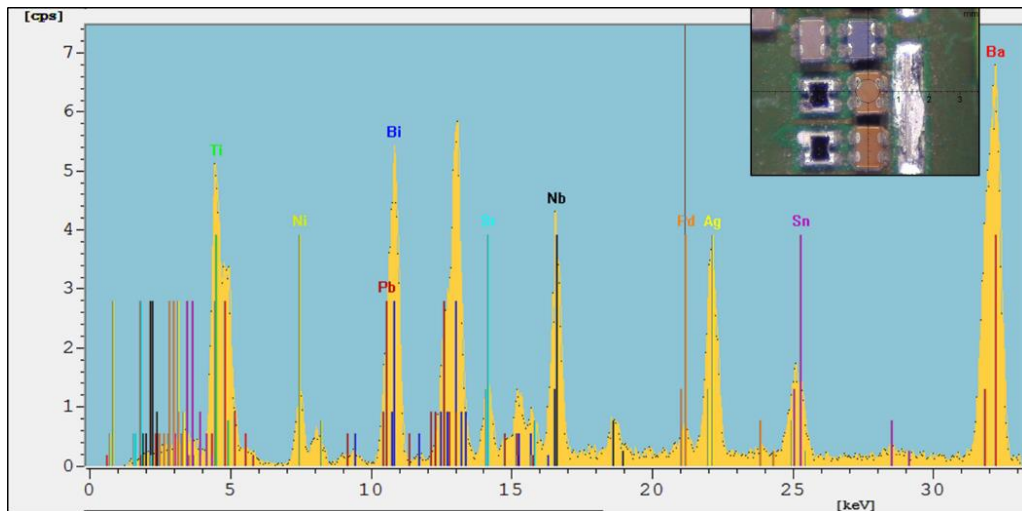
Figure 4.50 *X-ray emission spectrum of brown inductors on mobile phone PCBs containing Nb, Pd & Ag*
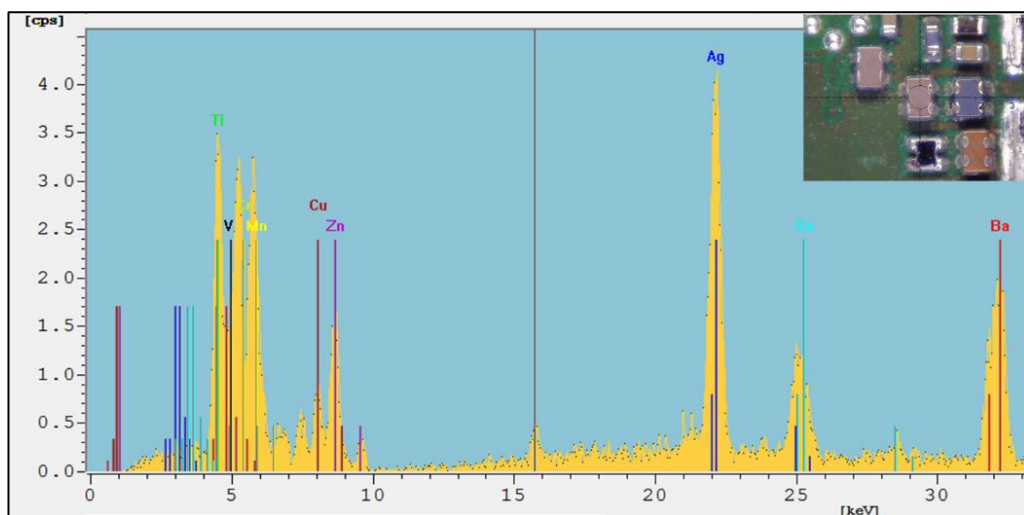
Figure 4.51 *X-ray emission spectrum of grey inductors on mobile phone PCBs containing Ag*
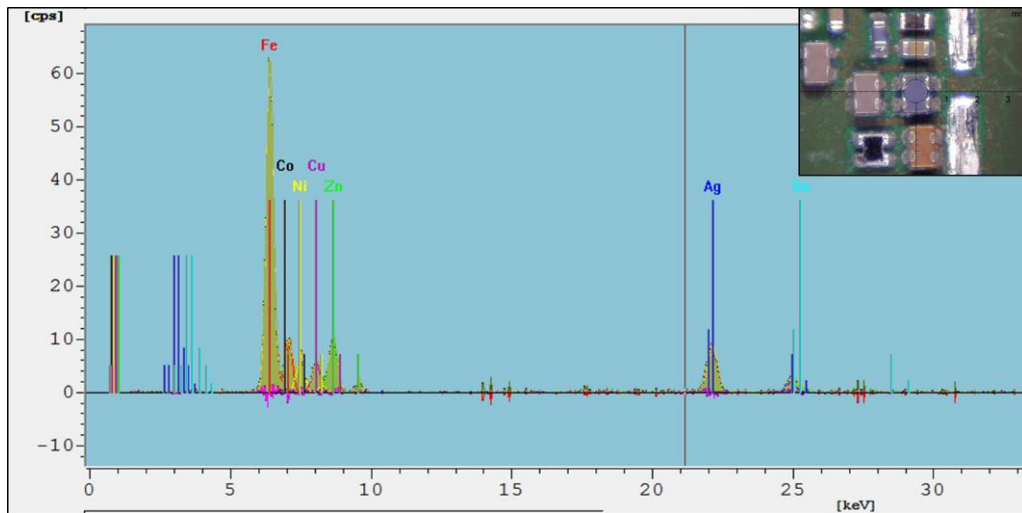
Figure 4.52 X-ray emission spectrum of purple inductors on mobile phone PCBs containing Ag & Co

Polarized moulded body diodes – These SMDs are infrequently found. To the naked eye it is easy to confuse these devices with Ta-capacitors due to the shape of their moulded plastic encapsulation. Diodes were found to contain Sb within the encapsulation plastic, probably in SbO_3 flame retardant (*Figure 4.53*).
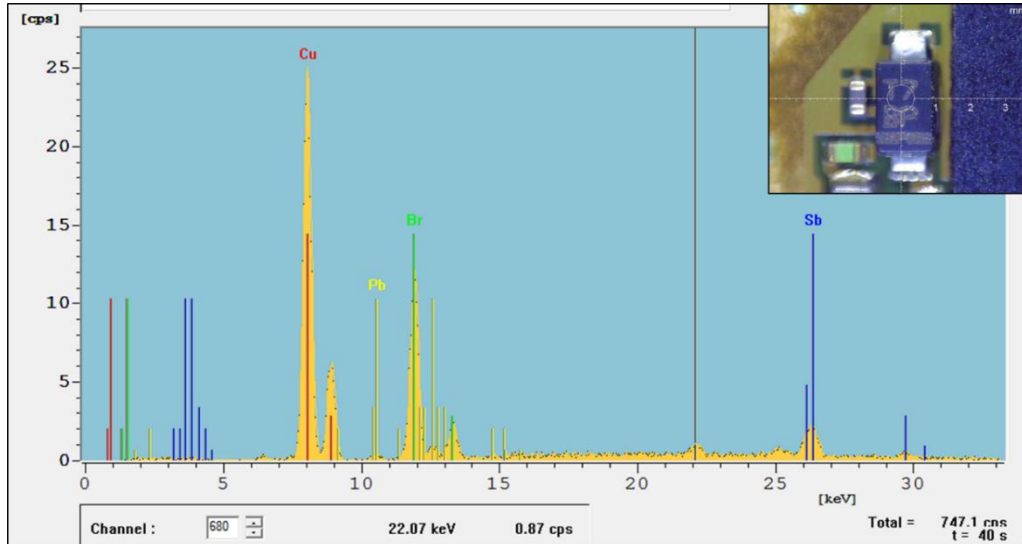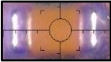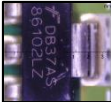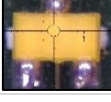
Figure 4.53 X-ray emission spectrum of typical polarized moulded body diode containing Sb

PCB Component Summary

A summary of CRMs found in PCB components is given in *Table 4.7*.

Table 4.7 *CRMs in PCB components*

Component	PMs		PGMs			REMs	Other CRMs					
	Au	Ag	Pd	Ru	Ir	Y	Co	Ga	Nb	Sb	Ta	W
Gold contacts	✓		(✓)									
Surface gold	✓		(✓)									
Solder		✓										
Chip resistors		✓	(✓)	✓			(✓)			✓		
ICs	✓	✓	(✓)							(✓)		✓
MLCCs												
						✓						
			✓						✓			
					✓				✓			
		✓							✓			
			✓						✓			
Transistors												
	✓	✓								✓		
	✓	✓								✓		
	✓	✓						✓		✓		
Ta-capacitors		✓								✓	✓	
Chip arrays	(✓)	✓	(✓)	(✓)								
Inductors												
		✓					✓					
		✓										
		✓	✓						✓			
Polarized diodes										✓		

✓ - consistently present in component; (✓) – sometimes present in component

Using this data, it is possible to give a visual representation of the distribution of CRMs in PCBs based on the library of components established. *Figure 4.54* shows the spatial distribution of CRMs in the main PCB of a TV.

Colour Code: | Au | Ag | Pd | Ru | Y | Co | Sb | Ir |
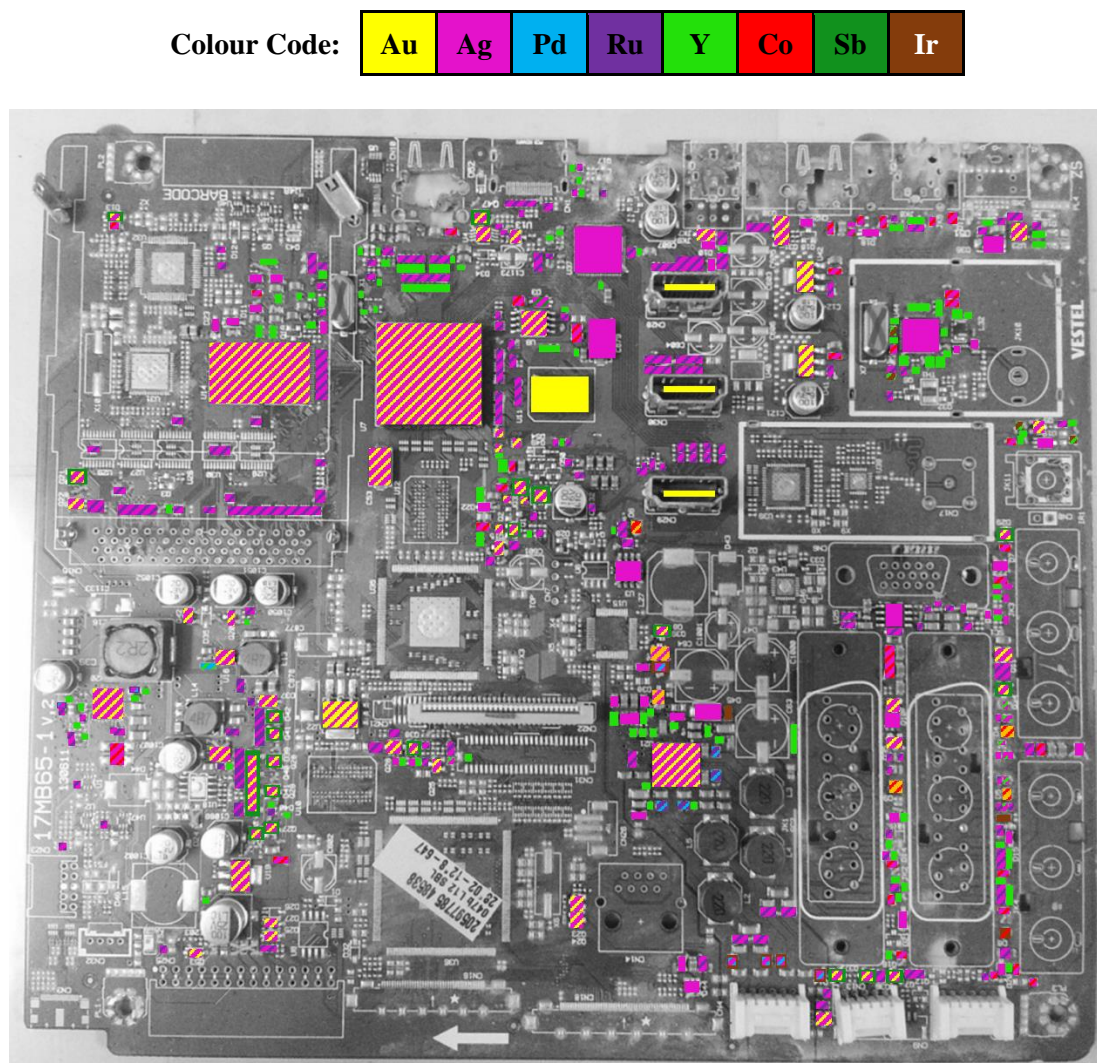
Figure 4.54 *Colour coded CRM distribution in TV main PCB*

It should be possible to develop software capable of analysing digital images of PCBs to identify and quantify components and calculate their value based upon knowledge of component compositions. Such software would be a powerful tool for rapidly identifying components on PCBs containing CRMs for selective disassemble and concentration, although this is outside the scope of this study.

Summary of CRMs identifies in WEEE samples.

Table 4.8 summarises the occurrences of CRMs in WEEE samples identified. Overall, the greatest variety of CRMs in items are found within their PCBs, particularly in those items where miniaturisation to a significant extent is observed. In addition to the CRMs found in PCBs: Sb has been identified in plastics as a flame retardant, Co is present in magnets and ferrite cores of magnetrons, magnesium-alloy is used for laptop housings, Y is present in the phosphors of LCD CCFL backlights, and Nd is present in NIB magnets of HDDs.

Table 4.8 Summary of identified CRMs in trial samples

Critical Material	Identified location
Antimony (Sb)	Was identified within plastics & numerous SMD s, probably as SbO_3
Cobalt (Co)	Co was identified in large concentrations (~19-21 wt%) within LIB cells, ferrous alloys in magnetrons (56 mg total), and within SMDs.
Gallium (Ga)	Ga was identified within LEDs
Magnesium (Mg)	Coated Mg-alloy laptop housings
Nb	CCFLs
Tantalum (Ta)	SMD Ta-capacitors
Tungsten (W)	Identified in ICs
Yttrium (Y)	Found in phosphors of CCFLs (1.7 wt% in CCFL) and in MLCC SMDs
Neodymium (Nd)	NdFeB (NIB) magnets for HDDs, 35wt% (11.4 g/HDD)
Iridium (Ir)	Found in some MLCCs
Ruthenium (Ru)	Found in chip resistor and chip array SMDs
Palladium (Pd)	Found in Au-alloy of contacts, solder, numerous SMDs (chip resistors, ICs, MLCCs & chip arrays)
Gold (Au)	Found in LEDs, contacts, coating alloys on PCBs, and numerous SMDs (ICs, transistors, chip arrays)
Silver (Ag)	Used in numerous SMDs (ICs, chip resistors, MLCCs, transistors, Ta-capacitors, chip arrays & inductors) and Pb-free solder

4.3.3 Evaluation of processes for isolation of CRMs from WEEE

As no CRMs were identified in power boards, and RSA security dongles have been found to be impossible to recycle in a cost-effective manner, these are not considered in this section. Due to the similar nature of the digital media device samples (i.e. mobile phones, MP3 players and cameras) disassembly processes for these are considered together.

Product Disassembly, analysis of components and CRM recycling potential

The following section outlines the disassembly methods used on each of the samples, an assessment of the cost of the process, and where routes for isolated materials could be found, an assessment of the value of material fractions generated based on quantities of CRMs in isolated fractions, as determined by XRF, AAS and ICP-MS analysis. PCBs are considered collectively.

Sanyo domestic microwave magnetron

Disassembly – Following confirmation of the presence of Co in magnets, three attempts were made to isolate them from whole magnetrons. The first, which was to unscrew the magnetron housing and remove the magnetron for disassembly, proved time consuming, as the housing did not easily separate because of the way its parts are fasten together (*Figure 4.55*). The second attempt was to smash the magnets with a hammer to allow their isolation in pieces. This process also proved unsuitable due to the attraction of the magnet fragments to the steel housing, preventing them from falling out of the housing once broken. The third attempt was to strike the magnetron housing with a hammer, deforming it sufficiently to removed it and access the magnets. This was the fastest and most suitable method, a single hammer strike enabling quick isolation of whole magnets.
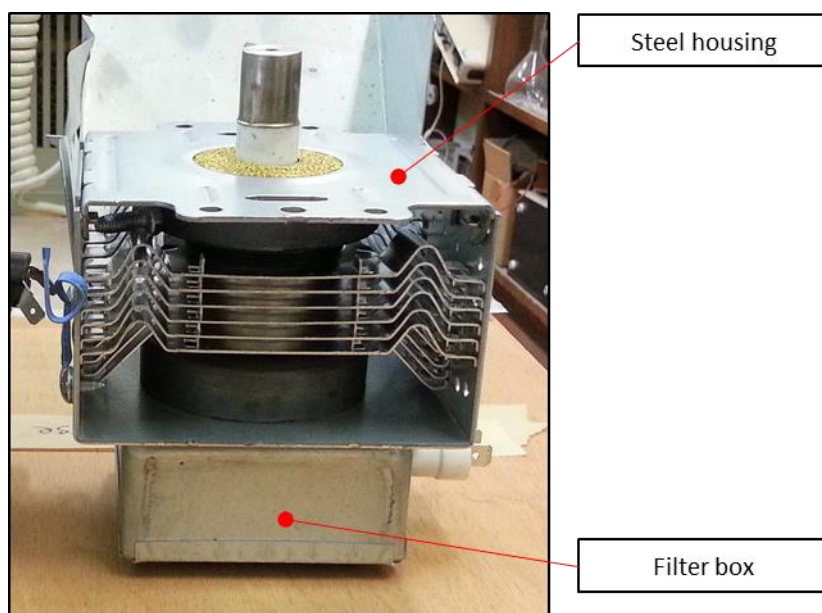
Figure 4.55 Sanyo domestic microwave magnetron

Three methods were attempted to isolate ferrite cores from the filter box, which is not easy to open because of the way the cover is fastened. Opening the filter box is therefore time consuming and costly. An attempt was made to break open the filter box with a hammer prior to removal of the magnets. Isolation of the cores following removal of the magnets was however found to be a better method. Once the magnetron is removed from its housing, copper wires forming the coils of the filter were left protruding from the filter box. Simply pulling these wires out of the filter box resulted in the fastest isolation of both magnets and ferrite cores, in a time of 120 s.

Recovery Potential - AAS analysis revealed that magnets and ferrite cores contain 22.1(±0.3) mg (0.01 wt%) and 6.24(±0.03) mg (0.5 wt%) of Co respectively, totalling 56mg of Co per device. An attempt was made to contact Swift Levick Magnets Europe, the Euro branch of the US company Arnold Magnetic Technologies, who were reported as the only company in the UK recycling cobalt-based magnetic alloys.[191] The company had gone into liquidation and no alternative process was identified. At the time of this study (2012-2013) magnetrons were shipped from Metech as whole items with other small domestic appliances for automated recycling to recovery their scrap metal value.[22] Given the recovery route employed, the magnetic alloy will adhere to the surfaces of ferrous fractions which are sent to scrap steel processes. The most common route for such material is for use in steel making as a coolant. The Co therefore will partition to the metal phase in BOF and EAF processes becoming alloyed with steel.[118] The fate of the ferrite cores is likely to be the same. Co cannot be separated from ferrous materials at EoL through traditional recycling routes, and so no additional value can be derived from isolating Co bearing components of magnetrons in material streams of their own.

Hard Disk Drives (HDDs)

Disassembly - Manual disassembly was carried out with a standard precision screw driver. The PCB was isolated from the HDD casing in a time of 55 seconds. The sheet aluminium cover was removed exposing the internal components of drive. NIB magnet steel supports were removed from the housing. This was not straightforward requiring the magnet supports to be levered out one at a time (two magnets were present in each HDD). Total time required to open the drive and isolate magnets attached to their steel supports was 185 s. No easy way was discovered to isolate the NIB magnets from their steel supports due to the force of attraction between the two. Isolation of HDD platters required an additional 73 seconds (*Table 4.9*).

Table 4.9 *Hard disk drive disassembly times*

Component	Time to isolate (sec)
PCB	55
NIB magnets	185
NIB magnets and platters	258
PCB and NIB magnets	240
PCB, NIB magnets and platters	313

A faster way to gain access to the magnets inside HDDs may be to remove PCBs, and chill the cast aluminium housing, embrittling it so that it may be smashed, granting faster access to the

magnets. Such a process would be analogous to the cryo-cracking method previously discussed. This would however require larger volumes of liquid nitrogen per HDD than will be required to treat mobile phones, camera and MP3 players due to the large size of HDD in comparison to these devices.

Recovery Potential   ICP analysis confirm each magnet contains 5.7(±0.2) g of Nd, 34.9±0.9 wt%, ~4-5% higher than indicated in 2½ inch HDDs by the Öko-Institut e.V.[19] This equates to 11.4 (±0.3) g of Nd per 3½ inch HDD.

At the time of this study (2012) it had been frequently stated that no commercial processes existed for recovery of REMs from HDD magnets.[191] However, discussions with one company revealed that there were markets for refining NIB, developed for processing production scrap from NIB manufacturing. Refinement is possible provided a sufficient quantity can be accumulated. It is speculated that a viable quantity for refining was ~ 300 tonnes. This quantity equates to approximately 184,000 NIB magnets, which would require approximately 92,000 HDD to be manually disassembled from hard drives (presuming two NIB magnets are present in every HDD).

At the time of this study much research was underway to develop a process for HDD NIB recycling, and to date there has been much progress. The hydrogen decrepitation method has received a great deal of publicity as a 'closed loop' process which enables production of new magnets by sintering recovered material. Much research is underway to improve this process.[200-204] In an attempt to enable cost-effective isolation of the magnets from HDDs, the US Critical Materials Institute has developed a robot capable of 'punching' the magnets from drives with high throughput.[58] Both processes allow magnetic materials to be isolated from HDDs whilst avoiding the major barrier represented by high cost of manual isolation of magnets from drives. Numerous other processes have been investigated for recovery of REMs from isolated NIB magnets as reviewed by Yang *et al*., 2017.[205]

Set top box front panel PCBs
Manual Disassembly - The LEDs of the boards (two blue, three green) were simply removed from the PCB with pliers within 20 seconds.

Recovery potential - It was not possible to find any commercial operations recovering Ga from LEDs, and it has been reported that no such process exists in the UK. Indeed, today the only recycling of Ga which occurs at commercial scale is from primary production. LED recycling is problematic. Small quantities of metals are used in each tiny device, which is

encapsulated. This results in problems with accessing the trace amounts of low value metals for recovery. In addition, an enormous number of LEDs would have to be isolated to amass a sufficient quantity for refining (were such a process available). Recent studies have shown that due to technical complexity of recycling Ga from LEDs, and recycling barriers throughout the whole recycling chain, no implementation of commercial recycling is likely in the near future.[206] It is therefore not viable to implement removal of LEDs from STB boards (or any other device). These relatively low grade FR-2 PCBs will be sent for smelting to recover Cu and any PMs, with LEDs in place resulting in loss of Ga to slag in the process.[118] The FP7 funded cycLED project, which aimed at improving the resource-efficiency of LED products, concludes that it is uneconomical at this time to recover any of the CRMs in LEDs (including In, PMs, Ga and REMs). This is due to cots barriers resulting from the dissipative nature of LED applications in WEEE, prohibitive costs of manual isolation, and losses through unintended co-separation in automated recycling.[207] LEDs therefore are an example of the dissipative application of CRMs resulting in non-viable recovery at end-of-life.

Sony Li-ion laptop batteries

Manual disassembly - Eleven samples of the Sony Li-ion battery packs from laptops were collected. These are disassembled from laptops as part of the standard recycling procedure employed by Metech. This is necessary to comply with depollution aspects of WEEE legislation. The question arose - could greater value be generated from disassembly of the battery packs into cells and component parts, rather than sending whole battery packs for recycling via a compliance scheme? Each unit contains six Li-ion cells. The cells were accessed by unscrewing the plastic housing and removing them from their plastic wrap. This process took 157 seconds. Included in the battery pack along with cylindrical Li-ion cells was a small PCB which was isolated in 5 minutes from the housing. This process was difficult as PCBs are permanently bonded in place with adhesive (*Table 4.10*).

Table 4.10 *Times taken for manual disassembly of CRM bearing components of Li-ion battery packs*

Unit	Time taken for isolation (s)
Cells from whole unit	157
PCB	291

Recycling potential

Li-ion cells – There is no capacity to recycle Li-ion batteries in the UK. Three national battery compliance schemes were contacted (G&P, Clarity Environmental, and Budget Pack), to investigate recovery routes in Europe (Holland, Belgium, Germany). Compliance schemes

were found to be the only possible route to recycling for Li-ion batteries. European battery smelters (e.g. Umicore) have minimum quantities they will accept for refining, and compliance schemes perform a crucial function in accumulating Li-ion batteries from across the UK, achieving sufficient quantities to ship. The transportation of Li-ion batteries must be conducted in accordance with UK and international regulation.[208] Compliance with these regulation results in high logistics costs.

The value of the batteries to recyclers was found to fluctuate greatly depending on the type of battery and its cobalt content.[209, 210] For this reason the Co content of batteries was measured by AAS (*Table 4.11*). Each cell was found to contain 8.30g of Co, 18.9 wt%, i.e. 49.8g (15.8 wt%) Co in the whole battery pack.

Table 4.11   *Cobalt content of Laptop Li-ion batteries*

Sample	Cobalt content	
	(g)	(Wt%)
Single cylinder Li-ion battery Cell	8.30(±0.01)	18.9
Whole battery pack	49.82(±0.06)	15.8

Great fluctuations in value have also resulted from volatile market values of Co, which had shown a net decrease over the two years previous to this study (2010-2012). Metech indicated that they used to regularly receive £30/tonne rebate for L-ion batteries, but at the time of the study received variable prices upon request.[211] Li-ion batteries represent a 'pure cost' to UK recyclers with a consignment fee of £80 being charged. Depending on battery chemistry and how costly they are to process, an additional charge may be incurred. Primary Li button cells such as the type found in the RSA security dongle and on PC motherboards are most costly to recyclers, costing up to £2000/tonne to have processed.

When Co prices were high, packet batteries and laptop batteries fetched a price at refineries of £100/tonne but currently (2017) no revenue from recovery is passed down the recycling process chain to recyclers. To see a positive value at refineries, 13-18 tonnes of batteries must be accumulated, which is unlikely to be viable for any one company performing manual pre-processing. If a single recycler could amass such a quantity of batteries then a profit may be generated if materials were sent directly to refineries, by-passing compliance schemes. Some older Li-ion batteries may fetch a profit due to their size and high Co content, but none of this type were included in the trial samples.

Due to regulations regarding handling and treatment of waste batteries, the Co content of the Li-ion batteries is recovered. However, graphite (another critical material) present in cells is

consumed in pyrometallurgical recovery. An alternative route for laptop batteries posing significant benefits in terms of critical materials conservation and revenue generation is sale for re-use in refurbished laptops or as replacements for products with users, once their functionality and storage capacity had been tested and verified as suitable.

As no value can be derived from the LIB cells, and isolation of their PCB is costly due to permanent bonding with the housing, it was deemed economically unfeasible to disassemble laptop Li-ion battery packs.

HP laptop screens

WRAP has published a study on end-of-life treatment of LCD displays, which focused on manual disassembly and shredding.[212] As manual isolation is costly in the UK, and shredding is disadvantageous in terms of recovery efficiencies for CRMs, methods were investigated which augment manual processes to achieve more rapid disassembly.

Disassembly   Manual disassembly of the LCD sandwich from its housing was easily achieved by removal of a series of screws and releasing a series of clip fasteners with the flat end of a screwdriver. This allowed the front bezel of the housing to be removed and the LCD sandwich to be unscrewed and removed from the housing. The main PCB was simply pulled from the back of the LCD sandwich, and the minor PCB detached from the bottom. The aluminium frame of the LCD sandwich in which the cold cathode fluorescent lamp (CCFL) is located was also unscrewed. This was detached by snipping through wires connecting it to the LCD. Times taken to isolate the CRM bearing parts of the screen using manual disassembly are given in *Table 4.12*.

Table 4.12 Time to manually isolate CRM bearing components of LCD displays

Component	Time to isolate (sec)	Cost (£)
AZ91D Mg-alloy housing	180	0.79
Minor PCB	224	0.99
Major PCB	248	1.09
CCFL	390	1.72

Disk Cutting - An attempt was made to isolate the CCFL and PCBs from the rest of the LCD unit by cutting the bottom section from the screen. This was followed by removal of the two side edges of the housing to open it for easy removal of PCBs. The first attempt to remove the bottom of the screen used a Dremel handheld multi-tool with rotating cutting disk attachment. This was extremely time consuming and after 10 minutes very little progress was achieved. The second attempt used the rotating cutting disk of a wet tile cutter to saw directly through

the screen parallel to its bottom edge, isolating the piece of housing containing the CCFL (*Figure 4.56*), which was prized open with a screw driver to access to the CCFL in a total time of 241 s. Repeated attempts always resulted in the CCFL being broken. This shows the method to be unsuitable, resulting in release of Hg from the CCFL posing an environmental H&S hazard.[212, 213] Removal and opening of the remaining two sides of the housing to isolate PCBs required an additional 141 seconds. A faster method of gaining access to the PCBs was to cut through the top and side edges of the housing avoiding the LCD sandwich inside. Using this method both PCBs were isolated from whole displays in a time of 154 seconds.

Figure 4.56 *LCD screen with the CCFL containing portion cut away*

Guillotine   Use of the guillotine to remove the top and side edges of the housing allowed the PCBs to be isolated in 65 seconds. This was by far the fastest method of opening the housings (*Table 4.13*) and requires no electricity, unlike the tile cutter.

Table 4.13 *Comparison of best times for LCD screen disassembly methods.*

Method	Isolation of CCFL (s)	Isolation of PCBs (s)	Isolation of CCFL & PCBs (s)
Manual disassembly	-	248	390
Tile cutter	241	154	382
Guillotine	-	65	-

Recovery Potential

Housing - Although the Mg-alloy housing is easily isolated using the guillotine, no companies in Europe processed painted magnesium alloy laptop housings. Most die casters in Europe would only process internal production scrap, which gives foundries a guaranteed source of supply of known composition at a stable price.

Magnesium Elektron in Manchester provide a recycling service for Mg processing scrap, but do not deal with post-consumer waste due to contamination issues. The paint from magnesium alloy laptop housings is likely to release dioxins which are not fully removed by the abatement plant. The presence of any copper wiring or stainless steel bolts/fixings would also downgrade the value of the scrap. This contamination would therefore mean that only small volumes of this type of material at a time may be accommodated in the process. Removal of such contamination from the housing would be costly. It is also questionable whether sufficient capacity exists to accommodate the volumes of Mg-alloy laptop housings that will enter the waste stream.

The recycling of coated Mg-alloy is problematic due to the difficulties encountered with complete removal of coatings using thermal processes of de-coating.[214-216] The only company identified to successfully process painted magnesium alloy laptop housings is Fujitsu Group in Japan.[217] They became the first in the world to achieve practical application of a technology for recycling Mg-alloy from housings of notebook computers collected in-house, and they began employing the technology in product manufacturing in Autumn of 2002. The paint is stripped off using solution treatment, and Al and Mn are added during re-melting to increase strength and corrosion resistance of the recycled alloy. The performance of the recycled alloy is almost equal to that made using virgin materials.[218] Shipping to Japan would require large quantities of laptop housings to be accumulated, and for this reason it is not a viable route to recovery for Metech. The problem of scale is less of a concern for specialist LCD recyclers who receive large quantities of screens and housings from AATF's.

CCFL: The presence of Hg, which is controlled by the RoHS directive, will complicate CCFL recycling and cause the process to be costly, requiring atmospheric monitoring and extraction systems, as well as special licensing. It is unlikely Metech would implement such a process given the volumes of material available to them and their inability to derive value from the CCFL. Metech will therefore continue to send whole laptop screens to specialist processors.

Digital Media Devices

The vast majority of recoverable value and CRMs found in MP3 players, mobile phones and digital cameras is concentrated in PCBs which are constructed from common SMD

components. For this reason, these products have been grouped into this single section. In addition to high-grade PCBs, all these items contain similar screens and packet Li-ion batteries. The PCBs are high-grade but despite this, they are not disassembled by Metech due to the costly nature of disassembly.

Disassembly

MP3 players **-** Complete manual disassembly of a Sony NWZ-s639F digital media player (MP3 player) into its parts was achieved in 105 s using a power screw driver. The time taken to isolate each of the CRM bearing parts is indicated in *Table 4.14:*

Table 4.14 MP3 player disassembly times

Component	Time to isolate (sec)	Cost (£)
Li-ion battery	52	0.23
Major PCB	62	0.27
Screen	94	0.41
Minor PCB	105	0.46

Cryo-cracking with liquid nitrogen was attempted on a similar Sony Walkman digital media player (*Figure 4.57*). Costs associated with use of liquid nitrogen are given in *Table 4.17*. The sheet aluminium casing on this player was not easily removed by this method. Repeated submersions were necessary before the casing was eventually opened by hammering. Time for isolation of the PCB was ~4 minutes. Repeated impact resulted in detachment of the larger ICs from the rest of the board. This made their recovery from debris generated in the process difficult. Failing to recover detached ICs results in loss of potentially recoverable value from PCBs along with CRMs. While the method is suitable for plastic digital media players, it is unsuitable for those with metallic casings.
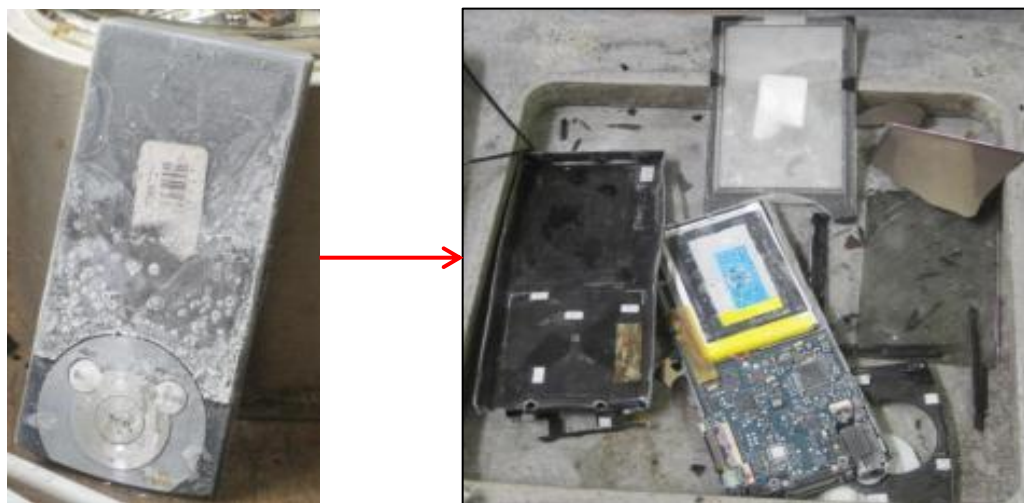
Figure 4.57 Liquid nitrogen cooling and smashing of MP3 player

Digital Cameras - Complete manual disassembly of the Sanyo X1220 digital camera with a power screw driver was achieved in 166 s. The times taken to isolate each of these components is indicated in *Table 4.15*.

Table 4.15 Digital camera disassembly times

Component	Time to isolate (sec)	cost (£)
Li-ion battery	8	0.035
Screen	120	0.53
PCB	166	0.73

Digital cameras exhibited mixed performances in cryo-cracking. Plastic casings are easily shattered after 20 s submersions in liquid nitrogen (*Figure 4.58*). If the PCBs are located near the rear (screen side) surface of the device, shattering the case in this way enables easy isolation. However, several of the cameras examined had PCBs located deeper within the structure of the camera behind other components, making isolation following cryo-cracking more difficult, requiring removal of additional screws, components and internal structural parts. One camera had an aluminium front casing which absorbed much of the impact when smashing, making removal of the plastic case more difficult.
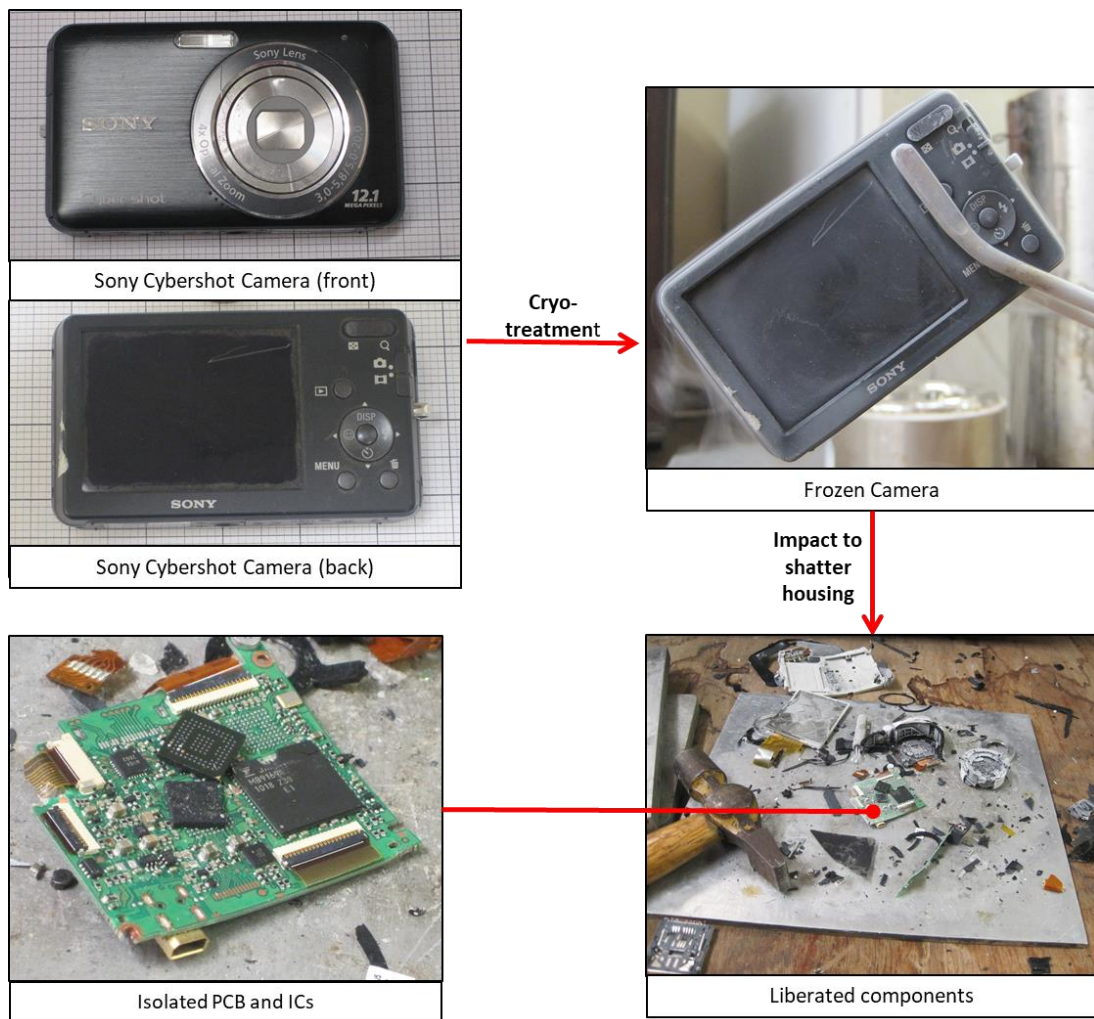
Figure 4.58 *Cryo-cracking of a Sony Cybershot digital camera to isolate its PCB*

Times for disassembly achieved with cryo-cracking for cameras with plastic cases are comparable to those for MP3 players, ~30s total. Cryo-cracking was also attempted on a digital video camera (*Figure 4.59*), which had proved problematic to disassemble. There are multiple PCBs in the device housed in different sections. These are relatively small as the functionality of the device is split between PCBs in the different parts of the camera. Isolation of all PCBs is time consuming. To achieve liberation of all components with cryo-cracking, repeated submersion in liquid nitrogen were required to shatter each housing section and isolate PCBs separately. PCBs were fastened to the device so isolation required further manual disassembly. The design of the device therefore prohibits easy isolation of PCBs through manual disassembly and cryo-cracking. A total of 60s submersion time was required, after which PCBs were still not easily isolated.

Figure 4.59 *Sony Xacti Full HD 10 MP digital video camera sample post cryo-treatment*

Mobile phones - A Nokia 6230i was selected for disassembly as a representative sample of the mobile phones currently received by Metech for treatment. Complete manual disassembly of the Nokia 6230i mobile phone sample to its CRM bearing components was achieved in 87 s with a powered screw driver. The time taken to isolate each of the constituent CRM bearing parts is indicated in *Table 4.16*.

Table 4.16 *Time to isolate CRM bearing components of mobile phones using manual disassembly*

Component	Time to isolate (sec)	Cost (£)
SD Card	8	0.04
PCB	87	0.38
Screen	87	0.38
Speaker Magnet	98	0.43

Casings of mobile phones were easily shattered following submersion in liquid nitrogen, and since very little of the structure of the devices was metallic the PCBs could be rapidly isolated. (*Figure 4.60*). Some loss of ICs occurred but the problem is not as serious as in items where repeated hammering is necessary to gain access to the PCBs. Cryo-cracking was well suited to isolation of PCBs from mobile phones, requiring only 20 s submersions in liq. nitrogen and a further 10 seconds of hammering to isolate the board.
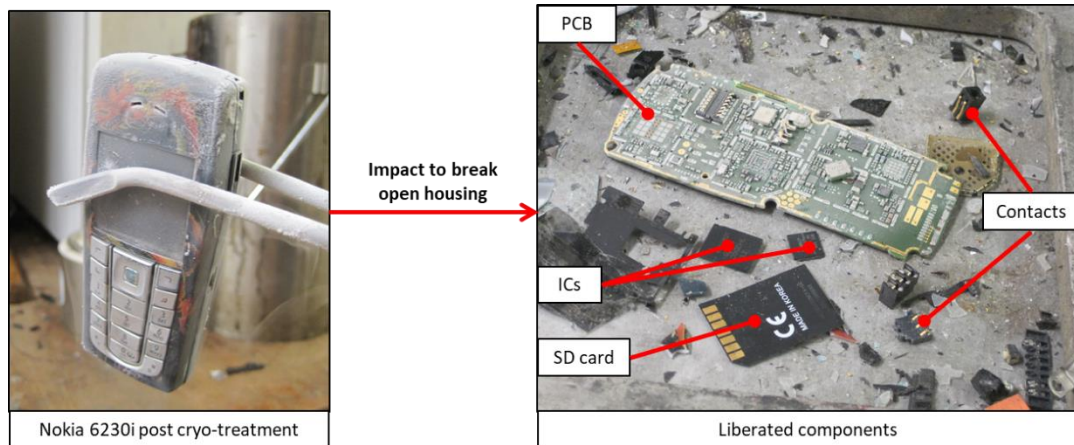
Figure 4.60. Cryo-cracking of Nokia 6310i mobile phones sample to isolate SM bearing components

General comments on disassembly methods

The equipment costs for manual disassembly are low. However, this process is time consuming resulting in high labour costs. Cryo-cracking enabled rapid isolation of high grade PCBs and lithium-ion batteries from digital media devices. Time trial results for isolation of PCBs with cryo-cracking are given in *Table 4.17*. Based on the time taken to perform the procedure, and costs of equipment and liquid nitrogen, the total cost of the process was ~10p/sample. This method was well suited to items with plastic housings and no major metallic structural features, e.g. mobile phones. Difficulty was encountered for items which have metallic structural features which remain ductile following cooling and obscure access to PCBs once housings are removed. However, consideration of H&S will be necessary before any industrial process based on this method can be implemented due to use of liquid nitrogen and the issue of flying fragments from items.

Table 4.17 Results of product disassembly following liquid nitrogen treatment and cracking

Item	Model	Item Mass (g)	PCB mass (g)	Immersion time (s)	Cost of process (£)
Digital Camera	Sony Cyber Shot: Steady shot DSSC-W310 12.1 MP (no battery)	115.99	6.10	20	0.102
Mobile Phone	Nokia 6350i (no battery)	75.8	12.99	20	0.102
Digital media player	Sony Walkman NWZ-A845 (including battery)	59.37	6.91	20	0.102
Video camera	Sony Xacti Full HD 10 MP (no battery)	115.24	11.06	60s*	-

* Required 3 submersions before all PCBs could be liberated

An enquiry to BOC revealed this process would cost around £3,000 investment for a liquid nitrogen dewar, with consumable costs of liquid nitrogen £2.29/L (sufficient to process ~200 products per litre of liq. nitrogen).[219] A breakdown of sample disassembly costs is given in *Table 4.18.s*

Table 4.18 Breakdown of costs for cryo-cracking

100 L of liq. nitrogen	£229.00
Delivery charge	£48.85
Total cost	£277.85
Units processed	20,000
Liq. Nitrogen cost per item	£0.0139

Liquid nitrogen is costly and it may not be necessary to cool items to -178 ºC. Investigation of embrittlement temperatures of commonly used WEEE plastics (e.g. PC-ABS) will provide data upon which it may be possible to develop less costly alternative cryo-cracking methods, e.g. using solid CO_2. Design and material composition of items should be assessed to determine suitability of individual items for cryo-cracking. This method could be scaled up for industrial use by freezing multiple items simultaneously and feeding them into an automated process to shatter casings while limiting losses of CRM bearing components. A jaw crusher may be a good solution.[220]

CRM recovery potential

Li-Ion batteries - The inability to derive additional value from LIBs has been discussed previously with regard to laptop battery packs. Co content for LIB types encountered in samples as determined by AAS is given in *Table 4.19*.

Table 4.19 Cobalt content of Li-ion batteries

Battery	Co content	
	(g)	Wt%
Cylinder Li-ion	8.30(±0.01)	18.94(±0.02)
MP3 packet Li-ion	2.46(±0.02)	20.8(±0.2)
Mobile phone packet Li-ion	4.17(±0.01)	19.44(±0.07)

Speaker magnets – ICP-MS analysis of the magnets showed each contains 133(±3) mg of Nd, equivalent to 27.9(±0.7) wt%. This concentration is comparable with NIB HDD magnets from notebook computers reported by the Öko-Institut e.V.[19] No commercial recovery route for these items could be found, and a great deal of time and effort is required to isolate them from

casings of the device. As discussed previously, at the time of the trial (2012-13) there was little chance of recovery of Nd because of a lack of available recovery infrastructure.

Screens – As previously discussed, at the time of thia study no organizations were operating recovery processes targeting indium in LCDs. Since the time of this trial, a cross-current leaching method has been developed by Rocchetti *et al*., which achieves economic recovery of In from LCDs.[221, 222] Dissolution of ITO from multiple screens in a single volume of nitric acid enables an economic quantity for recovery to be collected. How close this process is to commercialisation is unclear, and what quantity of screens would need to be amassed to ship for refining in Italy is also unknown. It is likely that limitations of scale will mean that Metech continue to send LCDs to specialist processors in the UK, who may then send larger quantities to this process once commercialised. SMDs and gold connectors on the 'flexible PCB' type connectors of screens can be included with PCBs for downstream recovery.

PCBs –Most waste PCBs are smelted to recover Cu, PMs and PGMs. There are economic and thermodynamic limitations to viable recovery of other CRMs in this process. The way in which metals partition between the liquid copper and slag phases during smelting is important in determining recycling potential.[118] Metals which do not dissolved in liquid copper have no chance of recovery in subsequent refining processes. Umicore's integrated smelting facility in Hoboken, Belgium is the most advanced plant of its kind, and in addition to the normal metals recovered Sb and In are target metals for recovery. Many of the PCBs from the UK find their way to this process, although there is competition for material between European and Asian refiners, and In and Sb may not be recovered from material sent to alternative recovery processes. Co, Ga, Ge, Y, Ta and W in PCBs are not recovered. For these reasons, there is little prospect of recovering CRMs from PCBs other than PMs, PGMs, Sb and In.

For CRMs in PCB components which are not targeted in recovery, isolation of these components from PCBs prior to smelting is the only viable option to prevent loss of these materials, and improve prospects for their eventual recovery. This strategy has been advocated by others for recovering CRMs from LEDs, Ta-capacitors, and Y from MLCCs.[207, 223] Correspondence with Delta Products, professionals dealing in minor metals recycling, revealed that a market exists for recovery of Ta from capacitors; however this is only viable for minimum quantities of 500 kg. [224] It was advised that the value of such a material would be equivalent to that of tantalite ore - £40-50k per tonne at the time of the trials. Ta capacitors weigh ~0.25 g each, meaning ~2 million capacitors would have to be isolated from PCBs to achieve a viable quantity for refining, requiring ~2,700 man hours at a cost of ~£44k (~£88k/t) to Metech. This strategy is not economically viable for Metech using manual isolation..

Capacitor Grade Ta powder is more valuable, ~£100k/t. If a process of isolating Ta from capacitors could be established, this may provide sufficient value to justify their isolation. Automation could also reduce costs of isolating capacitors, improving the economics of recovery. The process of isolating 500 kg of capacitors would take years at Metech with a long delay to any financial return seen given levels of material throughput at the time of the trial. This would be detrimental to cash-flow, and so such a process is unlikely to be adopted my recyclers operating at similar scales. Prospects for Ta recovery are better in organisations dealing with larger volumes of PCBs at high throughput, such as refiners, where isolation of Ta-capacitors from PCBs prior to smelting is a potential pathway to enhanced CRM recovery rates and avoid dissipative losses in recycling.

There is no economic justification for adopting equivalent processes to isolate LEDs (which contain Ga, REMs & PMs), or MLCCs (which contain Y), because no viable recovery options exist. It is important to point out that where SMDs contain both target and non-target materials of smelting processes, a dichotomy exists between the requirement to retain CRMs within the economy, and the desire to derive the maximum possible economic value from WEEE. Stockpiling of SMDs containing non-target CRMs of existing smelting processes in anticipation of a possible future recovery solution, when components have a high derivable value through smelting is not sensible for recyclers when the vast majority of material value can be exploited in current processes.

PCB component isolation methods

CRMs are often found in surface components and edge contacts of PCBs. Enhancing the value derived from recovery of these materials may be possible by isolating them from PCBs, thus concentrating them into a lower mass fraction. This will reduce refining costs (see *Section 1.5* re refining costs). It is also generally true that recovery efficiency increases with target material concentration.[106]

Contacts

Contacts soldered to boards - Manual isolation of gold contacts from the PCB and housing of the Nokia 6230i with pliers was achieved in 60 seconds at a cost of £0.26 (*Figure 4.61*). AAS analysis revealed the contacts contained 3.82 (±0.04) mg of gold in total and the isolated contacts fraction contains ~1300 ppm of Au.
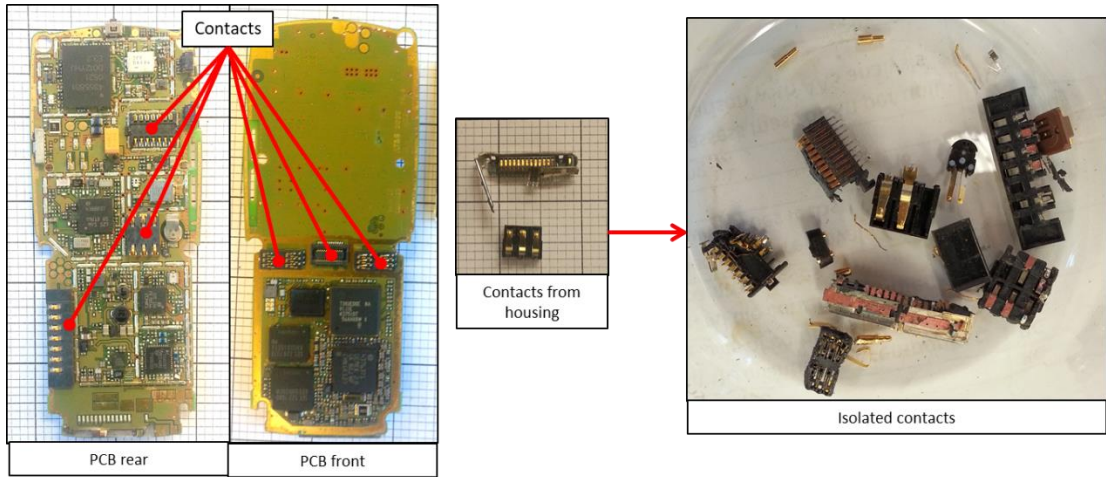
Figure 4.61 Isolation of contacts from Nokia 6230i mobile phone PCB and housing

PCB edge contacts - Both the guillotine and the tile cutter were used to separate the contacts deposited directly onto the PCB of a series of samples -graphics cards, TV LCD PCBs, server boards and Ethernet cards (*Figure 4.62*). The quantities of gold & copper found in each were analysed with AAS to establish their value (*Table 4.20*).

Figure 4.62 Gold edge connectors removed from graphics card

Table 4.20 Gold and copper quantity in samples and the value of these metals (based on market values, not revenue received from refiners)

Contacts from item	Au content (mg)	Cu content (mg)	Total value (£)
TV LCD PCB	1.16	1363	0.045
Ethernet card	4.11	231	0.137
Server board	22.2	408	0.736
Graphic card	2.95	63.2	0.098

Guillotine - *Table 4.21* shows times takes to cut the edge connector from a board and the costs of carrying out this operation. The method allowed rapid isolation of gold coated sections of PCBs and was a good tool for large mass high volume sections where the high value parts on boards such as edge connectors can be easily removed and bulked together. PCB guillotines are readily available. This process could possibly be automated by using image recognition of the gold edge connectors to align them with a guillotine blade.

Table 4.21 *Time to isolate gold edge contacts from PCB devices using a guillotine and cost of operation*

PCB	Contacts separation time per board (s)	Cost per board (£)
TV LCD PCB	8	0.0352
Graphics card	4	0.0176
Server board	6	0.0264
Ethernet card	4	0.0176

Wet Tile cutter - Despite this being a powered cutter it still took as long to remove edge contacts as the guillotine (*Table 4.22*). The tile cutter allows more intricate cutting of boards than the guillotine, and will cut through boards over 2 mm thick and 200 mm wide. However, this method presents more health and safety issues than the guillotine as it is dangerous for the user if care is not taken; it is noisy and the waste water will contain a slurry of toxic PCB dust which will have to be properly disposed of. It also has higher investment and running costs: The cutter costs £400, and replacement blades are £25-35 each. The power consumption during cutting was 880W.

Table 4.22 *Time to isolate gold edge contacts from PCB devices using a wet tile cutter and cost of the operation (based on energy demand and time of process)*

PCB	Contacts separation time (s)	Cost per board (£)
TV LCD PCB	8	0.037
Graphics card	4	0.019
Server board	6	0.028
Ethernet card	4	0.019

The Rubi ND-200 wet saw selected is suitable for industrial use and has the following advantages: It has a cutting table large enough to accommodate larger boards than the guillotine; clearance between the cutting table and the cutting wheel guard is adjustable and sufficient to allow it to cut around and/or through the majority of components found on PCBs;

the water supresses the generation of PCB dust and it can be topped up with a jug or hose rather than requiring permanent plumbing; and spare parts are readily available.

On a commercial scale, areas identified as containing concentrations of target materials could be cut away from the rest of the PCB using a guillotine, wet circular saw, laser, snips, a punch or a water jet. It is likely that this method would be used in conjunction with manual selective disassembly to speed up the process.

SMDs

Manual isolation - Manual selective disassembly of SMDs from PCBs involved no specialist equipment or initial capital outlay. Standard tools were used to successfully scrape or pull SMDs from PCBs. The results of times taken for removal of all surface components from MP3 player and LCD PCBs are given in *Table 4.23*. This method, used in conjunction with the image library would allow quick identification and 'cherry picking' of CRM bearing SMDs from PCBs prior to sending PCBs for recovery. This would be particularly advantageous for recovery of Ta capacitors, and components containing other CRMs such as Ge and Ga which are lost in smelting processes. However, as a means of depopulating entire PCBs, the method is time consuming and costly. For this reason, the method was only tested on two samples before being abandoned.

Table 4.23 *Time taken for manual removal of components from PCBs and process cost*

PCB	Time taken (s)	Cost of process (£)
MP3 player main PCB	240	1.06
LCD main PCB	600	2.64

De-soldering of PCBs (thermal methods)

Blow Torch - This method has low running costs: The Dremel Versaflam was available from £30 and the butane gas fuel is available in 200 ml canisters at a cost of approximately £2. The cost of gas is likely to be a low operational cost in any scaled-up process as a canister refills the Versaflame many times, which was not necessary over the duration of the trial. However, it was difficult to avoid burning boards with this method which presents a H&S issue. In addition, removing components from a whole board with this method was time consuming, requiring operators to slowly work their way across PCB surfaces to remove all SMDs. Results of time trials on PCBs using this method and the associated costs of the process are shown in *Table 4.24*.

Table 4.24 *Time taken for isolation of components from PCBs and process cost*

PCB	Time taken (s)	Cost of process (£)
MP3 player main PCB	36	0.1584
Mobile Phone	120	0.5279
Camera	266	1.170
LCD main PCB	60	0.2640

<u>Soldering Iron</u> **-** This method was very time consuming as it can only be used for the removal of one component at a time. Therefore, it is not a viable option to recover components for recycling on an industrial scale.

<u>Paint Stripping Gun</u> **-** Typically, the 2 kW heat gun took 15-30 s to reach a sufficient temperature to soften solder. Solder around individual components took a further 3-5 seconds to soften sufficiently to remove them. A disadvantage of this method was that the temperature of the gun could not be set and therefore over-heating and burning of SMDs and PCBs may occur, liberating hazardous emissions and posing a H&S issue. Running costs were high compared to other thermal methods, and the process was time consuming (*Table 4.25*).

Table 4.25 *Time taken for isolation of components from PCBs, energy demand and process cost using a paint stripping gun.*

PCB	Time taken (s)	Energy cost (£)	Cost of process (£)
MP3 player main PCB	60	0.003182	0.2671
Mobile Phone	180	0.009546	0.8014
Camera	300	0.01591	1.336
LCD main PCB	120	0.006364	0.5343

<u>Solder Bath</u> – When PCBs were placed on the surface of molten solder, solder holding SMDs to PCBs softened sufficiently for component removal in 10-20 s. This method could also be used with double sided boards as the majority of SMDs on the underside of PCBs in contact with the liquid solder surface remained in place until removed from the solder bath. Those that did detach remained floating on the surface of the molten solder and were easily sieved out again. *Table 4.26* shows times taken to remove SMDs from PCBs, cost of energy consumed and the total cost of the process.

During use, the solder bath used 500 W. It allowed rapid removal of components from a PCB without destroying them. The solder bath system could be scaled up for industrial use as there are many larger sizes available. Today, component removal from PCBs is a common practice

on manual recycling lines in China. With a larger bath a greater number of boards could be processed simultaneously, potentially reducing operational costs. Automation of the process could potentially increase the cost benefit and speed. However, the equipment cost (~£3k) and increased energy required to heat a larger volume of solder (~3-5kW) would need to be taken into account. The solder cost will be dependent upon the solder type. Lead solder can cost up to £40/kg, which should last for hundreds of boards. It would require occasional topping up of the solder during operation.

Table 4.26 *Time for isolation of SMDs from the surfaces of PCBs using a solder bath*

PCB	Time taken (s)	Energy cost (£)	Cost of process (£)
MP3 player main PCB	15	0.000199	0.0662
Mobile Phone	20	0.000265	0.0883
Camera	20	0.000265	0.088
LCD main PCB	15	0.000199	0.0662

NIR oven **-** The NIR oven used was successful at softening solder for removal of SMDs from PCBs. However, difficulty was encountered when attempting to find the correct balance of power and travel rate through the overn to soften solder without burning PCBs, which results in toxic emissions and environmental H&S issues. Further research would be necessary to optimize the operational parameters to soften solder without burning boards, and it is likely that these setting will vary depending on the alloy of solder employed on boards and the IR absorbing nature of the PCB substrate. For this reason, the method was found to be unsuitable for adoption by Metech. The high throughput possible lends itself to adoption at industrial scale however, and although outside the scope of this project, with further research, NIR ovens could be adopted for large scale depopulation of waste PCBs. The nominal power of the NIR investigated was 25kW. The machine cost £25k plus installation costs, e.g. extractor fans, fume hoods, and safety curtains.

Value of isolated components – To determine cost benefit of component isolation with each technique it was necessary to analyse the samples of isolated components from each PCB and establish their value. Isolated components from PCBs were therefore sent to BASF metals recycling (Cinderford) where Metech were sending PMR materials for refining. BASF conducted precious metal assay on the materials, and provided the results and refining terms from which a value for each batch of isolated components was calculated (*Table 4.27*).

Source of components	Mass (g)		Metal				Total	Treatment Charge (£/t)
			Au	Ag	Pd	Cu		
		Recovery efficiency	98%	95%	85%	98%		
		Refining Charge (£/kg)	200	25	475	-		
MP3 player	2.8169	Metal content (Wt%)	0.16	0.29	0.011	10.8		
		Metal content (g/t)	1,600	2,900	110	108,000		
		Value of contained metal (£/t)	57,544	2,015	1,579	590	61,728	1,800
		Refining charge (£/t))	320	72.5	52.25	-	444.75	
		Value of recovered metal (£/t)	56,393	1,914	1,342	578	60,228	
Mobile phone	3.4114	Metal content (Wt%)	0.146	0.131	0.066	16		
		Metal content (g/t)	1,460	1,310	660	160,000		
		Value of contained metal (£/t)	52,509	910	9,475	873	63,768	1,800
		Refining charge (£/t))	292	32.75	314	-	638.25	
		Value of recovered metal (£/t)	51,459	865	8,054	856	61,234	
Camera	2.1410	Metal content (Wt%)	0.047	0.08	0.004	24.7		
		Metal content (g/t)	470	800	40	247,000		
		Value of contained metal (£/t)	16,903	556	574	1,349	19,382	1,800
		Refining charge (£/t))	94	20	19	-	133	
		Value of recovered metal (£/t)	16,566	528	488	1,322	18,903	
LCD PCB	1.288	Metal content (Wt%)	0.115	0.29	0.014	19.6		
		Metal content (g/t)	1,150	2,900	140	196,000		
		Value of contained metal (£/t)	41,360	2,015	2,010	1,070	46,455	1,800
		Refining charge (£/t))	230	72.5	66.5	-	369	
		Value of recovered metal (£/t)	40,533	1,914	1,708	1,049	45,204	

Market values of metals used: Au = £35.9652 /g; Ag = £0.6949/g; Pd = £14.3566/g; Cu = £5.46/kg. Terms of refining: £1,800/t treatment charge then made on recovered metals (metal content of material x recovery efficiency) less refining charges for Au, Ag and Pd content of material

Methods used to concentrate CRM content in the isolated components

Microwave ashing

Dry ashing procedures using traditional muffle furnaces are time consuming, requiring hours to fully ash samples. When plastic/resin samples are to be treated, a pre-ashing process is also necessary which adds to process costs. However, microwave ashing uses microwave absorbing silicon carbide elements and samples can be ashed in less than an hour with no pre-treatment necessary. For this reason, ashing of isolated CRM bearing samples was trialled with isolated edge contacts from PCB samples. There are numerous suppliers of microwave muffle furnaces which cost in the region of £10-15k depending on required capacity.

Gold edge contacts isolated from PCBs using the guillotine and tile cutter were ashed (*Figure 4.63*). The mass reduction achieved and corresponding savings in treatment charges at the refinery are given in *Table 4.28.* Au & Cu content of isolated contact samples was determined by AAS, the results of which with calculated value increase for Metech associated with ashing 1 tonne of each based on BASF's refining terms are given in *Table 4.29*.

Figure 4.63 *Ashed gold edge contacts isolated from graphics card PCB*

Table 4.28 *Mass reductions and savings on treatment charges achieved for materials with microw...*

Samples	Mass (g)	Ashed sample mass (g)	Mass reduction (g)	% of original mass	Saving treatm charge
TV board contacts	3.3804	2.7471	0.6333	81%	337
Graphics card contacts	1.752	1.1705	0.5815	67%	597
Server board contacts	3.108	1.7329	1.3751	56%	796
Ethernet Card contacts	1.701	0.8293	0.8717	49%	922

Table 4.29 *Value gained from microwave ashing of 1 tonne of isolated contacts from samp...*
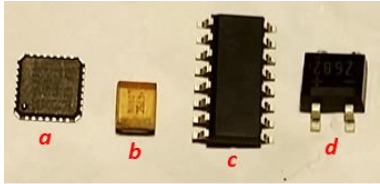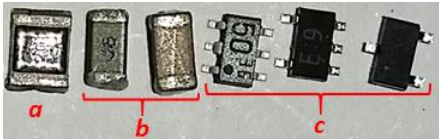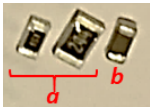
Sample	Mass (t)	[Au] (ppm)	[Cu] (kg/t)	Refining charges (£)	Recovered Au value (£)	Recovered Cu value (£)	Total charge (£)
TV board contact	1	345	403	69	12,151	2,157	1,869
Ashed TV board contacts	0.812	424	496	69	12,151	2,157	1,532
Graphics card contacts	1	2,350	132	470	82,812	706	2,270
Ashed graphics card contacts	0.668	3,517	198	470	82,812	706	1,672
Server board contacts	1	7,158	131	1,432	252,289	702	3,232
Ashed server board contacts	0.557	12,838	235	1,432	252,289	702	2,435
Ethernet card contacts	1	1,734	37.2	347	61,126	199	2,147
Ashed ethernet card contacts	0.487	3,557	76.2	347	61,126	199	1,224

The CEM microwave ashing oven costs £10-12k. Each run could hold 50 g of ashable material and consumed 1.06 kWh of electricity. The process significantly reduced volumes and masses of boards which could result in significant logistics savings when transporting materials to smelters in Europe. However, smelters will only accept minimum loads of 500 kg for refining, which could require ashing of >285,000 graphics card edge connectors and result in considerable expenditure before a return on processed material is received from refiners. This would be detrimental to healthy cash flow, particularly for smaller recyclers. This process also requires ventilation for the release of smoke which presents potential environmental and H&S issues. Any industrial process based on microwave ashing will require investment in a scrubbing system for removal of hazardous compounds evolved in the process, adding considerably to the capital investment required.

Sieving

The results of sieving are indicated in *Table 4.30.* All fractions produced were predominantly composed of PM and PGM bearing components in which these metals represent the most significant value by far. Each of the fractions can be recovered in the same downstream PM recovery process (either hydrometallurgical or pyrometallurgical). It is interesting to note that Ta capacitors are isolated in the 9.52-2.80 mm fraction. Were a viable downstream recovery option available for Ta in these components, then this seems a promising way of isolating them from large volumes of mixed SMDs. Although included in a fraction with PM rich components, the process of isolating the Ta-capacitors from these fractions may be easier than attempting to sort them from all components. This sorting may be possible with automated optical recognition systems, or XRF based intelligent sorting systems. The size range of components in this fraction is also relatively large, and use of more sieves with mesh sizes within this range may result in greater concentration of Ta within a narrower size range fraction. Loading the stack of sieves with SMDs and shaking for 60s incurrs a cost of £0.13. Further investigation into the value per unit mass of each fraction may reveal a cost benefit to the process if fractions of significantly different grade can be generated, through avoidance of treatment charges at refineries on higher grade fractions.

Table 4.30 SMDs and CRMs contained in sieved fractions

Fraction (mm)	SMDs		CRMs contained
>9.52		*Memory ICs*:	Au, Ag, Pd
9.52-2.80		a. *ICs:* b. *Ta capacitors*: c. *Small outline ICs*: d. *Transistors*:	Au Pd Ag Ag, Ta Au, Ag, Pd Au, Ag, Sb
2.80-1.68		a. Chip resistors: b. MLCCs: c. Transistors:	Ag, Pd, Ru, Co, Sb Ag, Pd, Ir, Y, Nb Au, Ag, Sb
1.68-1.40		*Chip Arrays*	Au, Ag, Pd, Ru
<1.40		a. *Chip resistors* b. *MLCCs*	Ag, Pd, Ru, Co, Sb Ag, Pd, Ir, Y, Nb

4.3.4   Cost Benefit Analysis

Isolating the Gold Contacts from Boards

CBA was conducted for methods used to isolate the gold edge contacts of PCBs generated as part of Metech's standard manual disassembly operations. The components considered were: TV main PCBs, graphics cards, server boards and ethernet cards. The guillotine and tile cutting operations were analysed alone, and in combination with the microwave ashing processes used to concentrate value in the contacts. The results are presented in *Table 4.31 & 4.32*.

The increase in revenue seen for materials as a result of reduced mass based treatment charges at the refinery does not compensate for the costs of electricity and labour incurred by ashings.

Table 4.31 *No of each PCB sample investigated required to generate 500 kg of ash from contacts, calculated costs of isolating conta[...] received for this material based on BASF refining charges (issued to Metech in 2012).*

| PCB | No processed | Operation | Costs (£) | | | Revenue for mate[...] |
			Labour	Power	Total	(£)
TV board contact	182,010	Guillotine separation	6,406	-	6,406	7,653
Graphics card contacts	427,168	Guillotine separation	7,517	-	7,517	60,806
Server board contacts	288,534	Guillotine separation	7,616	-	7,616	223,975
Ethernet Card contact	602,918	Guillotine separation	10,610	-	10,610	60,691
TV board contact	182,010	Tile cutter separation	6,406	33.98	6,440	7,653
Graphics card contacts	427,168	Tile cutter separation	7,517	39.87	7,557	60,806
Server board contacts	288,534	Tile cutter separation	7,616	40.40	7,657	223,975
Ethernet Card contact	602,918	Tile cutter separation	10,610	56.28	10,666	60,691

* does not consider the difference in revenues obtained from material flows of whole samples with contacts attached, and separate [...]

Table 4.32 *Cost-benefit analysis of isolating and ashing contacts to produce 500 kg of ash from the quantities of analyse[...]*

| PCB | Operation | Units processed | Ashing costs (£) | | | Total Cost (£) | Reve[...] mater[...] |
			Labour	Power	Total		
TV board contact	Guillotine separation + ashing	182,010	6,496	1,245	7,742	14,147	7,[...]
Graphics card contacts	Guillotine separation + ashing	427,168	7,902	1,515	9,417	16,934	27[...]
Server board contacts	Guillotine separation + ashing	288,534	9,469	1,815	11,283	18,900	224[...]
Ethernet Card contact	Guillotine separation + ashing	602,918	10,829	2,075	12,904	23,514	61[...]
TV board contact	Tile cutter separation	182,010	6,496	1,245	7,742	14,181	7,[...]
Graphics card contacts	Tile cutter separation	427,168	7,902	1,515	9,417	16,974	27[...]
Server board contacts	Tile cutter separation	288,534	9,469	1,815	11,283	18,940	224[...]
Ethernet Card contact	Tile cutter separation	602,918	10,829	2,075	12,904	23,570	61[...]

Disassembly of items for isolation of PCBs and SMDs

Costs associated with disassembly of samples to isolate PCBs are given in *Table 4.33* Manual disassembly is prohibitively expensive. The guillotine is much cheaper than the tile cutter for opening LCD housing.

Table 4.33 *Costs for isolation of PCBs from items using various disassembly techniques*

Item	Manual Disassembly	Cryo-cracking	Guillotine	Tile cutter
MP3 player	£0.46	£0.10	-	-
Mobile phone	£0.38	£0.10	-	-
Camera	£0.73	£0.10	-	-
LCD PCB	£1.09	-	£0.29	£0.68

The costs for isolation of SMDs from PCB samples are given in *Table 4.34*. The least expensive method by far is use of the solder bath. This method is also fastest with best outcome in terms of damage caused to components resulting in CRM losses.

The most cost-effective method for isolating components from whole samples is to use cryo-cracking for digital media devices with plastic housings, the guillotine for the HP laptop LCDs, and the solder bath for removal of SMDs. Combining the costs calculated so far with the calculated revenues for isolated SMDs from each device provides the total cost benefit of this process for the samples examined (*Table 4.35).* The proposed processes would only be cost effective for use on mobile phones, giving a cost benefit of ~£3k/tonne of isolated SMDs, or ~10p/phone. The higher value of phone components being sufficient to recoup costs incurred. Careful consideration of the recoverable value in mobile phones of different models should also be taken into account before the decision is made to utilise this process on any one particular model.

Table 4.34 *Per item costs of isolating SMDs from PCBs with various techniques*

PCB	Manual disassembly		Blow torch		Heat Gun			Solder bath		
	Time (s)	Cost (£)	Time (s)	Cost (£)	Time (s)	Energy (kWh)	Cost (£)	Time (s)	Energy (Wh)	C(
MP3 player	240	1.06	36	0.16	60	0.033	0.27	15	2.08	0
Mobile phone	600	2.64	120	0.53	180	0.100	0.80	20	2.78	0
Camera	620	2.73	266	1.17	300	0.167	1.34	20	2.78	0
LCD main PCB	600	2.64	60	0.26	120	0.067	0.53	15	2.08	0

Table 4.35 *Cost benefit of best cost options for disassembly and isolation of SMDs from PCBs in w*

Item	Process	Cost of isolating SMDs (£)	Revenue from SMDs (£)	per item
MP3 player	cryo-cracking & solder bath	£0.168	0.163	-0.005
Mobile phone	cryo-cracking & solder bath	£0.190	0.201	0.010
Camera	cryo-cracking & solder bath	£0.190	0.036	-0.154
LCD PCB	guillotine & solder bath	£0.352	0.055	-0.297

4.4   Conclusions

PCBs contain the largest variety of CRMs, particularly those of items which have been significantly miniaturised in recent years to increase functionality in smaller devices such as mobile phones.

XRF combined with digital imaging has proven useful for building a library of component images and x-ray emission spectra to inform future recycling processes which target CRMs for recovery. PCBs contain the largest variety of CRMs, particularly those of items which have been significantly miniaturised in recent years to increase functionality in smaller devices such as mobile phones.

In a study of pre-processing techniques that might enable greater value generation from WEEE, cryo-cracking of high value products whose manual disassembly is problematic has shown potential as a means of diverting CRM rich PCBs from automated recycling processes in which CRMs are dissipated and lost through unintended co-separation. The use of a guillotine to break through plastic housings and reduce costs associated with isolating CRM bearing components also shows potential. Isolation of SMDs from PCBs is best achieved by use of a solder bath; other thermal methods investigated are more costly, and/or present environmental H&S issues from burning PCBs if care is not taken.

The use of microwave ashing as a means of pre-concentrating CRMs in samples shows negative cost benefit showing its application for concentration of copper and Au in isolated edge contacts prior to refining. However, the method could potentially be suitable for components subject to such mass based treatment charges which high organic content. Ashing to remove the epoxy component from whole PCBs may result in sufficient logistics and refining charge savings to grant a cost benefit. This technique may therefore prove a suitable means for 'upgrading' of materials which contain PMs, PGMs and copper but fall below cut-off grades for PM recovery processes, facilitating greater recovery rates of these CRMs from WEEE.

Although CRMs have been identified throughout these electrical/electronic devices, many barriers exist to enhancing rates of recovery. While PMs and PGMs are recovered with high efficiency in smelting processes for PCBs, in general the dissipative nature of the application of CRMs in electronics seriously limits the potential for their recovery. Of the other CRMs identified in PCBs many partition into the slag during smelting for PMs/PGMs, rather than into the copper bullion collected for further refinement. CRMs identified in samples that are irrecoverably lost are Ga, Ge, Ta, Y, and Co. It is possible to isolate SMDs containing these

CRMs prior to smelting. However, at this time, there is little economic justification for the additional cost of such processes because of a lack of available recovery infrastructure for CRMs, and the fact that they are often found in combination with more valuable copper and PMs which are recoverable by smelting, but in a process in which other CRMs are lost. On solution may be to pursue development of hydrometallurgical recovery methods, through which losses of CRMs in smelting can be avoided, and through which a wider range of CRMs may be recovered. Lack of recovery infrastructure so far has resulted from the low recoverable value of CRMs in WEEE, due to low concentrations present and low market values, and although recycling of CRMs is fairly common from production scrap and other wastes, recovery from post-consumer wastes is rare. A 'chicken & egg' scenario exists in which isolating CRMs from WEEE in appropriate fractions for downstream recovery is not viable due to lack of recovery infrastructure, and recovery infrastructure is not in place as insufficient quantities of suitable WEEE derived materials are currently available to feed such a process. Price volatility for CRMs also results in greater risk to investment in CRM recovery processes. Poor design for disassembly also results in high costs associated with isolating CRM bearing component. The RSA security dongles investigated here are an example of poor design significantly limiting recycling potential.

5 Platinized counter-electrodes for dye-sensitised solar cells from waste thermocouples: a case study for resource-efficiency, industrial symbiosis and circular economy

Chapter summary

This thesis so far has dealt with the issue of how value can be exploited from WEEE through traditional recycling pathways. It will be shown in this chapter that through industrial symbiosis in which waste materials become raw materials for manufacturing, greater value can be generated from materials in WEEE than through traditional recycling process chains, resulting in sufficient economic advantage to drive recovery which is not economically viable through traditional recycling pathways. This demonstrates the greater value generation potential afforded by circular economy, in which 'wastes' are viewed as resources.

Future widespread deployment of photovoltaic (PV) technologies will make a significant contribution to sustainable energy generation, but the scale of future PV deployment will most likely be limited by access to 'critical' raw materials (CRMs). Circular economy represents a path for sustainable economic development with associated economic, environmental and social benefits. Adoption of circular practices by the PV industry such as industrial symbiosis will enhance access to CRMs through recycling, and reduce energy payback times, materials costs, levelised costs of energy generation (LCOE) and energy payback times (EPBT) for PV. Industrial symbiosis also enables partner organizations to valorise wastes and materials contained therein which may be uneconomical to recover through traditional recycling routes such as CRMs used in dissipative applications e.g. platinum in waste thermocouples (WTCs) filaments. Here, on a very small scale, the means to overcome these barriers is demonstrated through a proposed industrial symbiosis between Weartech International Ltd and the SPECIFIC IKC in South Wales (Figure 5.1). Small quantities of platinum in WTC filaments generated by Weartech (~43,000/year) can be economically recovered by conversion to chloroplatinic acid – an 'added value' product, for use by SPECIFIC in fabrication of dye-sensitised solar cell (DSSC) counter-electrode catalysts. 91±3% recovery of platinum from filaments as chloroplatinic acid hydrate (48.6±1.6 wt%Pt) has been achieved by aqua regia digestion of manually isolated filaments. Cost-benefit analysis shows the proposed process derives sufficient value from WTCs to cover Weartech's landfill costs for WTCs; provide ~5

days employment; and provide 63% materials cost savings for SPECIFIC in comparison to purchasing chloroplatinic acid. Suitability of WTC derived chloroplatinic acid for DSSC catalysts has been verified. EIS has shown counter electrodes created from 3 sources of chloroplatinic acid (WTCs, 99.998% Pt wire and purchased chloroplatinic acid) to have comparable charge transfer resistances (R_{CT}) and exchange current densities (j_0). The proposed process would divert >50g/year of platinum from landfill, enough to produce ~500 m^2 of DSSCs and supply clean energy for 12 homes in South Wales, and avoid up to 1400 kg CO_2 in emissions associated with primary production of an equivalent quantity of platinum.
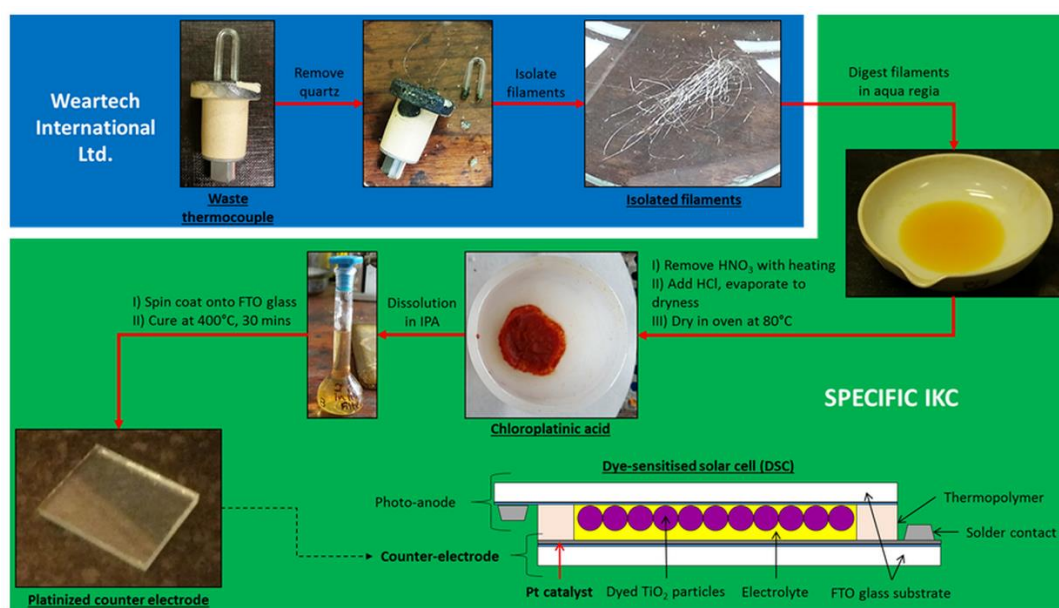
Figure 5.1 *Industrial symbiosis process for fabrication of dye-sensitised solar cell (DSSC) counter-electrode catalysts from waste thermocouples*

5.1 Introduction

The world faces the limits of current 'linear' economic models due to resource security issues, growing population and increasing per-capita consumption. Transition is necessary to a new 'circular economy': a resource-efficient industrial economy which decouples economic growth from resource consumption.[47, 225, 226] In a circular economy the concept of 'waste' is replaced with one of 'resource' and process waste is reduced through industrial symbiosis, whereby process waste becomes the feedstock of another process. In this way materials are retained in an economically productive capacity, cascading across multiple product lifecycles. Enhanced resource-efficiency will deliver synergistic economic, environmental and social benefits[47]. Of significant importance to sustainable economic growth and transition to a low-

carbon society is a secure supply of critical raw materials (CRMs),[53, 100, 188, 227] and widespread deployment of low-carbon renewable energy technologies. CRMs face future supply bottlenecks and their global recovery rates are currently low (*Figure 5.2*).[60, 118] CRMs are vital to the functionality of many low-carbon technologies upon which reductions in global emissions and achieving sustainability with our planet rely.[20, 53, 100, 118] The scale of deployment of renewable technologies, particularly photovoltaics (PV) may well be constrained by access to CRMs, and increasing CRM recovery rates will be crucial if demand for wide-scale deployment of sustainable technologies is to be met.[187, 228, 229]
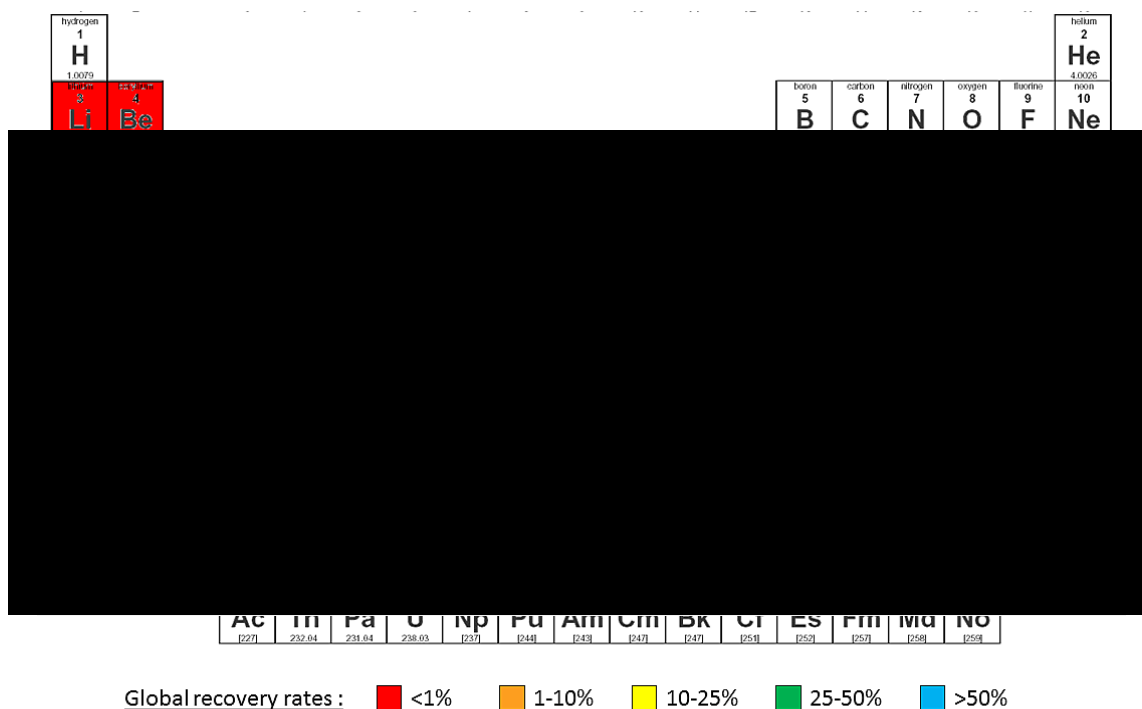
Figure 5.2 *Recycling rates of metals highlighted as critical in recent assessments (adapted from Graedel et al., 2011; Reck & Graedel, 2012)* [21, 53, 60, 100, 118]

Part of the reason for low recovery rates, even for valuable metals like Pt, is the use of these metals in dissipative applications, i.e. where they are present in low concentrations and the consequent high costs of recovery and low total recoverable value make traditional recycling routes unfeasible, resulting in loss of these elements from the economy. [62, 230-233]

Platinum is a CRM with high economic value (> $37/g LME 10/7/15, converted from GBP at 1.32 $/£.) reflecting its low abundance in the Earth's crust as well as the economic and environmental costs of its production (13,954 t CO_2/t of metal i.e. 4,100 times greater than copper).[16] *Table 5.1* gives global demand and recycling rates for platinum by end use sector. The high value of platinum has driven efficient recycling from applications such as industrial

chemical catalysts and bullion where use and management of these materials is carefully controlled and where recycling rates are very high, ~95%. On the other hand, recycling rates from electronics are very low, 0-5%, mainly due to the dissipative use of platinum in electronics, low global collection rates for WEEE, and poor product design for recycling & recovery.[234]

Table 5.1 Global demand for platinum by end use sector in 2015 and estimated end-of-life (EoL) recycling rates

Application	Global Demand		Recycling Rate (%)[59, 189]
	(mass/Troy Oz)10^{-3} [153]	% of demand	
Autocatalyst	3,011	40%	50-55
Jewellery	2,456	32%	90-100
Industrial total	1,629	22%	80-90
Chemical	494	7%	≤90[a]
Electronics	151	2%	0-5
Glass	163	2%	
Petroleum	100	1%	≤90[a]
Other Industrial	721	10%	10-20[b]
Retail Investment	474	6%	90-100[c]
Total	7,570		60-70[b]

a recovery from catalysts used by this sector; b Includes sensors, crucibles, medical/dental and decorative applications; c excludes coins and bullion- no typical end-of-life management, reuse is common

Low recycling rates are typical for many of the CRMs in electronics, where they are often used in trace amounts within complex systems. If cost-effective recovery of CRMs in WEEE could be achieved, then utilisation of this rich secondary resource could mitigate the issue of CRM supply bottlenecks and reduce costs and emissions associated with their production.[19, 20, 35, 63, 206, 222, 235, 236] Recycling of materials from WEEE for fabrication of solar cells is not only environmentally beneficial in comparison to primary resource based production, but offers a pathway to reduced energy payback times (EPBT), reduce levelised cost of energy generation (LCOE), and enhanced competitiveness and intangible value for PV manufacturers in a global market in which consumers are becoming increasingly environmentally aware.[61, 237, 238]

A significant application of platinum in industrial electronics is in thermocouple wire. The thermocouple temperature sensors market is estimated at $1.6 billion by 2018 with a current growth rate of 6.6%/year over the period 2014-2020.[239] Measurement of molten metal temperatures in foundries and steel plants is almost exclusively conducted using single use thermocouples (*Figure 5.3*) containing a pair of filaments, one of which is either pure platinum or PtRh6% alloy, and the other is platinum alloyed with 10-30% Rh depending on the required working temperature range. Recovery of platinum group metals (PGMs) from waste thermocouples (WTCs) is hindered by the small quantities of PGMs present in each thermocouple.[240] However, opportunities exist within circular economy for innovative

recovery models which valorise materials that may otherwise be lost when recovery through traditional recycling chains is not economic.[72] As we show here, a circular economy approach involving industrial symbiosis i.e. an association between two or more industrial facilities or companies in which the wastes or by-products of one become the raw materials for another,[71] may be used to drive cost effective recovery of platinum from waste thermocouples (*Figure 5.4*).
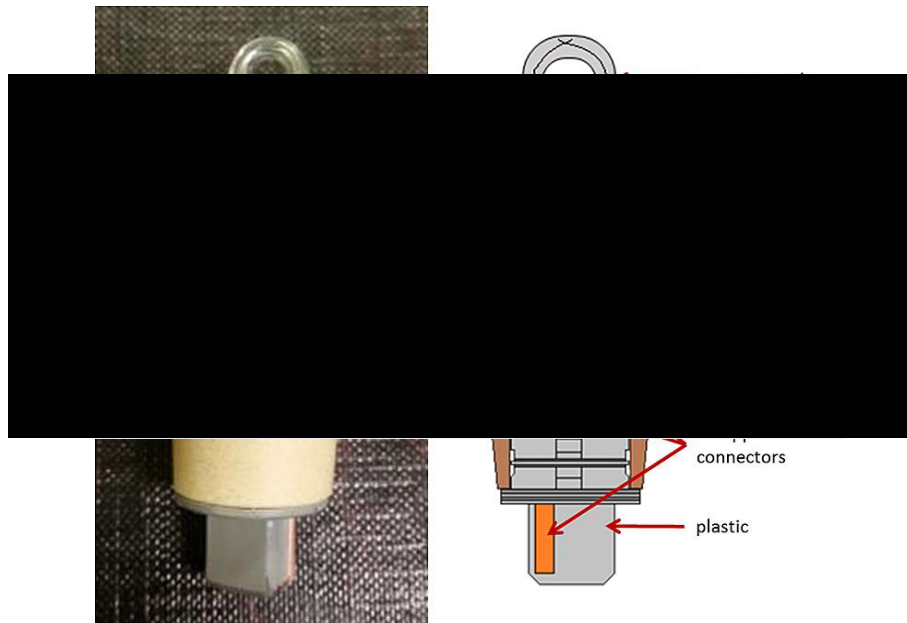
Figure 5.3 *Waste Heraeus Electro-Nite Positherm expendable immersion thermocouple (schematic diagram adapted from Van der Perre)[241]*
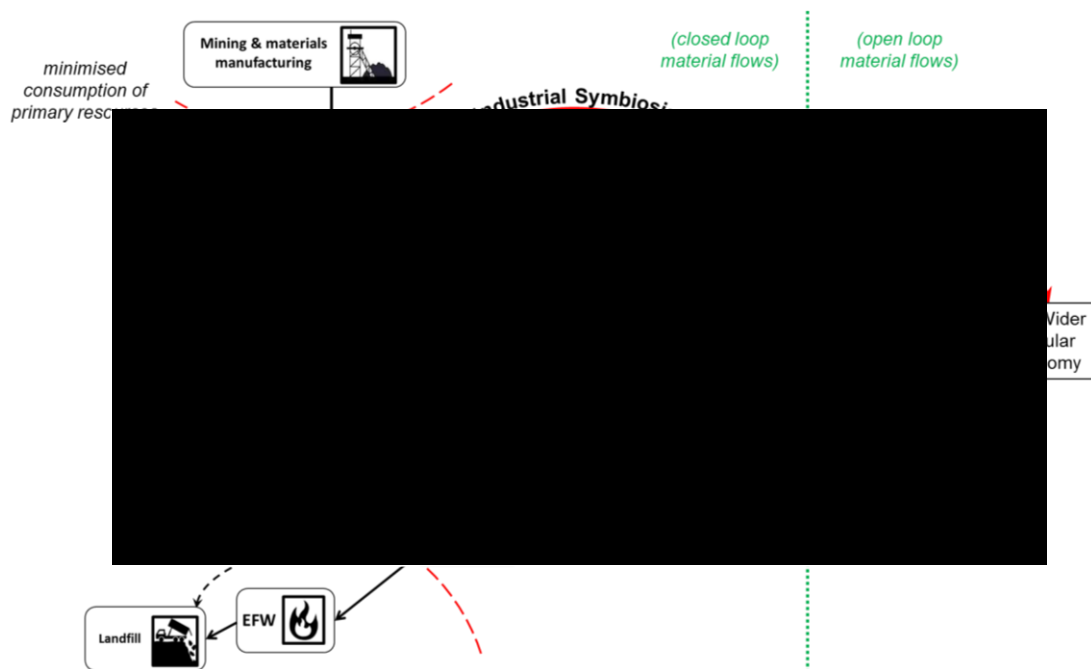
Figure 5.4 *Material flows in a circular economy drawing on secondary raw materials from the wider circular economy through industrial symbiosis (adapted from Ellen McArthur Foundation, 2013)[47]*

5.1.1 Industrial symbiosis strategy

Chloroplatinic acid is an important precursor in many applications of platinum.[242] It is more expensive than platinum ($102/g at ~38wt% Pt), and conversion of the Pt in waste thermocouples to chloroplatinic acid, an 'added value' Pt compound, could significantly increase the derivable value from Pt in the filaments. Following manual isolation of Pt filaments from WTCs it is possible to convert these to chloroplatinic acid by digestion in aqua regia[243] through reaction *5.1*, followed by removal of nitric acid from the resulting solution by boiling through reaction *5.2*, and evaporation to dryness following addition of HCl to yield solid $H_2PtCl_6.xH_2O$.[243]

$$Pt + 8HCl + 2HNO_3 \rightarrow H_2PtCl_6 + 4H_2O + 2NOCl \qquad [\mathit{5.1}]$$
$$3HCl + HNO_3 \rightarrow Cl_2 + 2H_2O + NOCl \qquad [\mathit{5.2}]$$
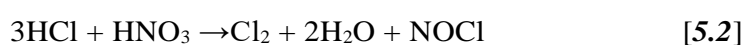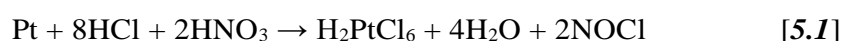
This simple process requires no specialist equipment other than a fume hood, producing no solid or liquid waste other than WTCs minus filaments. The potential for small scale recovery close to the source of generation of WTCs offers interesting possibilities at low economic and environmental cost in comparison to traditional recycling routes. If a suitable partner organization could be found that uses chloroplatinic acid, then an industrial symbiosis strategy could potentially lead to: increased levels of PGM recovery from end-of-life devices; reduced waste management costs for producers of WTCs; mitigation of materials criticality issues; and reduced environmental and economic costs for organisations using chloroplatinic acid.

Weartech International Ltd. operate a foundry in Baglan, South Wales and produce >43,000 WTCs annually. Conscious of resource security concerns over PGMs, Weartech sought a recycling route which recovers PGMs from WTCs, which are currently (2015) landfilled at a cost of $158.40/tonne ($132/tonne landfill tax + $26.40 gate fee) for lack of viable recycling options. A potential partner for this industrial symbiosis is the SPECIFIC Innovation and Knowledge Centre in Swansea University, which conducts research into optimisation of dye-sensitised solar cell (DSSC) performance and scale up of roll-to-roll production (R2R). Currently, SPECIFIC purchases chloroplatinic acid, in 1g quantities, for fabrication of DSSC catalysts[244] (*Figure 5.5*) at their site in the Baglan Energy Park, <2 miles from Weartech.
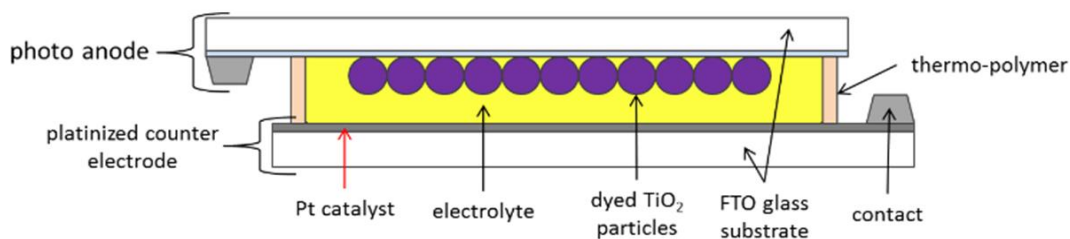
Figure 5.5 *Structure of a Dye-Sensitised Solar Cell (DSSC)*

To verify the suitability of WTCs as a source of platinum for SPECIFIC and the appropriateness of the industrial symbiosis strategy with Weartech, the following question must be answered: can chloroplatinic acid of sufficient quality for use in DSSCs be synthesised from WTCs in sufficient quantity and at sufficient cost-benefit to justify the process? Here we show that the answer to this question is 'yes' and that the barriers to recovery of Pt from this dissipative application in thermocouples may be overcome by local industrial symbiosis. We also use this example to illustrate the benefits of the circular economy approach.

Although here we focus on the example of Pt from WTCs for DSSC counter-electrode catalysts in a relatively small scale local operation between Weartech and SPECIFIC, chloroplatinic acid is important in numerous applications where platinum deposition is required. A major example for low-carbon technologies is in the preparation of catalysts for fuel cells.[245-247] Pt is also only one of the many elements facing future supply bottlenecks that may be sourced from available 'wastes'. In addition, small-scale local operations such as this are of significant importance to a healthy circular economy. Economies require a balance of various size businesses to thrive in the long term with larger enterprises bringing volume and efficiency and smaller ones offering alternative models when crises occur.[248] A multitude of similarly sized operations throughout the circular economy could deliver materials cost savings and domestic sources of CRMs for manufacturing as shown by this example, while providing economic resilience through diversity.[47]

5.2   Experimental

A 5.5 kg sample of WTCs was obtained from Weartech International Ltd., and was cone and quartered to give a representative sub samples of 82 individual WTCs for further study. Details of analytical techniques employed are outlined in section 2.2. Diameters of filaments were measured from SEM images, and alloy composition of filaments was measured using SEM/EDS. Pt concentration in chloroplatinic acid samples is given as the average of results from ICP-OES and AAS analysis. EIS is used to evaluate electrochemical performance of DSSC catalysts created from chloroplatinic acid from different sources.

5.2.1 Chloroplatinic acid synthesis

~100 mg of platinum filaments, or wire, was digested by boiling in 10 ml of aqua regia (3:1 HCl/HNO$_3$) for 3 hours. Following digestion, solutions were evaporated to near dryness to remove nitric acid, before dissolution of the residue in 10 ml 1:1 conc. HCl : water. Chloroplatinic acid was obtained from 5 ml of this solution by evaporation to dryness with further drying at 80 ˚C for 12 hours (*Figure 5.6, stage 2*). The remaining 5 ml of solution was retained for analysis and fabrication of DSSC counter electrodes.
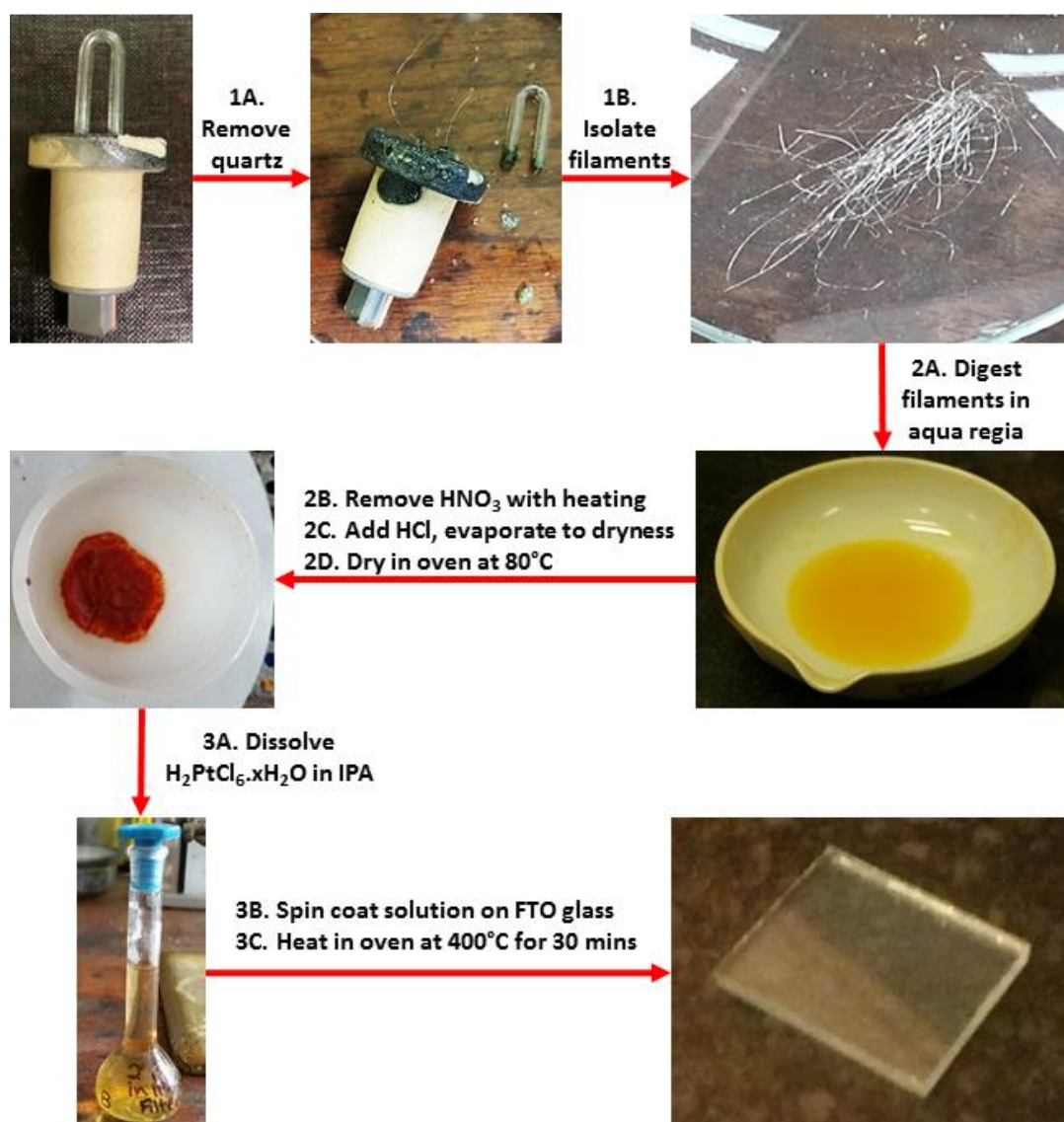
Figure 5.6 Procedure for synthesising DSSC counter electrodes from waste thermocouples (WTCs). The process includes 3 stages: 1) isolation of Pt filaments from WTCs; 2) synthesis of chloroplatinic acid from filaments; 3) creation of DSSC counter electrodes

5.2.2 Fabrication and characterization of platinized counter-electrodes

NSG Tec7 FTO glass (7 Ω/sq) was cut into 25 mm x 15 mm pieces. A small hole was drilled into the non-conductive surface adjacent to the upper right hand corner of a 1 cm^2 area at their centre to allow filling of cells with electrolyte. The glass was cleaned with distilled water & detergent, rinsing with distilled water and then IPA, before drying with compressed air. 100 µL of ~5 mM chloroplatinic acid in IPA was spin coated onto the FTO at 2,000 rpm for 40s, accelerating at 2,000 rpm/s and heated to 400 °C for 30 mins to create the platinized electrode (*Figure 5.6, stage 3*). Pairs of CEs were used to create 'dummy cells' (*Figure 5.7*),[138-142] sealed together with a 1 cm x 1 cm, 25 µm Surlyn™ gasket. Cells were filled with electrolyte (0.8 M 1-methyl-3-propylimidazolium iodide, 0.3 M benzimidazole, 0.1 M iodine, and 0.05 M guanidinium thiocyanate in 3-methoxypropionitrile) via channels drilled through the glass. Cells were sealed with Surlyn™ and a glass slip. An MBR electronics USS-9210 ultrasonic soldering system was used to apply CERASOLZER GS155 solder to the conductive side of each electrode at its terminus. Charge transfer resistances (R_{CT}) and double layer capacitances (C_{dl}) of the electrodes were measured using electrical impedance spectroscopy (EIS) on the dummy cells. The area tested by EIS analysis was 1 cm^2 per electrode as defined by the Surlyn gasket. Exchange current densities at each electrode (j_0) were calculated from measured R_{CT} values using e*quation 5.1*, where F is Faraday's constant, *T* is temperature, *R* the gas constant, and *n* the number of electrons involved in the reaction.[249]

$$R_{CT} = \frac{RT}{j_0 nF} \qquad \qquad Equation\ 5.1$$
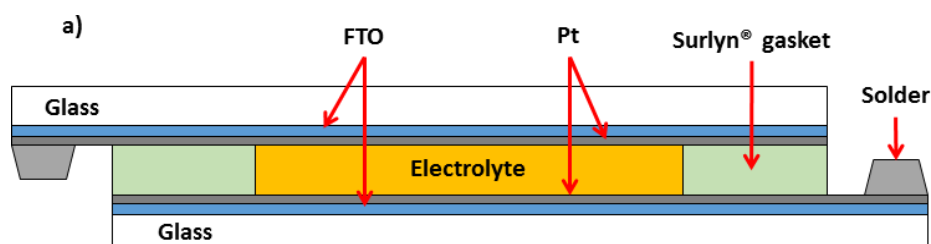
Figure 5.7 *Electrochemical symmetrical 'dummy cells' used for EIS measurements*

5.3 Result and Discussion

5.3.1 Isolation of filaments from waste thermocouples

Inspection of the sample from Weartech revealed the physical condition of WTCs to be variable with some in close to 'as new' condition (e.g. *Figure 5.3*) and others damaged extensively with some cracked, and/or quartz missing, and/or caked in the alloy they were

used to measure (*Figure 5.8*) Despite damage, most WTCs were found to contain both filaments in their entirety and WTCs without filaments were rare.
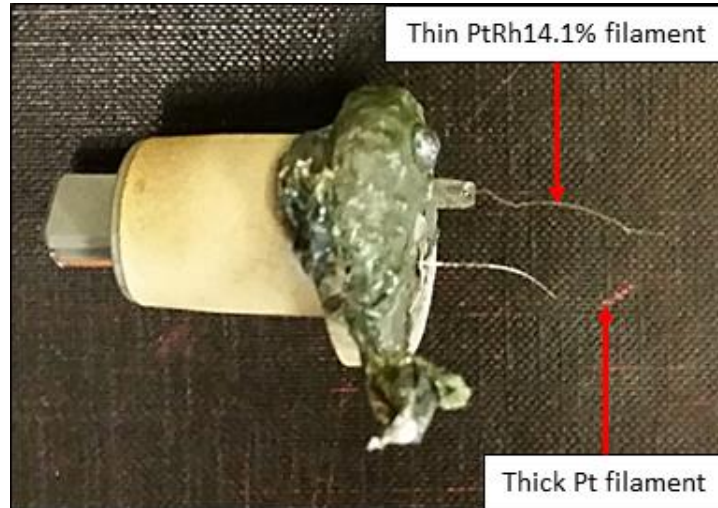
Figure 5.8 *Waste thermocouple in poor condition with exposed filaments and alloy compositions as determined by SEM/EDS.*

The quartz tube was removed with pliers to access the base of filaments protruding from the refractory cement. Filaments were snipped as close to their base as possible to minimise the quantity remaining within the refractory cement of WTCs (Figure 5.6, stage 1). This process was timed, and masses of isolated filaments were recorded for subsequent costing exercises. Microscopic analysis of isolated filaments revealed each WTC contained 2 filaments of different diameters, larger filaments with a mass of 1.1 (±0.3) mg and diameter of ~74 μm, and lighter thinner filaments with a mass of 0.4 (±0.1) mg and diameter of 40.5 μm. Diameters of thin and thick filaments were measured from images at 1,200 to 1,800 times magnification respectively (*Figure 5.9*). SEM/EDS analysis was used to determine alloy composition of the filaments (*Figure 5.11*).
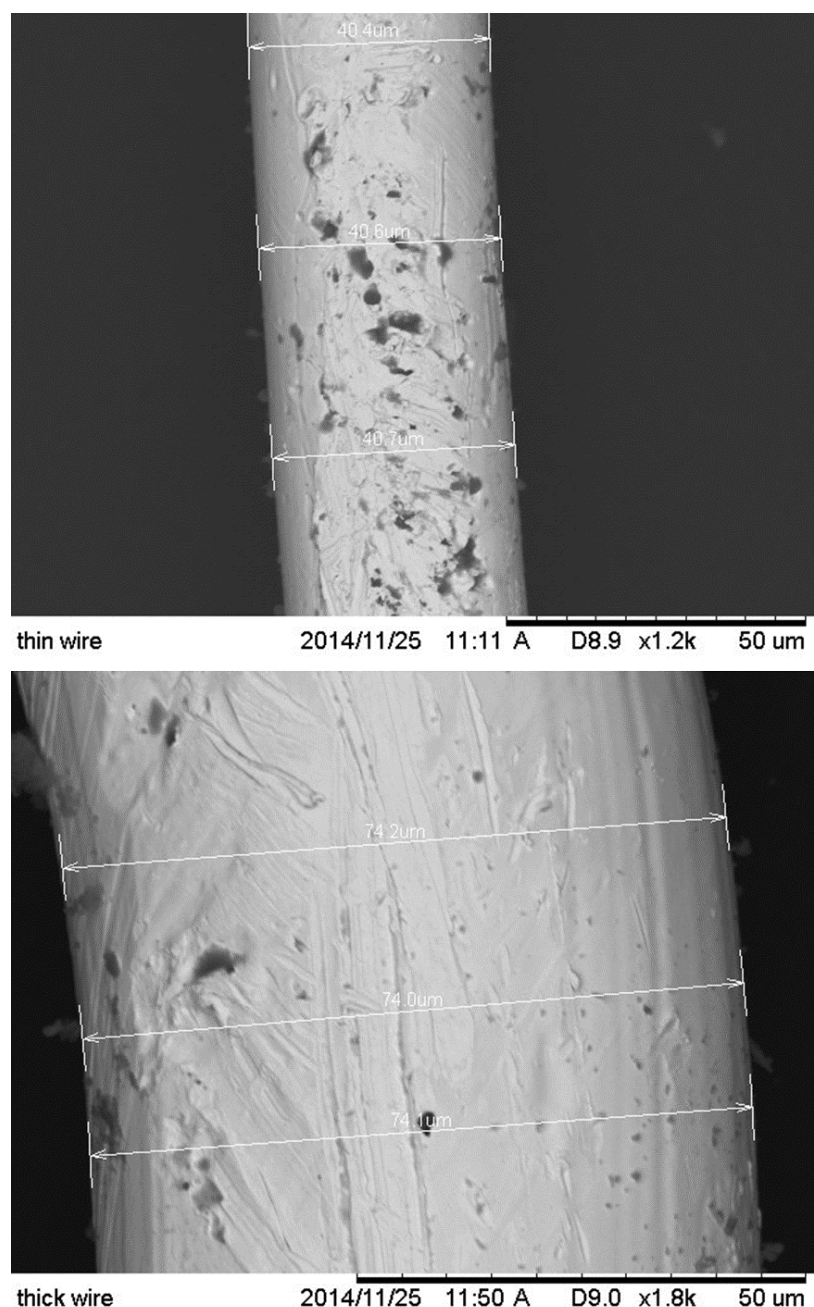
Figure 5.9 Diameter measurements of thin (left) and thick (right) waste thermocouple filaments from SEM images at 1,200 and 1,800 time magnification respectively

Alloy compositions of filaments were generated using Bruker Quantax software from X-ray fluorescence signals corresponding to L & M transitions for Pt, and L transitions for Rh in the resulting emission spectra of samples. SEM/EDS analysis revealed that heavier filaments are ~100% Pt (*Figure 5.10*), and lighter filaments are ~PtRh14% alloy (*Figure 5.11*), (close to the alloy composition of PtRh13% given for ANSI-type R thermocouple filaments in the manufacturer specification and within the tolerance of the EDS). [241] XRF analysis confirmed the thicker filament to be 100% Pt and the lighter filament to be PtRh12.75% alloy. Assuming

filaments are present in a 1:1 length ratio, then the average composition of filaments is Pt96%Rh4%.
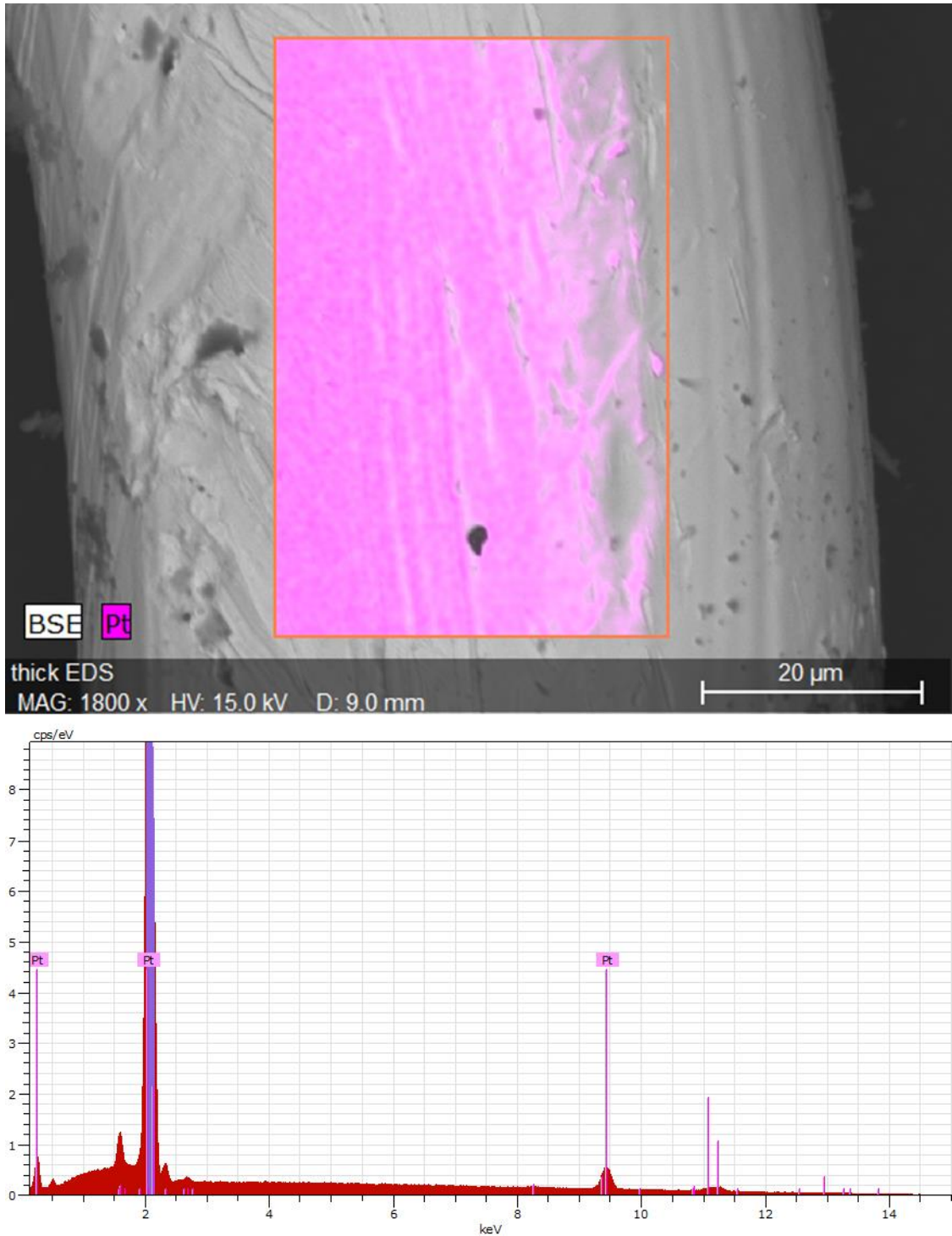
Figure 5.10 *Elemental map of Pt in thin waste thermocouple filament (top) with corresponding X-ray emission spectra and alloy composition analysis (bottom) produced using SEM/EDS*
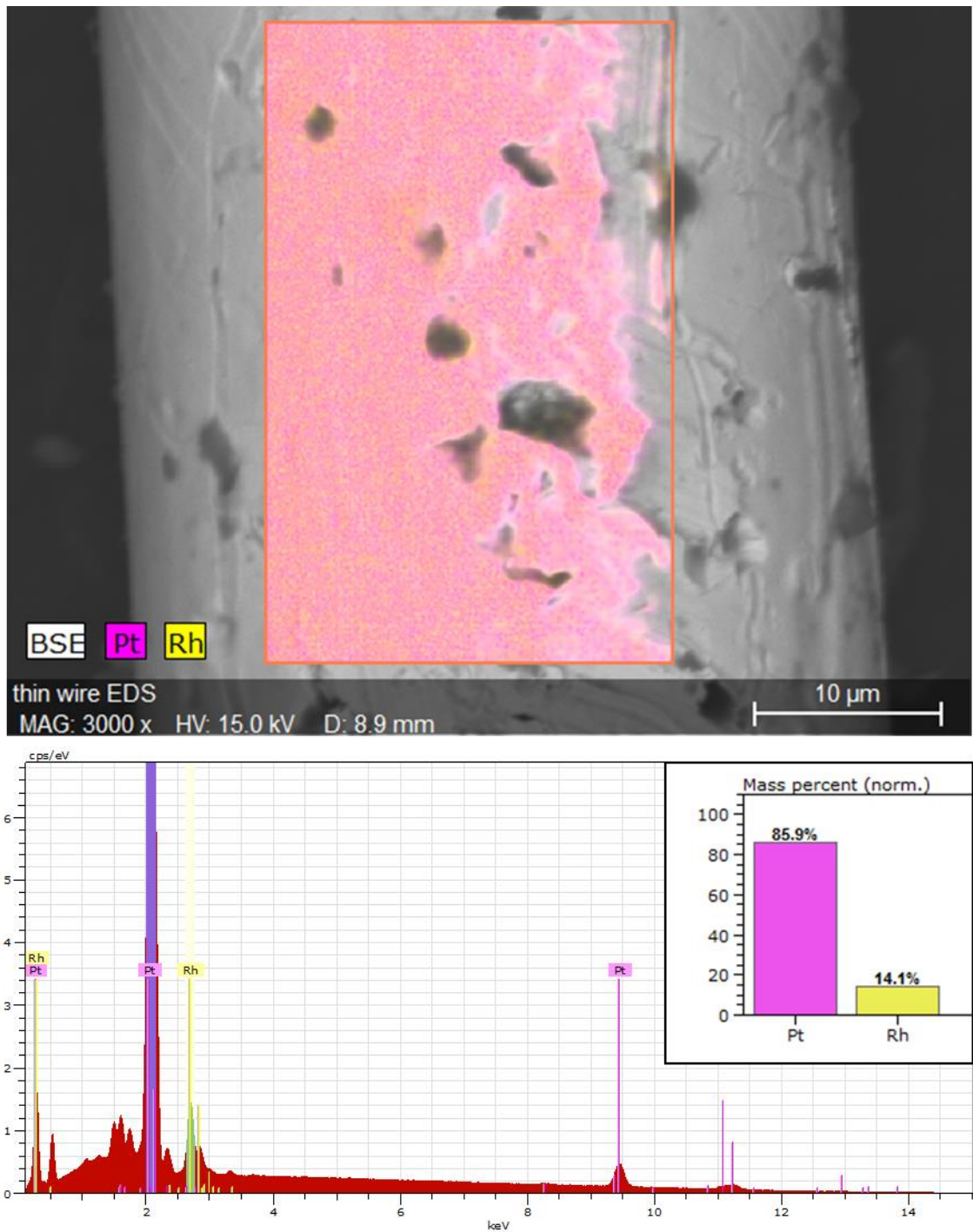
Figure 5.11 *Elemental map of Pt and Rh in thin waste thermocouple filament (top) with corresponding X-ray emission spectra and alloy composition analysis (bottom) produced using SEM/EDS/*

WTCs have an average PGM concentration of ~120 ppm, considerably higher than the majority of ores refined for Pt production (Nishnij-Tagil, Russia: 10-20 ppm; South African Bushveld complex: 3-20 ppm).[243] 97.3 (±0.3) mg of Pt bearing filaments were isolated from the 82 WTC sub-samples, an average of 1.2 mg per thermocouple.

5.3.2 Chloroplatinic acid

AAS analysis of the solution after filament digestion shows the average Pt content of WTC filaments to be 95 ($\pm$1)%, in line with expectation. *Table 5.2* gives details of yields and metal content for chloroplatinic acid synthesised from thermocouple filaments 99.998% Pt wire for comparison. Both chloroplatinic acid samples synthesised have significantly higher Pt content than purchased chloroplatinic acid currently purchased used by SPECIFIC (38.6($\pm$0.2) wt% Pt), probably as a result of the oven drying at 80°C.

Table 5.2 *PGM content of chloroplatinic acid and Pt recovery yield from WTCs and 99.998% Pt wire*

	Pt source	
	WTCs	**Pt wire**
<u>Metal Digested</u>		
Mass (mg)	97.3 ($\pm$0.3)	97.3 ($\pm$0.3)
Wt%Pt	95 ($\pm$1)	100
<u>Chloroplatinic acid product</u>		
Mass (mg)	173.2 ($\pm$0.3)	204.0 ($\pm$0.3)
Wt%Pt	49 ($\pm$2)	47 ($\pm$1)
<u>Pt recovered in product</u>		
Yield (mg)	84 ($\pm$3)	96 ($\pm$2)
%yield	91 ($\pm$3)	99 ($\pm$3)

5.3.3 Assessment of suitability for DSSC electrode manufacture

The role of the catalyst in a DSSC is to catalyse the reduction of tri-iodide to iodide at the counter electrode, *reaction 5.3*. This allows the iodide to regenerate the dye in the reverse reaction at the working electrode. The charge transfer resistance (R_{CT}) for the tri-iodide to iodide reaction can be measured using EIS (as discussed in *section 2.2.7*) and is indicative of the efficiency of the catalytic reaction.

$$I_3^- + 2e^- \rightarrow 3I^- \qquad\qquad [\textbf{\textit{5.3}}]$$

The mean values of R_{CT} for dummy cells created from chloroplatinic acid derived from different sources are given in *Table 5.3*. The slightly higher R_{CT} value observed for cells made from purchased chloroplatinic acid is likely due to a lower quantity of platinum deposited on the electrode surface as a result of the slightly lower concentration Pt solution used, possibly as a consequence of deliquescence of commercial chloroplatinic acid sample during weighing due to its highly hygroscopic nature. Column $j_0/[Pt]$ gives exchange current densities for the deposited Pt layer per unit concentration of Pt in IPA used to deposit the layer and within experimental error the results are the same.

Table 5.3 *Average charge transfer resistances (R_{CT}), double layer capacitances (C_{dl}) and exchange current densities (j_0) at the electrolyte│electrode interface for electrodes in 'dummy cells' created with platinum from different source; and corresponding j_0 expressed per unit concentration of Pt in IPA used for creation of electrodes ($j_0/[Pt]$).*

Chlorplatinic acid source	[Pt] in IPA (mM)	R_{CT} (Ω cm^{-2})	C_{dl} (μF)	j_0 (mA cm^{-2})	$j_0/[Pt]$ (mA cm^{-2}M^{-1})
• Pt wire	4.41(±0.06)	5.15(±0.31)	10.05(±0.46)	2.47(±0.15)	0.56(±0.03)
• WTC	4.70(±0.06)	4.80(±0.58)	10.73(±0.55)	2.65(±0.32)	0.56(± 0.07)
• Purchased from Sigma-Aldrich	3.84(±0.05)	7.00(±0.56)	9.20(±0.23)	1.82(±0.15)	0.47(±0.04)

Errors are standard error on the measn, (N=6)

The data in *Table 5.3* show that all three sources of Pt are equally suitable for the preparation of DSSC electrodes. The presence of Rh and any other contaminants in WTC derived chloroplatinic acid does not have any detrimental effect on the catalytic activity of platinized electrodes prepared using chloroplatinic acid from waste thermocouples. It was not possible to identify localised metal deposits on the electrodes using SEM across the 5,000-100,000x magnification range (the size range of ~1 μm to ~10 nm), and so we presume the metal particles to be smaller than ~10 nm, but what is most important for this work is that across this magnification range SEM showed no gross differences in electrodes made from recycled thermocouples compared to those made from pure Pt wire or purchased chloroplatinic acid.

5.3.4   *Supply and environmental impact*
Weartech International Ltd currently generate ~43,340 WTCs per year, which would yield 51.4 (±0.2) g of filaments, more than enough to support the current activities of SPECIFIC. Recovery of this quantity of Pt offsets demand for an equivalent quantity from primary sources, negating the requirement to mine and process between 2.5-17 tonne of ore and saving ~200-1400 kg CO_2. Counter-electrodes for highly efficient DSSCs require 5-50 μg/cm^2 of Pt,[142, 250, 251] therefore Weartech's WTCs could be used to create 100-1,000 m^2 of electrodes for DSSC annually. 500 m^2 of DSSCs is sufficient to provide enough solar electricity for ~12 households in South Wales, based on the local solar irradiance and a cell efficiency of ~12%.

5.3.5   *Cost benefit analysis*
The potential industrial symbiosis operation is indicated in *Figure 5.12*, and associated costs are given in *Table 5.4* with a cost benefit analysis given in *Table 5.5*. It is presumed that associated labour and overhead costs will be in line with those of Metech Recycling (UK) Ltd who operate a WEEE recycling facility near SPECIFIC and Weartech, and employ staff to conduct manual recycling processes at an overhead rate of $20.91/hour. Times for processing WTCs were scaled up from the time taken to process the 82 WTC samples. WTC filaments are then sold to SPECIFIC for conversion to chloroplatinic acid at a price which covers the

costs of this operation and disposal of processed WTCs in landfill ($158.40/tonne). Cost analysis for chloroplatinic acid synthesis by SPECIFIC takes account of: chemical costs (HCl ACS reagent grade, 2.5 L: $75.11; HNO_3 ACS reagent grade, 2.5 L: $115.63); transport costs ($0.59/mile); and electricity costs ($0.20/kWh, UK average 2015). Costs incurred for chloroplatinic acid synthesis are scaled up from production of 1 g of chloroplatinic acid. Cost of electricity for the oven used to dry the sample was not included as the oven used is in operation 24 hours a day regardless. No waste disposal costs are incurred in the chloroplatinic acid production as the process produces no solid or liquid waste. Labour costs for this process are not included in the cost benefit as minimal staff time is required for addition of acids to the process and during the digestion process and drying of the product. Administrative overheads for SPECIFIC associated with the process of procuring chloroplatinic acid are not included. A cost-benefit analysis was conducted by comparison of the total price of filaments and cost of chloroplatinic acid synthesis (per g), with the cost of purchasing chloroplatinic acid in 1 g and 25 g lots from Sigma-Aldrich.
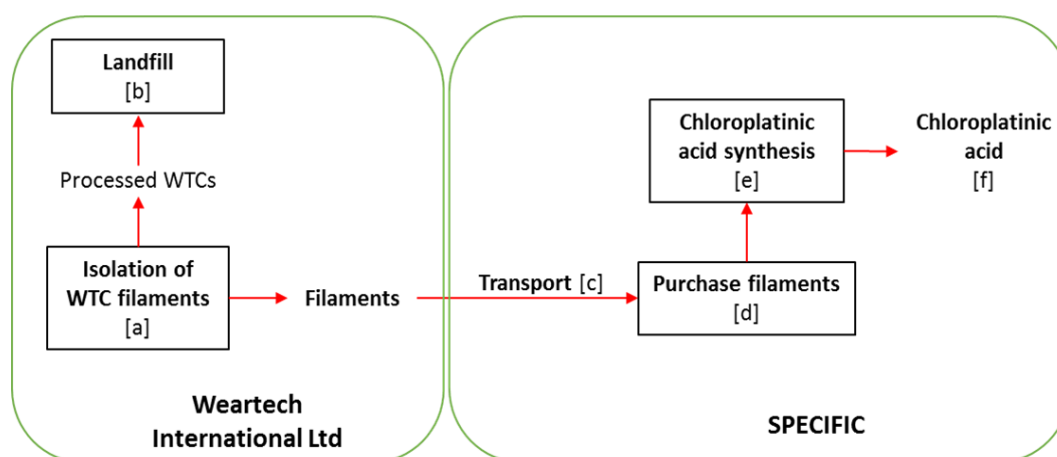
Figure 5.12 Industrial symbiosis operations and associated costs of each operation indicated by letters in square brackets: [a] Labour and overheads; [b] Landfill tax + gate fee; [c] transport; [d] price of filaments ([a+b]); [e] chemicals + energy; [f] total cost of chloroplatinic acid ([c+d+e])

Table 5.4 Cost analysis for production of 1 g chloroplatinic acid from WTCs

Operation	Costs	Weartech Costs	SPECIFIC Costs	% of Total Cost
[a]	Labour & overheads	$41.25		87.0
[b]	Landfill	$0.73		1.5
[c]	Transport		$0.32	0.7
[d]	Price of filaments ([a+b])		$41.98	88.6
	Chemicals		$3.70	7.8
[e]	Energy		$1.39	2.9
[f]	**Total cost** ([c+d+e])		**$47.39**	

Table 5.5 *Comparative cost of platinum as chloroplatinic acid synthesised from WTCs and purchased in minimum and maximum available quantities.*

Pt Source	Cost ($/g)	Wt%Pt	Pt cost ($/g)	Cost Benefit ($)
WTC	47.39	48.6	97.51	
Purchased $H_2PtCl_6.xH_2O$		38.6		
1 g quantity	102.56[252]		265.71	168.20
25 g quantity	41.03[252]		106.28	8.77

The cost of producing WTC derived chloroplatinic acid for SPECIFIC was calculated to be $47.39/g (*Table 5.4*), less than half the current price of chloroplatinic acid used by SPECIFIC when purchased in 1 g quantities (*Table 5.5*). The majority of cost is incurred in the manual isolation of filaments at Weartech. Despite this, there is sufficient cost benefit to justify ~5 days of employment per year at 37 hrs/week on UK national living wage, whilst also covering landfill costs.

Process costs could be reduced further by an increase of scale by extension of the process to take waste thermocouples from other foundries, steel works and glass works, along with the development of semi-automated isolation of WTC filaments. Although traditional automated recycling processes (grinding, with subsequent eddy current and density separation processes) without prior removal of filaments would render efficient recovery of Pt impossible,[18, 106, 116, 253] a semi-automated process for isolation of filaments from whole WTCs could accelerate the process whilst reducing costs. In addition, chemical costs - the second most significant in the process, could be reduced by processing greater numbers of filaments simultaneously. Although 10 ml of aqua regia was used in this case, a lower solid/liquid ratio could still achieve efficient digestion.

Additional cost benefit may be achievable through automated recycling of the remaining portions of WTCs. Comminution followed by eddy current and density separation techniques could produce Cu, plastic and refractory oxide fractions for recycling could valorise this material for Weartech which would generate additional revenue whilst eliminating landfill cost for Weartech.

5.4   Conclusions

Manual isolation of filaments from waste thermocouples (WTCs) with subsequent digestion in aqua regia and precipitation from HCl yields chloroplatinic acid of sufficient quality for use in production of platinized electrodes for dye-sensitised solar cells (DSSCs). This is achievable at sufficient cost benefit to justify implementation of the proposed industrial symbiosis

strategy between Weartech (WTC producers) and SPECIFIC (consumers of chloroplatinic acid). Through conversion of WTC filaments to the 'added value' product, chloroplatinic acid, sufficient value is derivable to cover Weartech's landfill costs; provide ~5 days employment; and enable SPECIFIC to achieve 63% materials cost saving on chloroplatinic acid in comparison to the current scenario in which chloroplatinic acid is purchased from Sigma-Aldrich.

In addition, >50 g of Pt can be diverted from landfill annually. This enhances resource-efficiency and mitigates materials criticality issues by decoupling supply from primary production. Recovery of this quantity of Pt offsets demand for an equivalent quantity from primary sources, negating the requirement to mine and process between 2.5-17 tonne of ore and saving ~200-1400 kg CO_2. Additional environmental benefits result from avoidance of long global logistics chains necessary for supply of chloroplatinic acid through traditional routes. Enough chloroplatinic acid can be synthesised annually from this single foundry alone to produce ~500 m^2 of DSSCs, sufficient to make the electrodes necessary for solar cells to supply clean energy for ~12 households in South Wales. Utilisation of secondary materials from within the circular economy in this way will result in reduced energy payback times (EPBTs) and cumulative energy demand (CED) for photovoltaics whilst reducing the cost and emissions associated with electricity generated.[238]

The proposed strategy exemplifies the environmental, economic and social benefits available through adoption of circular practices and industrial symbiosis, which make use of secondary materials available within the local economy by valorising wastes. The general approach taken provides a mechanism to improve CRM recovery rates from WEEE and other wastes which are uneconomic to process through traditional recycling pathways.

6 Third Generation Photovoltaics – Early Intervention for Circular Economy and a Sustainable Future

"We need to accept the fact that natural resources are limited and that we are not using them in a sustainable way. Growing population and per capita consumption are challenging the very essence of our consumer society. Our responsibility, individual and collective, is increasing and is incomparable to the responsibility mankind was facing a century ago. Change is unavoidable. Change in the way we produce, consume, in the way we live... It is essential for our future industrial competitiveness not only that we produce products using less raw materials, less energy and less water, but also that we are able to replace virgin materials and imports with supplies of secondary raw materials where they are available, and that we produce products that can be re-used, repaired, refurbished and recycled. This is what we mean by circular economy"

Janez Potočnik[225]
European Commissioner for Environment, 2010-2014)

Chapter summary

Work presented so far focuses on recovering the inherent value of WEEE through means which are very much 'reactionary' i.e. using end-of-life (EoL) practice alone to recover value and manage potential environmental impacts. There has been no consideration of how greater value generation and superior EoL outcomes for future EEE may be achieved through feedback of knowledge from EoL operations to other stages of product lifecycles including design & manufacturing. This chapter introduces the concept of lifecycle optimisation for circular economy, in which EoL treatment will be very much 'pre-meditated' rather than reactionary, with products and components designed to accommodate upgrade, repair, refurbishment, remanufacturing and recycling. This results in superior 'circularity', with enhanced retention of items, components and materials within the economy through multiple successive product generations resulting in greater resource-efficiency. This enhancement of the industrial ecology of EEE is necessary in the interests of global sustainability and mitigation of climate change and global resource security issues. Here, lifecycle optimisation for emerging printable photovoltaic (PPV) technologies is considered as an example of how this may be achieved for EEE.[238]

PPV, which include dye-sensitised solar cells (DSSCs), organic photovoltaics (OPV), and perovskite solar cells, are promising green energy technologies in their infancy which hold the promise of low cost energy generation for the future. At this early stage in development, full lifecycle optimisation, taking account of all parts of the product lifecycle, must be

conducted to maximise the resource-efficiency benefits associated with the use of PPV and create truly sustainable renewable energy technologies. Here we examine the advantages of lifecycle optimisation for 3GPV technologies along with key aspects of design; materials selection; manufacturing processes; likely applications of the technologies; and potential recycling and refurbishment strategies. In so doing, features which are conducive to circular economy and challenges for resource-efficiency for these technologies are identified along with potential solutions and priority areas for future research in the field.

The findings detailed in this chapter resulted from a multi-disciplinary sandpit organised and co-chaired by the author entitled: '3rd Generation Photovoltaics: Early Intervention for Circular Economy and a Sustainable Future', hosted at the SPECIFIC IKC, Baglan, South Wales on 7th-8th of April 2016. The aim of the 2-day sandpit with stakeholders involved in all stages of PV life cycles including manufacturers, academics, resource managers, circular business model and eco-design specialists. The purpose of the sandpit was to develop a framework for future R&D which promotes whole lifecycle considerations informed by experts from all stages of the product lifecycle, whilst creating new and strengthening existing collaborations for future funding applications to pursue the progress in this area.

6.1 Introduction

We are on the brink of significant climate change and face the limits of current linear economic models. Transition is necessary to a resource efficient 'circular economy' (CE) with widespread deployment of sustainable green energy technologies. Embracing the waste hierarchy for EoL EEE and prioritising reuse and repair > refurbishment/upgrade > remanufacturing > recycling, results in greatest resource-efficiency benefits and larger savings in embedded costs (economic and environmental) of products and components. This is the basis of the superior economic value potential of CE. Whenever costs of reverse logistics and returning products to market are lower than production costs in linear models, circular systems afford greater value than linear systems.

The economic benefits of CE will also increase over time as prices of primary raw materials rise,[49] as seen for CRMs in recent years. CE presents opportunities for substitution of virgin materials by cascading products, components and materials across multiple product lifecycles. Resource-efficiency benefits result from using cascading materials in new applications; more of the embodied costs (labour, energy, materials) are retained than in traditional recycling pathways. This creates opportunities for organisations to valorise 'waste' through industrial

symbiosis, as described in *Chapter 5*. Resource-efficiency gains from use of post-consumer materials/components are enabled by design for disassembly and materials separation, which reduces costs of reverse cycles and maintains materials quality and longevity within the circular economy. [47] Environmental impacts associated with the use of toxic materials in devices can also be mitigated with appropriate circular practices. Additionally, intangible company assets such as brand value may be enhanced as consumers become increasingly environmentally aware.[49]

Growing recognition of these benefits, rising/volatile resource prices[49] global resource criticality concerns,[53] and rising production costs has made CE an attractive prospect, particularly for manufacturers who rely on supplies of critical raw materials (CRMs). Organizations such as First Solar who produce CdTe PV have therefore adopted business models that unlock the power of CE and generate value through development of appropriate recycling technologies, long product lifecycles, and linking value chains with other industries and supply chain partners.[254]

Commercial viability of photovoltaics (PV) is based on the levelised cost of electricity (LCOE) generated, determined by the power conversion efficiency (PCE), cost and lifetime of PV products (*Figure 6.1*). Resource-efficiency benefits afforded by CE can potentially reduce the economic and environmental costs of module production, enhancing commercial viability and increasing competitiveness with other energy technologies. The use of recovered components and materials can reduce module costs; and design for refurbishment, upgrade, repair and remanufacturing extends module lifetimes. Energy payback time (EPBT), emissions associated with electricity generation (CO_2eq/kWh) and the cost of energy generation ($/Wp) can all be reduced through adoption of circular practices. Studies have shown that EPBT for Si wafer based PV technologies are reduced by half through use of recycled materials.[255] For CdTe PV, it has been predicted that as power conversion efficiency increases and volumes of EoL modules increase, demand for CdTe for PV could be satisfied by secondary supplies from EoL modules alone.[256] The value of take-back and recovery in this case is enormous. The magnitude of these benefits resulting from lifecycle optimisation is determined by the effectiveness of eco-design, which is greatest when implemented at the earliest possible stage in development of new technologies and performed in collaboration with experts from all parties involved in product lifecycles.
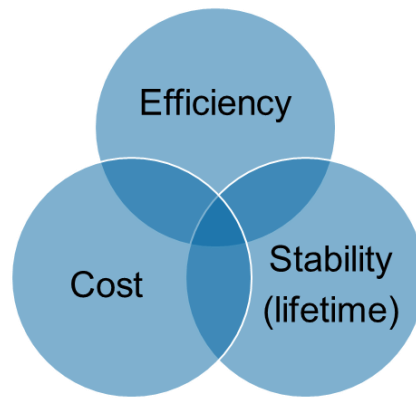
Figure 6.1 *The commercialisation challenge for photovoltaics*

3rd generation photovoltaics (3GPV) include dye-sensitised solar cells (DSSC),[257] organic photovoltaics (OPV),[258] and lead halide perovskite solar cells[259] which are promising low cost green energy technologies in their infancy. The advantages 3GPV offer over previous PV technologies include: the use of low-cost abundant materials; the possibility of roll-to-roll (R2R) printing technologies for manufacturing; flexible light-weight devices; suitability for building and product integration; superior performance in diffuse light conditions; and a range of aesthetic possibilities such as tuneable colour and transparency. As a technology in its infancy, 3GPV has high potential for lifecycle optimised for CE. In addition to appropriate business models and reverse logistics systems, enabling technologies and product design will also require careful consideration and optimisation.

Although viewed as a 'green' technology, 3GPV has environmental impacts associated with its production and may contain hazardous components. Widespread deployment will require a continued supply of CRMs and full lifecycle optimisation for CE is necessary at this early stage in development to create truly sustainable technologies. This includes: minimization of environmental impacts associated with production; development of EoL strategies and processes; design for longevity; cradle-to-cradle design optimisation; selection of low impact materials; and substitution of primary resources and CRMs. This is achievable through the process of eco-design[168] which considers: selection of low impact materials; optimisation of production techniques and reductions in material usage; optimisation of business models and logistics systems; reduction of impacts during use; optimisation of initial life stages of products through design for longevity, upgrade and repair; and optimisation of end-of-life systems.[122, 260, 261] Full lifecycle optimisation also requires cross-sector collaboration between all parties involved in product lifecycles including academics, manufacturers, waste managers, designers and logisticians, to enable cascades of reuse, remanufacturing and recycling, and to

ensure appropriate circular flows of products and materials for optimal economic, environmental and social outcomes.

Here we present an assessment of key features of design, production, reuse and recycling of 3GPV, and the future priority research areas necessary to ensure truly sustainable photovoltaic energy generation. These include: likely applications, architectures and manufacturing processes; attributes of these technologies which are conducive to circularity; appropriate materials selection; potential recycling/remanufacturing processes & strategies; and potential barriers to circularity/sustainability.

6.2 Current PV generation technology

First generation crystalline silicon (c-Si) PV devices are the dominant product on the market today (>90% market share), due to high PCE and stability. Devices are however fragile, expensive and have relatively high embodied energy compared to successive generations of PV.[262] Second generation 'thin-film' technologies, which include amorphous silicon (a-Si), cadmium tellurinde (CdTe), copper-indium-sellenide (CIS) and copper-indium-gallium-diselinide (CIGS), have begun gaining market share. They accounted for ~7% of global PV production in 2015, and some projections show an increase to 50% by 2030.[228] Although offering lower PCEs than c-Si PV, 2nd generation PV requires less materials and energy for manufacturing and offers lower cost electricity generation, short energy payback times (EPBT) and reduced emissions associated with electricity generation.[263] In addition, flexible devices can be created. Despite these advantages, manufacturing involves costly vacuum processes and devices contain toxic materials (e.g. Cd, Pb) and CRMs (e.g. In, Ga, Te), which may limit widespread deployment of these technologies.[256]

In light of these issues, we are now witnessing the emergence of 3GPV, or printable PV (PPV), which are thin-film devices based on molecular photoactive layers, potentially manufactured from earth abundant materials using cheap roll-to-roll (R2R) production. These technologies have attracted an enormous amount of research over the past decade.[264] Early versions of DSSC and OPV devices for niche applications are now commercially available, although much research into new materials, improved device performance and superior manufacturing processes is on-going. Perovskite solar cells,[265] the newest of the PPV technologies, are yet to emerge on the market because of issues of stability. However, lab based devices have reached efficiencies of 22.1%,[264] which is comparable with record cell efficiencies for competing thin-

film technologies. Perovskite cells hold the promise of low cost and high efficiencies if stability issues can be addressed.

6.3   Architectures and operation

3GPV modules are composed of individual solar cells, which are electrically connected and encapsulated in ethylene vinyl acetate (EVA) or glass to form flexible or rigid modules respectively. The various 3GPV technologies share common features in terms of cell architectures and materials sets. Substrate and electrode materials are common across all technologies as are encapsulating materials. Some of the active materials are common across technologies, although a wide range of active materials and architectures have been explored in research, complicating the issue of materials selection in future devices. Here we limit discussion to 'sandwich' cells (*Figure 6.2*), with working and counter electrodes on different substrates.

Figure 6.2 a) Dye-sensitised solar cell (DSSC - Grätzel Cell); *b*) solid-state dye-sensitised solar cell (ssDSSC) (adapted from Snaith, 2013)[265]

DSSCs have been created with various architectures and materials sets.[244] Generally, these are composed of two electrodes, the photo-anode, and a cathodic counter electrode (*Figure 6.2a*). One electrode must be transparent e.g. coated glass, or a plastic such as polyethylene terephthalate (PET) for flexible devices. The second electrode can be made of either a similar substrate or a metal foil.

The photo-anode is composed of a substrate coated with a mesoscopic layer of a semiconductor, commonly TiO_2, which is dyed with a sensitiser species capable of absorbing visible light. The counter electrode is either a transparent conductive oxide (TCO) coated substrate, with a catalytic layer of Pt, or a metallic substrate such as Ti. Electrodes are sealed together with a thermopolymer, and the cavity between is filled with a liquid electrolyte of an iodine/triiodide or cobalt complex redox couple.[266] When illuminated, absorption of a photon by the dye creates an exciton (electron-hole pair). Rapid injection of the electron from the dye into the conduction band of titania follows, enabling the electron to diffuse through the TCO of the anode, around a circuit, and back to the counter electrode. The oxidized dye is reduced by the electrolyte, which is in turn, reduced at the Pt of the counter electrode in the reverse reaction *6.1*. DSSCs are commercially available.

$$I_3^- + 2e^- \rightarrow 3I^- \qquad \qquad [\textbf{6.1}]$$

Solid-state DSSCs (ssDSSCs) (*Figure 6.1b*) are not yet commercialised. Their structure and function is analogous to liquid DSSCs with the electrolyte replaced by a solid hole transport material. These can be organic or inorganic species capable of reducing oxidised dye species and transporting the exciton hole to the counter electrode. A compact titania layer is also used between mesoporous titania and the TCO on the anode which functions as an electron transport layer (ETL) and blocking layer preventing short circuiting through contact of the hole transport materials with the transparent conductor of the anode. Devices use fluorine doped tin oxide (FTO) glass or indium doped tin oxide (ITO) PET as transparent electrode substrates, and metal laminates as counter-electrodes such as Ti. The catalytic Pt layer is not necessary in a ssDSSC.

Perovskite solar cells use methylammonium lead halides ($CH_3NH_3PbX_3$; X=Cl, I or Br) as absorbers. These crystallise in a perovskite structure which gives the cells their names. The first perovskite cells used DSSC type architectures with perovskite infiltrated in a titania scaffold as a sensitiser, referred to as mesosuperstructured solar cells (MSSCs) (*Figure 6.3a*).[267] Later it was found that perovskites themselves function as excellent electron transport materials[268, 269] and porous perovskite heterojunction (*Figure 6.3b*) and perovskite p-i-n heterojunction cells, (*Figure 6.3c*) without titania/alumina scaffolds, have been created.[265] The most efficient devices use Au as a contact. Both organic and inorganic hole transport materials have been used..[270, 271]
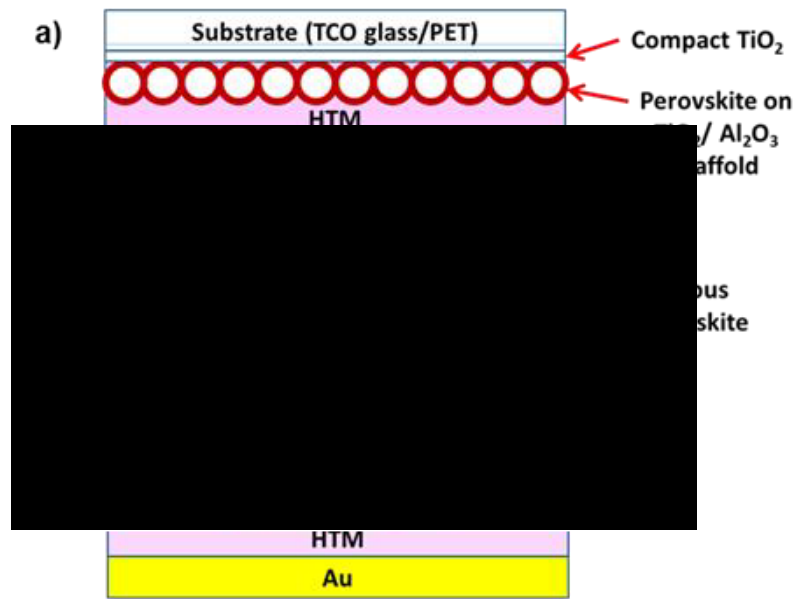
*Figure 6.3 Example architectures of Peroskite solar cells: **a**) perovskite based mesosuperstructured solar cell (MSSC); **b**) porous perovskite heterojunction; **c**) perovskite p-i-n heterojunction (adapted from Snaith, 2013;[265] HTM: hole transport material*

Between the electrodes of OPV devices are two organic materials with extended conjugated π-orbital systems. The first is generally a polymer, such as 3-hexylpolythiophene (P3HT), which acts as a light absorber. The second functions as an ETL, typically a fullerene compound such as phenyl-C61-butyric methyl ester (PCBM). These organic materials can be deposited as individual thin films (*Figure 6.4*), or can be combined and deposited as a single film polymer blend.[272]
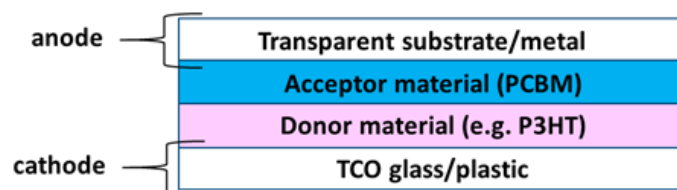
Figure 6.4 Organic photovoltaic (OPV) solar cell device architecture

6.4   Applications of 3GPV

Currently, poor stability and low conversion efficiencies prevent the production of commercially viable large area 3GPV cells, and commercial 3GPV devices emerging on the market are for niche applications. Building integrated photovoltaics (BIPV) to date have been mounted on south facing roofs to achieve good efficiency. 3GPV can be applied vertically to

walls and windows. Retrofitting existing buildings which were not designed to bear the additional weight of other forms of PV is also possible. Interesting new product integration possibilities for 3GPV also exist, particularly at the dawn of the internet of things where electronics will communicate wirelessly and require off-grid energy supply. Additional possibilities exist for combinations with existing PV technologies in tandem devices with enhanced PCEs.[273]

In the immediate future DSSCs will likely find most use in integrated applications. One example is the GCell produced in Wales.[274] This flexible product has found applications in solar backpacks for charging consumer electronics, keyboard folios for iPads and more recently in the first energy harvesting ibeacon, designed for indoor use (*Figure 6.5*). Sony has produced prototypes of their indoor Hana-Akari (flower lamps), which use glass based DSSCs to charge batteries to power LEDs (*Figure 6.6*). An example of BIPV DSSCs include the façade of the SwissTech Conference Centre (*Figure 6.7*).

Figure 6.5 *The DSSC 'GCell' produced by G24Power (top left) and its product intergrated applications in: solar backpacks (top right), ipad keyboard folios (bottom left), and ibeacons (bottom right); images coutesy of www.gcell.com*[274]

Figure 6.6 *Sony Hana-Akari (flower lamps) for indoor use powered by glass based DSSCs in the external flower decorations.*
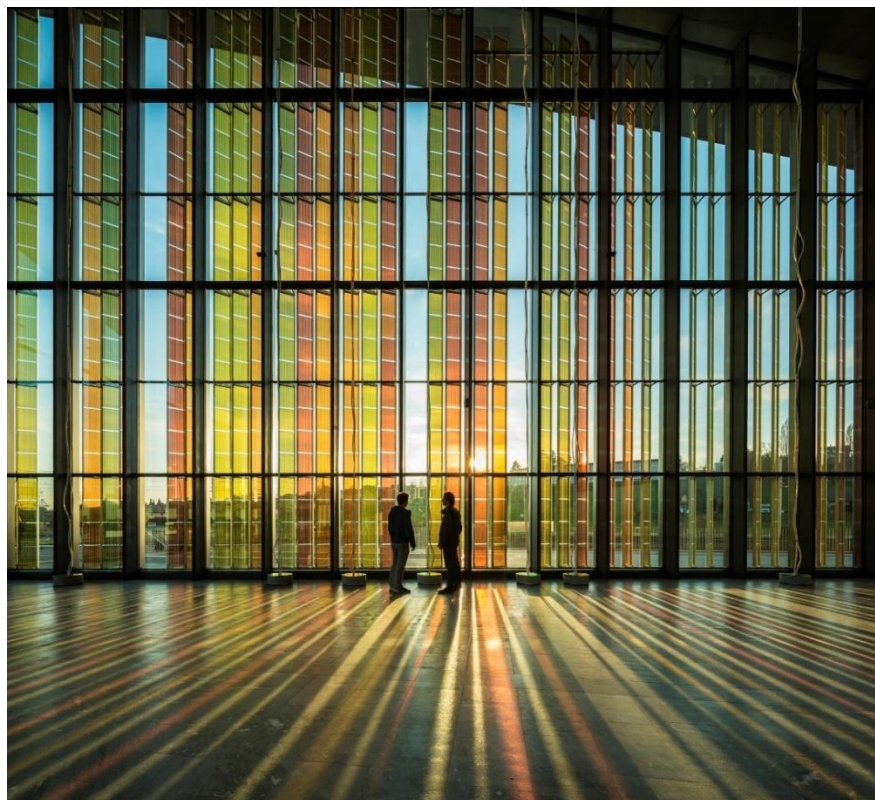
Figure 6.7 *Coloured DSSC façade of the Swisstech Convention Centre*

The first perovskite products will probably be 'tandem cells', in which a perovskite device is combined with existing PV technologies. This is the goal of Oxford PV who are developing

and commercialising thin film perovskite solar cells for printing directly onto Si or CIGS modules (*Figure 6.8*).
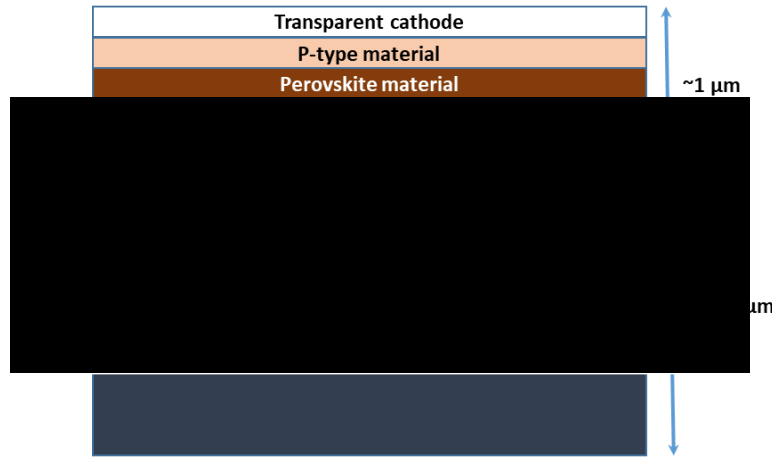
Figure 6.8 *Structure of a tandem perovskite-Si solar cell (adapted from Oxford PV)[275]*

Flexible OPV products have emerged on the market including Heliatek's Heliafilm® for use in BIPV applications, and in the automotive sector for integration with car roofs.[276] Solar phone chargers, solar adhesive tapes and flexible solar foils are also commercially available (*Figure 6.9*).[277] Such products are suited to retrofitting of buildings, windows and consumer electronics.

Figure 6.9 *Heliatek's OPV Heliafilms® (top left) suitable for: retrofitting buildings (top right;, product integration in mobile phone chargers (bottom left), and solar tape for retrofitting products (bottom right).[276]*

6.5 Manufacturing processes

3GPV is cheap because it can be made using R2R production with solution deposition of materials on flexible substrates.[278] Rolls of substrate are run through a series of sequential deposition techniques in which the layers of the cell are deposited as thin films (10 nm – 10 μm), with the final coated product recoiled at the end of the line (*Figure 6.10*). The result is rapid production at relatively low cost. Substrates include metals, such as steel for functionalised building envelopes, and ITO PET for transparent devices. A variety of solution based coating techniques are possible including: bar coating, screen printing, spray deposition, dip coating, slot-die coating and inkjet printing. Coating is followed by thermal treatment to drive-off solvents and cure films. Convection ovens and hot plates have been employed, but higher throughputs, shorter processing times and greater energy efficiency is achievable with NIR curing.[279] Photonic flash annealing is another promising option currently under research.[280] For glass-based devices, R2R is not a possibility and glass must be processed in sheets.
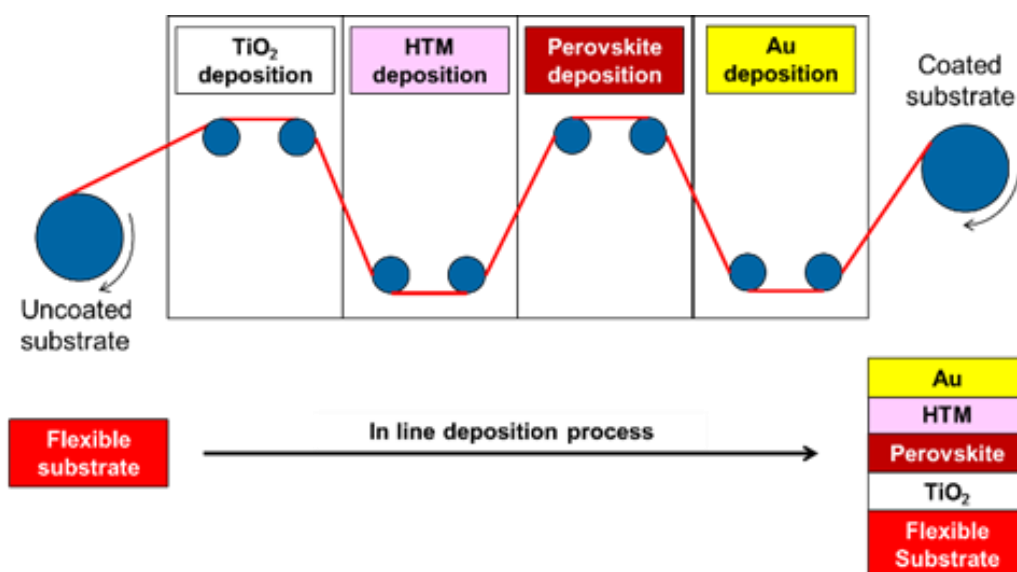
Figure 6.10 *Principle of roll-to-roll production of planar p-i-n perovskite cell as shown in Figure 6.3c.*

Solution deposition of active materials allows precise quantities of materials to be deposited, with little waste resulting from each print. This is in contrast to the large volumes of waste generated in producing Si wafers which is notoriously problematic to recycle.[229] Despite the suitability of R2R production for resource-efficient manufacturing, there are still issues which

need to be addressed: some components, such as gold cathodes, require vacuum deposition techniques which are relatively high in cost, energy demand, and material wastage; masks used in deposition processes retain material; there is the waste issue of production scrap; and solution based processing involves solvent loss. Many of the solvents used, such as DMF and chlorobenzene are hazardous and much research is underway to replace these. New environmentally-friendly solvents are becoming commercially available, such as Cyrene® derived from wood cellulose, which exhibits similar solvent properties to DMF and may be suitable for use in the manufacture of perovskite cells.[281, 282]

A particular advantage of solution deposition is that devices manufactured in this way are often capable of being recycled by 'reverse manufacturing', i.e. selective sequential dissolution of the layers using the same solvents as used for deposition. Solutions of recovered materials may then be used to manufacture new cells. This has been demonstrated at lab scale for perovskite cells by Binek *et al*. (*Figure 6.11*).[283]
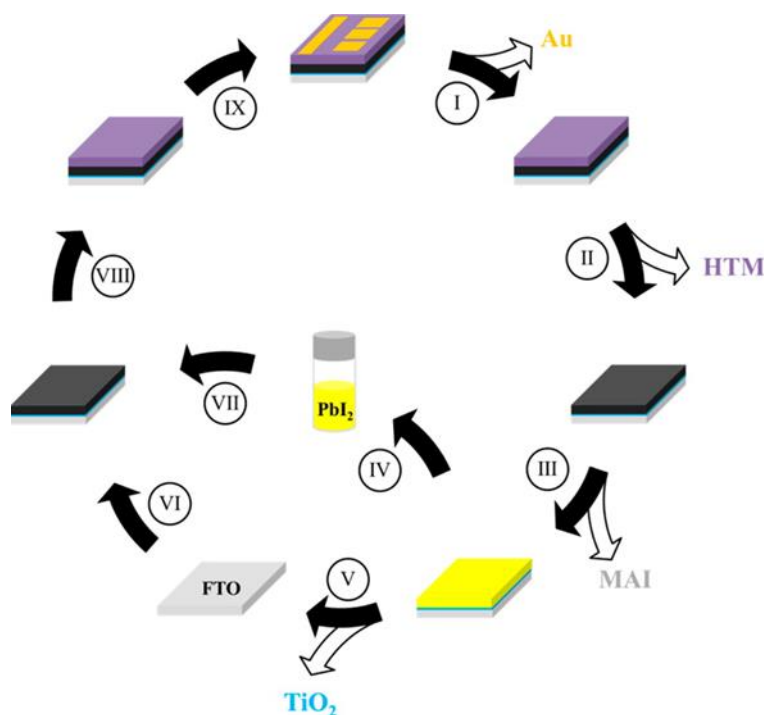
Figure 6.11 Recycling procedure for perovskite solar cells. (I) Removal of Au electrode with adhesive tape. (II) Removal of the HTM by immersing in chlorobenzene. (III) Transformation of the perovskite into methylammonium iodide (MAI) and PbI₂ and extraction of MAI in water. (IV, V) Removal of PbI₂ and TiO₂ using dimethylformamide (DMF). (VI) Preparation of a new TiO₂ film. (VII) Formation of the perovskite film on recycled FTO from recycled PbI₂. (VIII) Preparation of the HTM layer. (IX) Evaporation of the Au top electrode. (Reprinted with permission from Binek et al.,[283] Copyright (2016) American Chemical Society).

6.6 Materials selection

In the interest of circular economy and sustainable economic development, materials selection must take account of compatibility with EoL processes. Numerous studies have shown that substrates represent a large proportion of the embodied environmental and economic costs of PV cells,[258, 283-286] and that these costs are lower for PET substrates than glass.[257] Recovering substrates for reuse is therefore important and delamination of modules is necessary. Mechanical delamination usually destroys substrates and thermal delamination degrades PET.[229] LCA has also shown that laminate materials represent a significant proportion of the embodied costs of thin-film modules[286] and so their recovery is also desirable. A requirement therefore exists to develop new delamination methods, new laminate materials, or alternative flexible transparent substrates which are compatible with thermal delamination. Chemical dissolution of EVA with sulfuric acid, and lactic acid has been demonstrated for second generation PV modules. There is also a case for the use of glass (flexible glass is available although expensive and fragile) in favour of PET despite its higher embodied cost, because of net resource-efficiency benefits over time resulting from viable recovery and reuse of glass substrates using existing delamination processes. Active materials may also be degraded, particularly in thermal delamination processes, and consideration of the benefit of their recovery by mechanical or chemical delamination in preference to thermal delamination is also necessary. The use of metals as electrodes also requires careful consideration. These are readily recyclable, however their initial deposition in devices is usually by relatively high cost, high energy, high waste, vapour deposition techniques, unless cells are printed directly onto metallic substrates.[287]

3GPV technologies use numerous critical raw materials (CRMs). The traditional TCO used in devices has been ITO. However, due to rising prices and the global criticality of indium and demand for ITO for flat screens, this has been replaced by FTO on glass in solar cell applications. Replacement with FTO on PET has been problematic because the high temperature physical vapour deposition (PVD) process used for FTO deposition degrades PET. Mitigation strategies enabling ITO substitution may result from research into new low temperature methods for deposition of TCOs, such as RF magnetron sputtering.[288-290] Substitution with graphene coated PET may be a solution, however its cost is currently prohibitive for commercial application. Carbon-nanotubes which can be printed on substrates have also been explored as TCO alternatives.[291] Another CRM issue arises from the use of Ru in dyes for DSSCs,[244] and there is much work on fully organic dyes as replacements.[292] However, further investigation is necessary into their degradation mechanisms and whether they can, after degradation, be converted easily back into their functional forms for reuse.

An alternative strategy to substitution for mitigating resource criticality issues is to decouple supply from primary production by developing secondary supplies from within the circular economy, including supplies from EoL devices and cascaded materials derived from wastes available within the circular economy (industrial symbiosis). Examples of lab scale processes for production of 3GPV materials from waste include the production of perovskites from Pb-acid car batteries,[237] production of carbon based counter electrodes from batteries,[293] use of conductive glass from LCD screens as DSSC counter electrodes,[294, 295] and the generation of platinized counter electrodes for DSSCs from waste thermocouples described in the previous chapter.[230] The use of WEEE as a raw material may lead to significant materials costs savings and even additional revenue for PV manufacturers. Producers of such WEEE, particularly the items described here which result in disposal costs for those producing them, may be happy to pay PV manufacturers to take such material if the cost is below current disposal costs.

Biologically derived alternatives to oil based plastics are an attractive prospect. Transparent flexible substrates composed of cellulose nanocrystals (CNCs) have been used in OPV cells and shown to have high transparency and suitable surface roughness for this application (relatively high surface roughness has hampered efforts to fabricate viable devices based on paper substrates).[296] In addition, OPV devices on CNC substrates have been shown to be readily recyclable because due to their solubility in water.[297] Where plant derived materials are used, the carbon sequestration benefit will also contribute to reducing GHG emissions associated with electricity generation.

6.7 Product integration

It is likely that the lifetimes of buildings will be considerably longer than the target lifetime of 25-30 years for 3GPV. Full integration into buildings therefore presents issues once modules degrade and reach EoL, and a 'roll-on/roll-off' approach may be useful. OPV lifetimes (currently ~5 years), are more aligned with those of consumer electronics products and so these devices may be most suitable for product integrated applications. DSSCs on the other hand present an interesting opportunity in terms of *in-situ* refurbishment. DSSCs fail due to degradation of electrolytes and dyes. But modified cells (*Figure 6.12*) can be flushed of electrolyte with dilute NaOH and re-dyed in a period of 5 mins with no loss of functionality, in-fact evidence suggests that this treatment enhances PCEs in comparison to virgin cells.[298-300] Modification of DSSC design to accommodate a re-dying process presents possibilities for *in-situ* refurbishment and upgrade in BIPV applications.
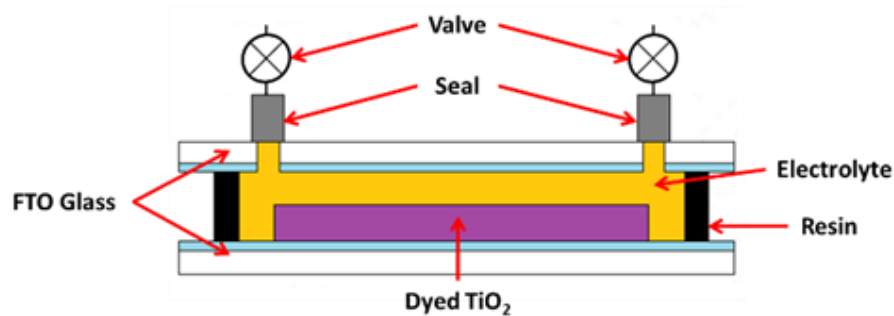
Figure 6.12 Modified DSSC for replacement of dye and electrolyte.

Product integration of PV will also results in complex EoL issues. It is likely that much 3GPV will end up incorporated into low value small domestic appliances that are commonly recycled with automated pre-processing in which shredding will result in dissipation and loss of PV materials. To address this issue, design optimisation of EEE so that PV can be easily isolated from appliances at EoL is necessary. This will require cooperation between PV manufacturers and their clients, EEE manufacturers who purchase PV for integration into products. The cost benefit of returning PV from where it is globally distributed to EEE manufacturers for reuse in new/refurbished products or PV producers for recycling is likely to be poor due to the low inherent material value of 3GPV devices small enough for product integration. The 'refurbishability' of DSSCs again presents interesting opportunities for product integration. As DSSCs could potentially be 'recharged' they could retain value after degradation which may justify isolation from products and return to manufacturers for refurbishment using reverse logistics system resembling those currently used for printer cartridges for example. This 're-charging' strategy for DSSCs also presents opportunities for upgrade as new dyes become available which enhance the PCE of cells.

6.8   Conclusion

3GPV technologies hold great potential as a sustainable renewable energy source for the future. With full lifecycle optimisation for circular economy enabled by eco-design which takes account of EoL, reuse of substrates, laminates and active materials in successive product generations may be possible. Materials costs savings achieved by this, combined with the possibilities of upgrade and refurbishment to extend product lifetimes could result in the lowest levelised cost of electricity from PV technology to date.

DSSCs show great potential as the first 'refurbishable'/upgradable PV device due to the ability to replace dyes and electrolytes repeatedly with no observable loss in functionality over many

product generations. The numerous aesthetic possibilities for 3GPV technologies suggest interesting possibilities in building and product integration.

Priority research areas to enable full lifecycle optimisation include: methods of module lamination/delamination which do not degrade material components; substitution of CRMs; processes for generation of secondary resources from 'wastes' available within the CE and EoL of cells; development of biologically derived cell components such as CNC based substrates; methods which enhance resource and energy efficiency of R2R manufacturing such as solvent capture and recovery of production scrap; and product design for modularity, recyclability, reusability, refurbishability, upgradability and remanufacture.

The examples discussed for PPV highlight the value of intervention at the earliest opportunity in development of EEE to optimise entire product lifecycles for circular economy. This will avoid the complex problems associated with managing current WEEE arising when technologies reach EoL and enhance the industrial ecology of the EEE industry. This enables greater value from technologies past the point of initial sale, a crucial aspect to enhancing resource-efficiency through circular economy. Consideration of EoL strategy, product longevity, and integration with the wider circular economy when designing products in tandem with manufacturing and EoL processes will lead to cost-effective reuse of products and components, and more efficient recycling of materials. The resulting greater value generation from EEE at EoL could drive enhanced resource-efficiency, thereby facilitating sustainable economic development and a solution to the global WEEE problem for the future.

7 Sustainable Solar Energy Storage for Rural Africa

Chapter summary

Previous chapters have demonstrated that greater resource-efficiency and value generation from WEEE may be achieved through lifecycle optimisation of EEE for circular economy. However, a transition towards circular economy will be a gradual and continuous process, which will have little immediate impact on the global WEEE problem. In the short term, consumers themselves have a role to play through selection of the most appropriate EEE for given applications. This requires informed consideration of product design and materials contained, as well as available infrastructure for extending the working life of items and managing items appropriately at EoL for best resource-efficiency outcomes. This is not a simple task, as often consumers and those responsible for procurement within large organisations do not possess sufficient knowledge or expertise to make informed decisions on the matter, or easily differentiate between competing technologies. Lack of knowledge by user of EEE may also result in poor operation resulting in shortened product lifetimes, and management and disposal at end-of-life in an inappropriate manor.

Photovoltaics, notably silicon PV, are becoming increasingly important in providing localised energy for rural communities in Africa. Although viewed as 'green', these technologies have environmental impacts associated with their production, use, and disposal, and full lifecycle optimisation for the circular economy is necessary to make every aspect of these technologies truly sustainable. One of the key questions when considering installation of solar energy systems is what is the best energy storage technology to use. Here various battery technologies are discussed in terms of their suitability for circular economy and functionality for small scale domestic installation in South Africa. This discussion is within a framework for selection of appropriate battery technologies for use in PV systems for off-grid electrification of rural sub-Saharan Africa. Using South Africa as an example location, selection is informed by careful examination of materials content, cost, local available skills & knowledge, and infrastructure for management and processing of batteries in a manner conducive to circular economy and greatest benefit for local economies and communities.[301]

7.1 Introduction

In 2016, ~10% of households in South Africa had no access to electricity.[302] This equates to around 5.5 million people from a population of 55 million. Most of these households are in rural areas.[303] In January 2017 the author co-organised and chaired a workshop: 'Eco-Design of Printable Photovoltaics – the Building of an African Infrastructure' in Durban, South Africa, to discuss the multidisciplinary research necessary to develop a functioning circular economy for photovoltaic solar energy systems for rural Africa. The key question which arose from the workshop, more significant than choice of solar cell technology was: "What is the most suitable battery technology for sustainable solar energy storage for small scale domestic use in rural Africa?"

In Swansea University the SPECIFIC Innovation and Knowledge Centre (www.specific.eu.com) team has constructed a building on which new technologies for solar energy collection and storage are monitored and validated. This ~200 m^2 building demonstrates the 'buildings as power stations' principles under development by SPECIFIC using technologies embedded into building envelopes to generate, store, and release energy.[304] The building has a 17 kWp roof integrated photovoltaic (PV) installation, transpired solar air collectors integrated into the external south wall for heating, and 60 kWh capacity of aqueous hybrid ion batteries (C2C certified) for clean and safe energy storage (*Figure 7.1*).[305] In Africa, a team from Swansea University installed a small scale off-grid solar energy structure with 1.4 kWp of integrated PV in an orphanage in Mutende, Lulamba, Zambia (*Figure 7.2*).[306] Two 12 V, 102 Ah lead-acid batteries were used for electricity storage. They seemed an obvious choice given they were readily available, easily replaced, durable, and provided the required capacity. But was it the best choice technology?

Roof integrated CIGS PV

Aquion salt water batteries

Transpired solar collector
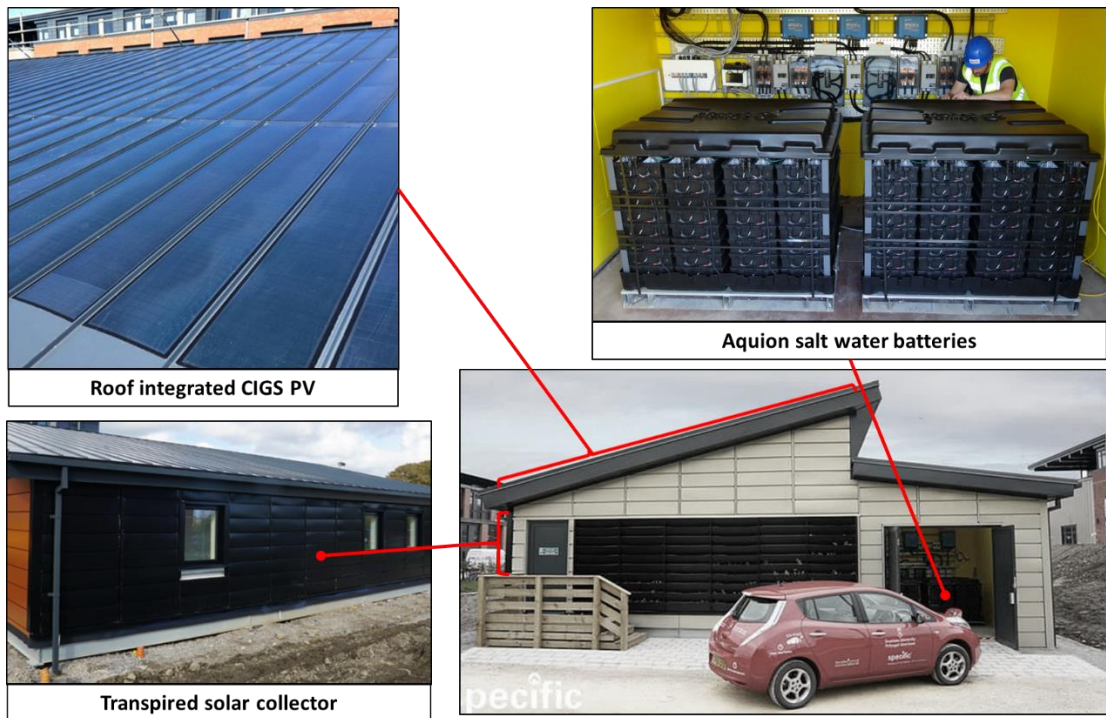
Figure 7.1 *Integrated technologies on the SPECIFIC 'Active Classroom'*

1.4 kW-peak photovoltaic roof

Solar-powered system with an integrated battery to provide:
- **Lighting under the shelter**
- **Music system with charging outlet for USB devices**

Independent solar-powered lighting around the structure

Games table for evening entertainment!

Invertor & charge-controller with battery storage & mains outlet

Figure 7.2 *Off-grid solar energy structure with 1.4 kWp of integrated PV in an orphanage in Mutende, Lulamba, Zambia*

7.2   Defining the System

To establish the specification of off-grid systems, the energy requirements of households to be met must first be defined. In recent years, South African energy suppliers introduced a scheme

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to provide 50 kWh/month 'free basic electricity' to grid-connected households, with a plan to develop off-grid solar powered systems providing 50 kWh/month to rural households.[303] 50 kWh/month is ~1.67 kWh/day, significantly lower than the average daily consumption of ~8 kWh/day by grid connected homes in South Africa, but sufficient for basic commodities such as lighting TV, radio, cell phone charging, washing, and possibly refrigeration (*Table 7.1*).

Table 7.1 Example daily energy consumption for small domestic appliances

Item	Usage	Energy consumption (kWh/day)
TV (32 inch LCD)	5 h	0.35
Small DC fridge (50 W)	24 h	1.2
Compact fluorescent light (one 14W bulb)	5 h	0.07
Cell phone charger (5 W)	3 h	0.01
Washing machine (500 W)	1 h	0.5
Total Energy Consumption		**2.13**

If 90% of this energy was required overnight, then ~1.5 kWh energy storage is needed. Allowing for an annual load growth of 2%/year over the 20 year lifetime of the PV system requires ~2.1 kWh of battery storage. (It is interesting to note that increase in electricity demand is such that this year, 2017, the proposed on-grid 'free electricity' allocation in Durban is 65 kWh/month, ~2.1 kWh/day). Battery technology is developing rapidly; here the focus is on systems which could be put in place immediately.

Operational conditions have a strong influence on battery performance and lifetime, and South Africa is a tough environment in terms of ambient temperatures both day-to-day and over the year. To mitigate this, it is proposed that batteries be buried at a depth of ~1.5 m where the insulation and thermal lag due to soil cover, is expected to limit temperature variations to ~12-25 °C.[307]

To give some idea of what is involved, the battery and photovoltaic requirements have been modelled using the Photovoltaic Geographical Information System[308] with Durban as an example location. The cost of a system capable of generating a minimum of 50 kWh/month has been estimated. A 600 Wp photovoltaic system (optimised in terms of orientation and angle) coupled with a 12 V, 250 Ah lead-acid battery with a minimum state of charge cut-off limit of 40% and a daily power consumption of 2 kWh would yield an average of 56.5 kWh/month and 678 kWh/year. Using a value of 1.3928 R/kWh (0.096 €/kWh) as the cost of electricity (provided by Prof. Bice S. Martincigh, School of Chemistry & Physics, University of KwaZulu-Natal, Durban, RSA, as a typical cost for electricity in Durban) gives a yearly value of €65.09 for the 678 kWh. The estimated cost of this system is: 0.34 €/W for a multi-

Si module,[309] totalling €205.32 for 600 Wp; €345.15 for a 250 Ah lead-acid battery based on commercially available batteries in South Africa; and €65 for a charge controller and cables. This gives a total initial system cost of €615. Over a period of 20 years, given the typical number of cycles from a lead-acid battery, the battery would need to be replaced 4 times (5 batteries in total), roughly once every 4 years, bringing the 20-year cost of the system to €1,996. *Figure 7.3* shows the cost of the system over time with these battery changes and the value of the electricity produced assuming all costs remain constant. It is evident from that most of the system cost is attributable to the batteries (~87%). To make the system cost effective, reduction of lifecycle cost is necessary. The role of circular economy as a means of reducing these estimated costs is discussed below.
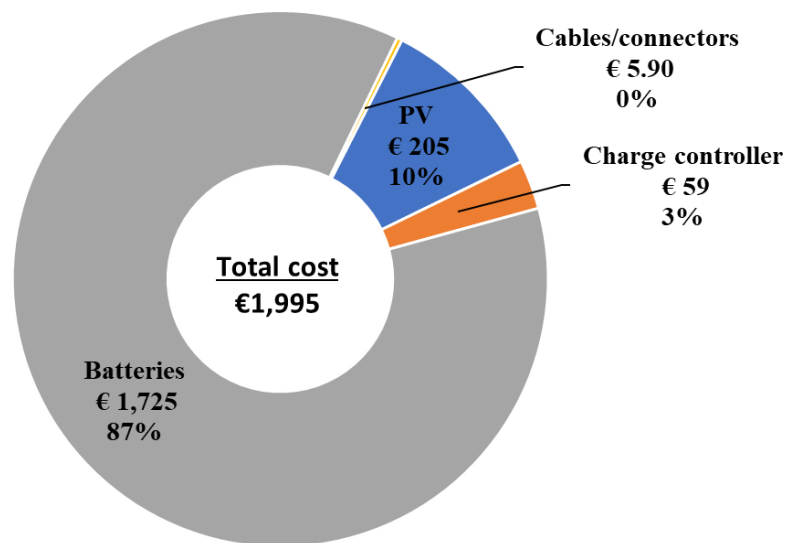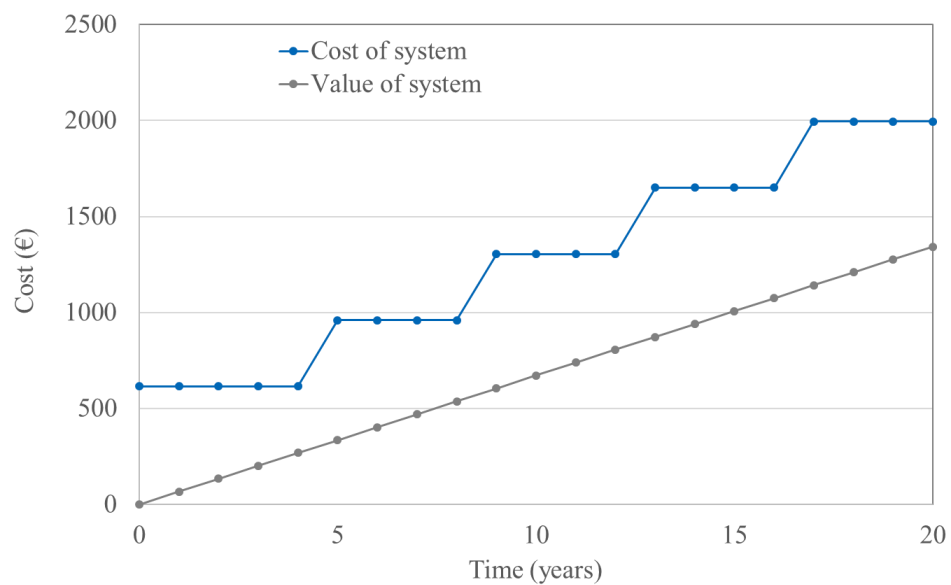
Figure 7.3 *An estimated cost of an off-grid DC, PV system in Durban, South Africa, consisting of 600 Wp silicon module, a 12 V, 250 Ah lead-acid battery and a charge controller and cables (top); and breakdown of cost of system (€) over 20 years (bottom)*

7.3   Battery Choices & Cost

Four main battery technologies dominate stationary energy storage applications (*Table 7.2*).[310] Lithium ion (Li-ion) batteries represent the majority of installed storage capacity and are commonly used in domestic photovoltaic systems. The merits of lead-acid batteries for application in rural Africa have already been highlighted in the discussion of their use for the Swansea University Zambia project. Vanadium redox flow batteries (VRFB), require pumps for electrolyte flow and additional energy and storage capacity to support this. This along with the additional mechanical complexity of VRFB systems makes them unsuitable for small-scale applications. High temperature NaNiCl batteries are unsuitable because of the hazards associated with molten metal electrodes.

Table 7.2 Globally installed stationary energy storage capacity by battery type (data from Baumann et al.)[310]

Battery Technology	Installed Capacity	
	(MW)	(GWh)
Li-ion	~1300	1.27
Hight temperature NaNiCl	171	1.01
Valve regulated lead-acid (VRLA)	196	0.173
Vanadium Redox-flow batteries (VRFB)	114	412

Cost is of paramount importance for application in rural South Africa, and *Table 7.3* compares costs for three candidate technologies for the proposed system i.e. lead-acid, Li-ion batteries and the Aquion saltwater battery (*Table 6.3*). Commercially available lead-acid batteries are significantly cheaper than LFP or Aquion batteries (~10 and 5 times respectively). The easy availability and low capital investment costs of lead-acid batteries are very attractive, but lead-acid has comparatively low cycle lives, in comparison to Li-ion and Aquion batteries and a high sensitivity to deep discharge. Significant oversizing of capacity is therefore required. And the relatively short lifetimes for lead-acid batteries mean that these must be replaced 4 times over the lifetime of the proposed system, resulting in a total cost of €1,726, which is still only one quarter and one third the price of the longer lifetime LFPs (€7,104) Aquion batteries (€5,040) respectively.

Table 7.3 Comparative costs of commercially available batteries over 20-year lifetime of system

Battery	Cost (€/Ah)	No. replacements	Total cost (€)
VRLA	1.38	4	1,726
LFP*	14.21	1	7,104
Aquion	6.72	2	5,040

***LFYP** - lithium-iron-yttrium-phosphate battery; **VRLA** – valve regulated lead acid battery*

Of course, economies of scale and direct bulk purchase from manufacturers may result in lower these battery prices and the use of a 'circular economy' approach can give cost savings by: utilising remanufactured, refurbished or repurposed batteries; purchasing batteries manufactured from recovered materials (obtained at lower cost than virgin materials); and valorising end-of-life batteries to recoup costs by diverting them to refurbishment, remanufacturing and recycling processes.

7.4 Carbon Footprint and Lifecycle Impact Consideration

A comparison of carbon footprints of lead-acid and different types of Li-ion battery production for the system is given in *Figure 7.4* (equivalent data for Aquion batteries could not be found). When the need for replacement batteries is considered, lead-acid batteries account for a greater contribution to the carbon footprint of the system than Li-ion alternatives, except for lithium titanate batteries (LTO). Lithium-nickel-cobalt-aluminium batteries (NCA) would contribute least to the carbon footprint of the system over its lifetime. It should be noted that, utilisation of recovered materials for battery manufacturing would reduce emissions associated with production.
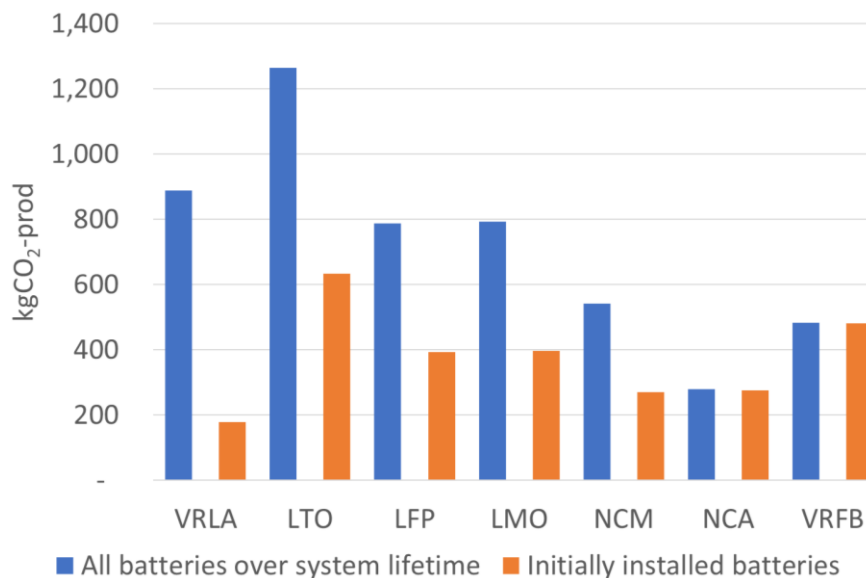
Figure 7.4 *Carbon footprint of batteries for the system including replacements (based on data from Baumann et al.[310]. VRLA – valve regulated lead-acid; LTO – lithium-iron-phosphate with lithium titanate anode; LFP - lithium-iron-phosphate with carbon anode; LMO - lithium-manganese-oxide; NCM – lithium-nickel-cobalt-manganese; NCA – lithium nickel-cobalt-aluminium-oxide).*

Carbon footprint of the production of batteries is useful for a comparison of global warming potential. However, this is a limited picture of the environmental impacts of batteries. Further consideration of emissions during production from primary resources should be made e.g. the

production of Li-ion batteries from primary raw materials results in considerable SO_2 emissions and water contamination.[311]

Additional consideration of the hazardous nature of materials within batteries and their potential impacts if improperly managed during use and end-of-life is necessary. Issues relating to end-of-life of Li-ion batteries arise from their metal content e.g. Co present in cathodic materials; fluorine, arsenic or sulfonated compounds present in electrolytes; and the extremely reactive alkali metal – Li. Improper treatment of lead-acid batteries at end of life results in the release of Pb and sulfuric acid to the environment. These materials can directly impact human health through contamination of water & soil and accumulate in food chains when batteries are landfilled or recycled improperly.[117] This is of particular concern for rural of sub-Saharan Africa where batteries are installed in isolated underdeveloped area making collection problematic and recycling practices lack basic precautions to prevent emissions of these substance to the workplace and environment, and those recycling facilities that are licensed face serious competition from the informal sector which formerly consisted of small scale backyard recycling operations which are now increasingly replaced by industrial scale informal smelters.[312, 313] Pb-poisoning of workers is common and fatal in some cases.

The issue of hazardous waste arising from increased deployment of batteries for solar home systems in Africa is significant. In 2016, 1.232 million tonnes of Pb-acid batteries were shipped to Africa containing >800,000 tonnes of Pb (equivalent to 10% of global production).[312] The African Renewable Energy Initiative that was launched in 2015 has a 300 gigawatt target for 2030, and solar will form a major part of installed capacity. Nigeria alone has a target of 30 GW of installed solar capacity, which will require an initial installation of over 40 million batteries, and if Pb-acid batteries are used to support the systems, 280 million batteries will have to be installed, recovered and recycled over the lifetime of these systems.[314]

The discussion so far suggests lead-acid batteries are the cheapest option by a significant margin, however their use results in greater global warming potential over the 20-year lifetime of the system than most Li-ion alternatives.

Optimum battery use requires some knowledge of the technology, as does proper handling of waste batteries.[312] Thus, any system installation also requires: i) an additional basic education and training package on the benefits of solar energy, and proper operation, maintenance and replacement of components; and ii) full system performance monitoring and analysis for problem/fault prediction/finding.

7.5 Resource-efficiency and Circular Economy

7.5.1 Critical Materials

Critical raw materials (CRMs) used in batteries are shown in *Table 7.4* with their current supply risk index from the British Geological Survey. The high supply risk associated with vanadium may present future resource security issues for VRFBs, further justifying its elimination as a potentially suitable technology for the proposed application. Li-ion batteries face resource security issues due to Li, Co and graphite, as do Aquion cells which contain graphite. In the interests of global resource security, it is questionable whether technologies containing CRMs should be utilised without further consideration of available infrastructure to support collection and closed-loop recycling, refurbishment and remanufacturing. Lead-acid batteries contain no CRMs.

Table 7.4 Supply risks of materials in batteries, those highlighted in orange have been identified as CRMs in recent assesments

Element	Relative supply risk index[315]	Relevant battery technology
V	8.6	VRFB
Co	8.1	LIBs (NMC and NCA)
Li	7.6	All LIBs
Graphite	7.4	LIBs (LFP, LMO, NMC, and NCA), Aquion
Mn	5.7	LIBs (LMO NMC), Aquion
Ni	5.7	LIBs (NMC and NCA)
Pb	5.5	VRLA
Fe	5.2	LIBs
Ti	4.8	LIBs (LTO)
Al	4.8	LIB

Supply risk index runs from 1 (very low risk) to 10 (very high risk); LIBs – Li-ion batteries; highlighted elements included in EU20 critical list.

7.5.2 End-of-life prospects & compatibility with circular economy

Closed-loop recycling of lead-acid batteries is well established in South Africa. First National Batteries operate a network of collection points across South Africa, which divert lead-acid batteries to their smelting facility in Benoni for recycling. Recovered Pb and plastics are used to manufacture new batteries with optimised design for disassembly.[316] This suggests end-of-life costs will be low in comparison to other batteries which cannot be recycled domestically, and that lead-acid batteries are an appropriate choice for circular economy in South Africa, with environmental, economic and social benefits afforded through closed-loop retention of the materials within the South African economy. Materials cost savings resulting from use of recovered components/materials should rise with volumes of lead-acid-batteries recycled in the future, resulting in cheaper batteries for the proposed photovoltaic system. Several

businesses within South Africa operate a lead-acid battery reconditioning service which reverses the sulfation process that limits their working life. This presents opportunities to extend the longevity of lead-acid batteries and reduce battery replacement costs over the system lifetime. With this infrastructure in place, opportunities should be explored for utilisation of automotive lead-acid batteries in a second life for the proposed systems which may be obtained and refurbished at lower cost than they can be purchased, with associated environmental, social and economic benefits resulting from the initiation of new industry.

To the best of the author's knowledge no Li-ion battery recycling exists in Africa. Li-ion batteries are collected and shipped to Europe for recycling, at considerable economic & environmental cost. South Africa also has no Li-ion battery manufacturing through which to valorise recovered materials in closed-loop material flows.[317] This indicates Li-ion end-of-life costs in South Africa will be comparatively high with significant logistics costs incurred and little of the social and economic value inherent in Li-ion batteries exploited within South African local economies. High costs increase the likelihood of improper end-of-life management, and the resulting potential for impacts on health and the environment is high. However, the South African government has funded research seeking to develop domestic Li-ion battery recycling.[317] Were such an industry to emerge, the derivable economic, environmental and social benefits from Li-ion battery recycling within South Africa could be improved significantly. No future prospects for Li-ion refurbishment exist at this time. It may be possible to source used automotive batteries for reuse in the proposed system at reduced costs with associated environmental benefits to the proposed system.[318] As an emerging technology yet to be deployed in Africa, Aquion batteries have few prospects for end-of-life treatment within the continent in the near future.

7.6 Conclusion

From this preliminary examination of battery technologies for sustainable small scale (50 kWh/month) domestic installation in South Africa it seems that the current best choice is lead-acid batteries despite lower efficiencies and lifetimes than Li-ion and Aquion batteries. This is justified by the ready availability of lead-acid batteries in South Africa through domestic manufacturing; low cost; and existing infrastructure for refurbishment and closed-loop recycling. To maximise the circular economy benefits and achieve economic viability for the proposed PV system, South African energy companies should engage key organisations involved at all stages of lead-acid battery lifecycles, and consider appropriate business models

to maximise return of batteries at end-of-life such as 'lease and takeback' schemes or deposit schemes for batteries.

Future developments for Li-ion batteries initiated by the South African government may in time enhance the benefits of Li-ions for this application, however high costs, critical materials issues and poor prospects for refurbishment and remanufacturing cast doubt over the suitability of this technology for the proposed system.

Whichever battery technology is used, optimum battery use and management over their lifecycles requires knowledge of the technology. Thus, any system installation also requires an additional basic education and training package on the benefits of solar energy and the proper operation, maintenance and replacement of components; and full system performance monitoring and analysis for problem/fault prediction/finding.

This evaluation is South Africa specific, and based upon local availability of systems and infrastructure to support circular economy around batteries for PV systems. The primary purpose of the work presented is not to identify the most appropriate battery technology for the circular economy for the whole of sub-sahran Africa through examination of the South African context, but to stimulate consideration of the issue by others within the framework applied here, taking account of geographically specific considerations so that optimum solutions to battery selection and end-of-life management can be developed and key areas for further development to support circular economy around off-grid PV systems.

8 Conclusion

The 'global WEEE problem' represents a significant sustainability challenge for humanity. Most of the 41.8 million tonnes of WEEE generated annually around the globe is still unaccounted for and its improper treatment by informal sectors has resulted in significant impacts on the environment and human health.

Initially, this EngD project was focussed on the measurement and assessment of value in WEEE for a local firm, Metech Recycling (UK) Ltd to inform operations and increase the value derived from recycling. However, over the period of study, the author became increasingly convinced that this, while important work, is only a small part of the solution to the global WEEE problem. The emphasis of the project shifted over time in recognition of the fact that linear throughput of materials used by the EEE industry to manufacture new products which replace WEEE represents a resource-efficiency crisis that must be urgently addressed, and that the answer to the 'Global WEEE problem' lies in the replacement of current linear economic models with circular economy.

The study of temporal trends in precious metal content of WEEE described in *Chapter 3* shows that quantities of gold and silver in DRAM modules have been stable over the time period 2000-2010, but that copper content has risen, and a very significant decrease in palladium content has occurred as a result of miniaturisation of MLCCs, although Pd content of modules (and other PCBs utilising MLCCs) may eventually begin to slowly rise again when additional MLCCs are incorporated to support advanced functionality. Global sales of desktop PCs and therefore DRAM modules are diminishing as laptops and tablets gain greater market share. Thus, the total size of the 'reserve' of metals in PC DRAM modules is decreasing and therefore so is their recycling potential. Based on projections of global PC sales, it is likely that the annual number of waste DRAM modules produced will decreased in proportion with PC sales.

Gold and silver make up the major value fraction of recoverable value in computers, laptops and tablets, and were there to be a decrease in content of these metals in the future, then major discrepancies between recycling potential projections and the resulting future reality could arise, to the detriment of waste management operations and legislation based upon such projections. The immediate technological changes which may lead to a reduction in gold and silver content are continuing miniaturisation and thrifting in manufacturing, and cloud based computing and data storage. Miniaturisation may well decrease the absolute gold content of a device, but miniaturisation of the whole device may result in sustained or even increases in

recycling 'grade' of devices overall. Similarly, while cloud based computing will decrease the required functionality of PCs, laptops and tablets and therefore the material value, this will be accompanied by increased volumes of servers in data centres which generally represent higher grade material than PCs. This may mean the shift to cloud computing results in a concentration of precious metals in data centres which may make recycling more efficient.

When considering recovery of critical raw materials from WEEE as discussed in *Chapter 4*, XRF combined with digital imaging has proven useful for building a library of component images and x-ray emission spectra to inform future recycling processes which target CRMs for recovery.

Cryo-cracking of high value products whose manual disassembly is problematic may be useful as a means of diverting CRM rich PCBs from automated recycling processes in which CRMs are dissipated and lost through unintended co-separation. The use of a guillotine to break through plastic housings and reduce costs associated with isolating CRM bearing components also shows potential, while isolation of SMDs from PCBs is best achieved by use of a solder bath. The use of microwave ashing to pre-concentrating CRMs can provide sufficient cost benefit through mass reduction prior to refining which incurs mass based treatment charges.

While CRMs have been identified throughout the WEEE samples examined, the dissipative nature of applications of CRMs in EEE is a major barrier to recovery. Many CRMs in PCBs partition into slag during smelting for precious metals recovery, rather than into the liquid copper carrier metal for refinement from collected copper bullion. CRMs which are irrecoverably lost this way include Ga, Ge, Ta, Y, and Co. It is possible to isolate SMDs containing these CRMs prior to smelting, but there is little economic justification for the additional cost of this because of a lack of available recovery infrastructure for CRMs, and the fact that the more valuable copper and PMs are recoverable simply by smelting, even though this results in permanent losses of the other CRMs. One solution may be to pursue development of hydrometallurgical recovery methods through which a wider range of CRMs may be recovered. A 'chicken & egg' scenario exists currently in which isolating CRMs from WEEE in appropriate fractions for downstream recovery is not viable due to lack of recovery infrastructure to valorise CRMs in those fractions, and recovery infrastructure is not in place as insufficient quantities of suitable WEEE derived materials are currently available to feed such processes. Poor design of EEE for disassembly also results in high costs associated with isolating CRM bearing components from WEEE, another barrier to their recovery.

One important feature of circular economy is industrial symbiosis in which waste from one process becomes feedstock for another, and the work described in *Chapter 5* on platinized

counter-electrodes for dye-sensitised solar cells from waste thermocouples develops a local example of this. The process developed essentially 'activates' waste thermocouples (WTCs) produced by Weartech as a cost-effective source of chloroplatinic acid for production of platinized electrodes for dye-sensitised solar cells (DSSCs) in Swansea University SPECIFIC-IKC labs. Sufficient value is derivable to cover Weartech's landfill costs; provide ~5 days employment; and enable SPECIFIC to achieve 63% materials cost saving on chloroplatinic acid in comparison to buying from Sigma-Aldrich. ~50 g of Pt can be diverted from landfill annually negating the requirement to mine and process between 2.5-17 tonne of ore and saving ~200-1400 kg CO_2. The proposed strategy exemplifies the environmental, economic and social benefits available through adoption of circular practices and industrial symbiosis, which make use of secondary materials available within the local economy as secondary CRM sources by valorising them to a greater extent than can be achieved through traditional recycling chains, thereby improve CRM recovery rates from WEEE. The principle of direct generation of added-value precursor compounds for manufacturing to enhance derivable value from materials in wastes is applicable to other materials and waste streams which are otherwise uneconomic to process through traditional recycling pathways. This highlights the importance of industrial symbiosis as a means to enhance recovery of CRMs and other metals used in dissipative applications in general.

The work on early intervention for circular economy for third generation photovoltaics decribed in *Chapter 6* identifies the need for eco-design at the earliest stages of product development. Although photovoltaics represent a 'green' energy solution, whole lifecycle optimisation for circular economy of photovoltaic systems is necessary before this technology can be considered truly 'sustainable'. Priority research areas to enable full lifecycle optimisation include: methods of module lamination/delamination which do not degrade material components; substitution of CRMs; processes for generation of secondary resources from 'wastes' available within the CE and EoL modules and solar cells; development of biologically derived cell components such as CNC based substrates; and methods which enhance resource and energy efficiency of R2R manufacturing such as solvent capture and recovery of production scrap. Consideration of EoL strategy, product longevity, and integration with the wider circular economy when designing products in tandem with manufacturing and EoL processes will lead to cost-effective reuse and remanufacturing of products and components, and more efficient recycling of materials. The resulting greater value generation from EEE at EoL could drive enhanced resource-efficiency, thereby facilitating sustainable economic development and a solution to the global WEEE problem for the future.

Along with the generation of solar energy there is a need for energy storage, and sustainable energy storage is at least as important as sustainable generation, particularly for small scale generation. From the preliminary examination of battery technologies for sustainable small scale off-grid domestic PV installation in South Africa described in *Chapter 7,* lead-acid batteries are determined to be the best choice because of low cost, domestic manufacturing, and an existing infrastructure for collection, refurbishment and closed-loop recycling into new products with design for disassembly. Pb-acid batteries are more compatible with existing local knowledge, skills and infrastructure to support circular economy than alternative battery technologies, so greater potential exists to generate economic, social and environmental value from Pb-acid batteries than alternative technologies. Optimum battery use and management throughout their lifecycles to maximise their longevity and retention of batteries and constituent materials requires knowledge of the technology. Basic education and training on the benefits of solar energy and the proper operation, maintenance and replacement of components must therefore accompany any system installations to ensure component longevity is maintained, and that EoL components are managed appropriately. Full system performance monitoring and analysis for problem/fault prediction/finding is also required. While this evaluation was specific to South Africa the framework for evaluation which takes account of local conditions is generally applicable to all EEE. It is hoped this work will stimulate consideration of these issue by others so that optimum solutions to battery selection and end-of-life management can be developed. Key areas for further development to support circular economy around off-grid PV systems include investigation of appropriate reverse-logistics and business models which suit low population density rural areas and will facilitate maximum collection rates of EoL PV system components, suitable legislation to govern EoL management of system components, and a thorough evaluation of how the informal sector may be incorporated into a functioning circular economy.

In the broader context, circular economy represents a solution to the global WEEE problem and a means to enhance the industrial ecology of the EEE industry. By effective exploitation of the inherent value of WEEE, significant economic, environmental and social benefits can be derived, whilst limiting detrimental impacts resulting from its hazardous nature.

Treatment processes which are conducive to circular economy provide opportunities for greater valorisation of WEEE than is possible through traditional recycling process chains. Upgrade, refurbishment and repair of WEEE extends its life so that it can be reused. This, as well as remanufacturing with retention of as many original components as possible; cascading components and materials across product lifecycles; and recycling with the greatest efficiency possible including industrial symbiosis approaches, conserves primary raw materials and

natural capital and retains materials within WEEE in an economically productive capacity. Greater value generation afforded through such processes provides a financial incentive which may deter illegal exports, and reduce quantities of WEEE processed in 'back yard' recycling operations reducing impacts on human health and the environmental resulting from WEEE. The extent to which economic value is exploited form WEEE determines the magnitude of associated environmental and social benefits, and so the waste hierarchy should be embraced and prioritised.

Circular material flows require sufficient economic value to be derived from WEEE at EoL to finance the costs of necessary logistics and processing. Reuse, remanufacturing and recycling must all exploit as much of the inherent value of WEEE as possible. To date, little remanufacturing of WEEE occurs and effective reuse of WEEE and its components is often prohibited by inadequate product design. To overcome these barriers in the future, full lifecycle optimisation of EEE will be necessary to ensure that problems associated with management of WEEE today, are avoided in the future. To enable this, eco-design of products to accommodate efficient disassembly, upgrade, refurbishment, remanufacturing and component/materials recovery must be undertaken. Manufacturing and remanufacturing must be optimised in tandem with recycling so that recovered materials from EoL products can be efficiently cycled back into manufacturing. Product design must also accommodate this. Complete lifecycle optimisation such as this is most effective when intervention at the earliest possible stage in design of new products occurs. This should take account of suitable secondary materials available for manufacturing, compatibility of materials with recycling and remanufacturing processes, substitution of CRMs where possible, failure mechanisms of technologies, and the applications of technologies. Appropriate reverse-logistics and business models are essential to ensure efficient collection so circular material and product cycles are realised from which maximum value can be exploited. This is only possible with a collaborative multi-disciplinary approach involving experts and stakeholders in all aspects and stages of product lifecycles.

For existing WEEE which has not benefited from lifecycle optimisation and eco-design for reuse, upgrade, repair and remanufacturing, efficient recycling of all materials, particularly precious metals in PCBs which represent the greatest part of recoverable economic and environmental value, is of paramount importance. The economic value afforded through recovery of these materials grants viable recovery of other strategically and environmentally important components such as CRMs which on their own are of insufficient value for economic recovery. Effective recovery of these materials is possible only with costly manual pre-processing, and so exploiting the maximum value from items is necessary to ensure as

much WEEE as possible falls above the cut-off grades for manual processes. Without viable manual processing, the derivable economic value and efficiency with which CRMs and other 'high-tech' metals can be recovered is limited.

Exploitation of the maximum value of WEEE through recycling relies on knowledge of the total available quantities of target materials in the waste stream, and their location within individual WEEE items. This information about the 'urban mine' is analogous to 'prospecting' of primary resources when planning mining operations. Detailed knowledge of the material composition of future WEEE and material value contained therein, and volumes of specific categories and types of items that will be available in the future waste stream is required. This will inform planning of future recycling strategies capable of exploiting the maximum possible material value from WEEE. As the nature of the future waste stream cannot be known with certainty, predictions must be made based upon available knowledge of current trends in manufacturing practices, lifetime distribution data for EEE products, likely changes in consumption patterns following the emergence of new technologies onto the market, and data on quantities of EEE placed on the market. This must take account of temporal trends in manufacturing which may result in reductions in precious metal content in WEEE, which in combination with rising costs of recycling could result in major barriers to manual recycling of WEEE in the future. Data on historic temporal trends in material composition of items can be used to improve the accuracy of such predictions which currently use static compositional data for existing items.

In the interests of sustainable economic development, the strategic value of WEEE must also be exploited to a far greater extent through efficient recovery of CRMs. In general, the low economic value of CRMs and dissipative nature of their applications in EEE renders recovery economically unviable through traditional recycling processes. Shredding of WEEE results in dissipative losses of CRMs through unintended co-separation with bulk material fractions, so processes are necessary which enable isolation of CRM bearing components from WEEE in their own distinct material streams for recovery. At this time, a lack of such processes as well as those for recovery of CRMs identified in WEEE prevents viable recovery.

Enhancing CRM recovery rates from WEEE requires efforts to reduce pre-processing costs for isolating and concentrating CRM bearing components from WEEE, and to enhance the derivable value from CRMs through recovery. Innovative separation processes for isolated components, such as sieving with further mechanical separation which avoids shredding, or intelligent liberation/sorting systems which make use of optical recognition and established knowledge of CRM content of components, or online XRF analysis to identify and isolate

CRM bearing components in WEEE, are required. Processes which enable cost-effective recovery of CRMs from output fractions of pre-processing must also be commercialised so that isolated CRM bearing fractions from WEEE may be directed to them. Hydrometallurgical processes offer superior control and flexibility in this regard than established pyrometallurgical recovery processes. In addition, recovery processes which derive greater value through circular economy are required for viable recovery for materials that are currently lost due to low economic value.

Demand for CRMs from the EEE sector is a major contributing factor to the critical status of high-tech metals. One method of addressing materials criticality is to harvest and reuse components, offsetting demand for virgin components manufactured from primary raw materials. This more 'closed-loop strategy' may result in greater value generation from the isolated components. In the future, cost-effective isolation of such components may be achieved through robotic automation should sufficient quantities of similar items be gathered to justify the capital investment. One example of such a technology is Apples's 'Liam' the robot, designed to disassemble Apple's own products. It will be difficult to stimulate a demand for such second-hand components who's functionality may be questionable, and who's cost is likely to be comparable to, if not higher than new components manufactured at massive scale. The solder bath method could be used to recover components from PCBs for this purpose, however, further study of the impact of this high temperature process on functionality of recovered components is necessary.

The value available through circular economy and cascading materials across product cycles may be sufficient to drive CRM recovery in the future. Added-value opportunities through industrial symbiosis (and other cascades of reuse) in which CRM bearing components of WEEE are used as feedstocks for manufacturing holds the potential to generate sufficient value for economic CRM recovery. Such opportunities will enhance derivable value from WEEE and therefore lower cut-off-grades for manual recycling, whilst improving global resource-efficiency and mitigating resource criticality for manufacturing. Local industrial symbiosis solutions may also reduce the environmental impacts of materials recycling when economic and environmental costs associated with logistics throughout existing global recycling process chains are avoided. Processes which cycle materials into emerging 'green' technologies are particularly valuable in terms of sustainable economic development. Clean energy technologies, including wind turbines, electric vehicles, photovoltaic cells and fluorescent lighting, currently consume about 20% of global CRM production, growth of emerging technologies will increase this quantity significantly in the future. Securing secondary sources of CRMs for such applications will be crucial for reducing global emissions and combating

climate change. As such, new strategies for generating additional value from CRMs in WEEE through recovery for use as raw materials for clean-energy technologies will be essential to meet demand and increase the resilience of these emerging industries to global resource security issues, thereby safeguarding jobs and futureproofing technologies.

The issue of criticality is one that can be addressed through a number of strategies apart from enhanced recovery. Research into suitable substitutes for CRMs should be explored, as well as new manufacturing processes which enable utilisation of alternative materials in mass production The use of FTO in solar cells in place of ITO containing critical indium is a good example of an industry reacting to the issue of 'resource criticality'. Optimisation of logistics (and reverse-logistics) to minimise damage of products on their way to the market place, and during take-back will also result in less generation of WEEE and reduce demand for virgin CRMs.

The EC's ongoing Eco-design Working Plan initiated as part of the Circular Economy Package aims to investigate measures for implementation which would mandate appropriate product design measures to support circular economy.[319] This opportunity to establish overarching legislation to drive progress in this area should be capitalised upon. This would result in legislative pressure on OEMs to adopt such practices in addition to existing extended producer responsibility (EPR) imposed by the WEEE directive. This is particularly important when the implementation of EPR as collective producer responsibility (CPR) is common. Where possible, CPR systems of compliance should be altered to individual producer responsibility (IPR) systems, providing a direct economic incentive to OEMs to design products in a way which reduces EoL costs by enabling reuse, upgrade, repair, remanufacturing and efficient recycling.

Major impacts on the global WEEE problem through exploitation of the inherent value of the waste stream must be facilitated by significant improvements in collection efficiencies and diversion of collected WEEE from inappropriate recycling practices in the developing world. Education about the WEEE problem at hand is also vital to ensure that we, the users of EEE, make appropriate decisions when it comes to disposal of items. Equally valuable is the education of those involved in informal WEEE sectors in the developing world so that they may take measures to protect themselves and the environment from the hazards associated with materials from WEEE. Such education would go a long way to motivating those involved in the informal WEEE sector to make more responsible choices concerning the practices they use to treat WEEE. Many who conduct backyard-recycling do so out of necessity, with few alternative employment opportunities available to them. It is therefore essential that solutions

to the global WEEE problem embrace the informal sector, and that value exploited from WEEE is shared amongst all parties involved in the lifecycle of EEE to the benefit of global society and the environment.

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Appendix A - Evaluation of Fischerscope XDAL

This section outlines assessments made of the Fischerscope XDAL instrument's ability to detect and quantify CRMs in WEEE samples.

Qualitative analysis: direct measurement of CRMs in devices

Standard spectra of CRMs were obtained from metal foils of Pd, Pt, Au, Ge, Co, Ta, Ag, W, In, Mg, Nb and Y. Attempts were made to detect these foils through i) 0.1 mm Al foil and ii) 0.1 mm 18/8 stainless steel foil, using manufacturers recommended setting for detection of trace metals. (50 keV with a beam diameter of 0.3 mm and Al primary filter applied). The results are given in *Table A*.1. All elements tested were visible through aluminium, with reduced peak intensity in the cases of W, Nb and Y. Through the stainless-steel foil only Ag, In and Ge were visible. Results suggest that it may be necessary to cut open encapsulated components or grind them to powder before scanning. The same may be true for SMDs encapsulated in glass, plastic, or ceramic.

Table A.1 Detection of metals through steel and aluminium foils.

CRM	Nature of electronic transitions	Emission energy (keV)	Visibility through 0.1 mm Al foil	Visibility through 0.1 mm 18/8 stainless steel
Pd	$K\alpha_1$ $K\beta_1$	21.18 23.82	Clearly visible	Clearly visible with diminished peak height
Pt	$L\alpha_1$ $L\beta_1$	9.42 11.07	Clearly visible	Not visible
Au	$L\alpha_1$ $L\beta_1$	9.71 11.44	Clearly visible	Not visible
Ge	$K\alpha_1$ $K\beta_1$	9.89 10.98	Clearly visible	Barely visible (only with maximum expansion and zoom on spectra)
Co	$K\alpha_1$ $K\beta_1$	6.93 7.65	Clearly visible	Not visible
Ta	$L\alpha_1$ $L\beta_1$	8.15 9.34	Clearly visible	Not visible
Ag	$K\alpha_1$ $K\beta_1$	22.16 24.94	Clearly visible	Clearly visible (diminished peak height)
W	$L\alpha_1$ $L\beta_1$	8.40 9.67	Clearly visible with reduced L_α/L_β peak ratio	Not visible
In	$K\alpha_1$ $K\beta_1$	24.21 22.28	Clearly Visible	Visible
Nb	$K\alpha_1$ $K\beta_1$	16.62 18.63	Visible	Small peaks visible
Y	$K\alpha_1$ $K\beta_1$	14.60 16.74	Visible	Not clearly visible

Quantitative analysis of powder samples

A) Relative composition

To investigate the precision, accuracy and limitations of the XDAL in determination of relative masses of elements, and to evaluate different methods of quantification, ground samples of Ta capacitors were analysed.

Sample preparation - Twelve 100 µF 10V 107A Ta capacitors (*Figure A.***1**) were collected from PCBs (total mass = 1.7242 g) and ground to a powder (for details of grinding procedure see *section 2.1.1*). To assess precision of the XDAL in measuring rel.% composition of target materials over a range of concentrations, the TaCap powder was mixed and ground with graphite to give samples of: 50/50; 25/50 and 10/50, TaCap/graphite, w/w.
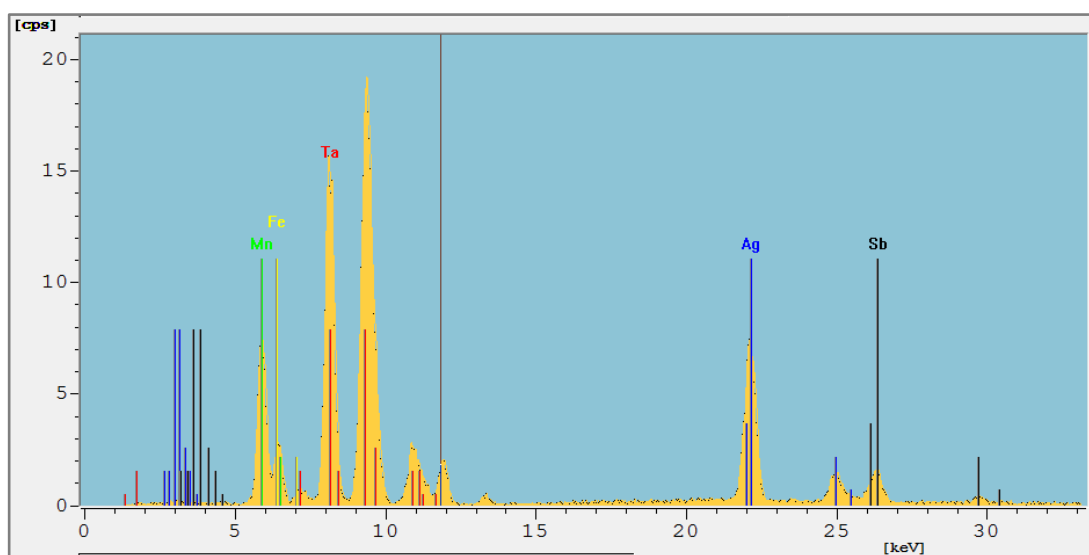
Figure A.1 X-ray emission spectrum of 100%-TaCap powder

Effect of scan time - *Figure A.***2** shows spectra at 2s and 200s scan times. Results from repeat XRF analyses of the same area of the 100%-TaCap powder, are given in *Table A*.2. Measured composition stabilises by about 16 scans (*Figure A.***2** and *Figure A.***3**).
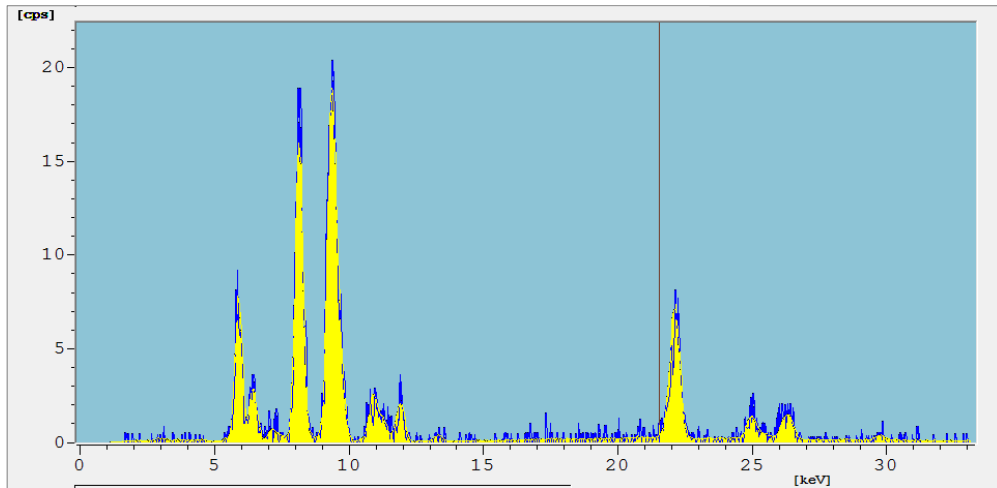
Figure A.2 *Comparison of spectra obtained from the same area of 100% TaCap with 2s (blue) and 300s (yellow) scan times, showing improved S/N with increased scan time; blue 2s scan time spectra is jagged and noisy compared to the yellow 300s scan*
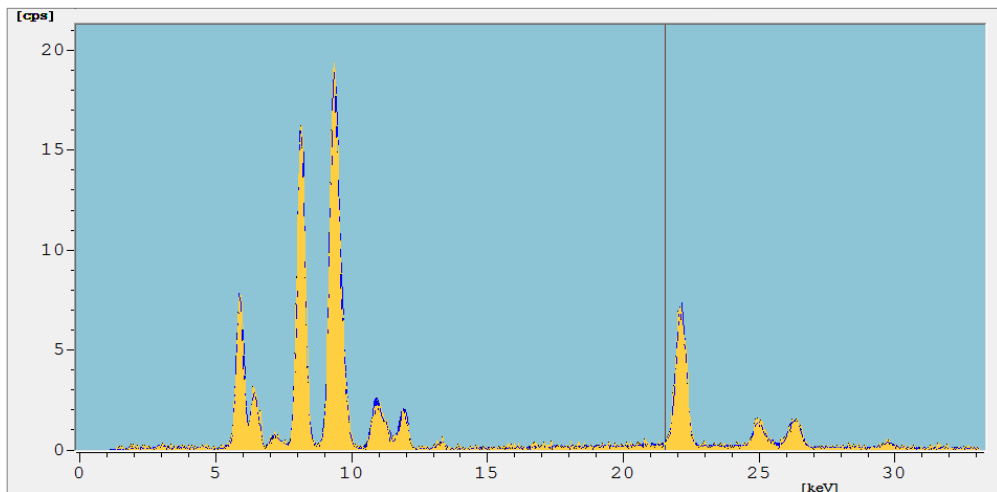
Figure A.3 *Comparison of X-ray emission spectra of 100%-TaCap powder measured with 16s (yellow) and 300s (blue) scan times*

Table A.2 *Variations in measured relative mass percentages (rel. %) of detected elements in 100%-TaCap powder with scan time.*

Scan time (s)	Ta	Ag	Mn	Fe	Sb
2	60.50	5.97	25.09	5.00	3.44
4	58.43	6.59	29.47	3.57	1.94
8	57.84	6.31	29.98	3.22	2.64
16	57.54	6.75	28.91	3.98	2.82
32	57.47	6.42	29.58	3.78	2.75
64	57.51	6.57	29.43	3.67	2.82
132	57.95	6.72	28.74	3.86	2.73
300	57.59	6.57	29.08	3.98	2.78

Instrument precision - *Table A*.3 gives compositions from 6 repeat measurements using 16s scan times on a single region of 100%-TaCap powder. The instrument precision for determination of each element decreases with elemental % composition; it is typically a few 10^{-1}% for elements of high % composition and up to ~10% for elements which make up only a few % of the sample composition.

Table A.3 *Repeat measurements of relative masses of detected elements in a single area of 100%-TaCap powder using 16s scans.*

Scan	Relative mass percentage %				
	Ta	Ag	Mn	Fe	Sb
1	57.54	6.75	28.91	3.98	2.82
2	57.60	6.64	29.35	3.83	2.58
3	57.56	6.51	29.03	3.89	3.01
4	57.97	6.52	28.68	4.05	2.78
5	57.81	6.45	29.52	3.58	2.65
6	57.65	6.40	28.82	4.51	2.62
Mean	57.69	6.55	29.05	3.97	2.74
SD	0.17	0.13	0.32	0.31	0.16
RSD	0.3%	2.0%	1.1%	7.8%	5.9%

Evaluating Method Precision – *Table A*.4 shows the results obtained from 16 s scans at 12 different sites in a single sample of 100%-TaCap powder. Copper was only automatically detected at site 12, and results for each element show high 15-60% relative standard deviations across the 12 sites. To investigate how relative abundance of elements in samples may affected the precision of results, the process was repeated for 50%- and 25%-TaCap powders in order to compare results with those obtained for 100%-TaCap powder (*Table A*.5). Cu was not detected in 50%-TaCap powder, and was detected at only one site in 25%-TaCap powder. Sb was not detected in 25%-TaCap powder. It is interesting to note that for the 25%-TaCap powder the RSD of results obtained for all detected elements has decreased greatly. This may be due to the method of producing the 25%-TaCap powder which may produce a more homogeneous sample because of the addition of graphite as a diluent with additional grinding.

Sampling and sample heterogeneity dominates analytical precision for these powder analyses. Grinding of samples for quantitative analysis of CRMs using the XDAL with this method will not result in quantitative data of suitable precision to base recycling process changes upon. The instrument is therefore suitable for qualitative identification of CRMs only.

Table A.4 *Relative percentage masses of detected elements at 12 sites of 100%-TaCap powder measured with 16s scan times.*

Area	Rel. %					
	Ta	Ag	Mn	Fe	Sb	Cu
1	57.69	6.55	29.05	3.97	2.74	ND
2	68.74	3.28	22.13	3.34	2.51	ND
3	68.91	3.18	21.9	2.95	3.06	ND
4	67.73	1.64	25.13	4.06	1.44	ND
5	65.96	3.28	26.34	2.7	1.71	ND
6	62.97	1.39	28.17	5.81	1.68	ND
7	57.37	0.96	32.83	7.15	1.7	ND
8	58.64	3.42	28.19	6.26	3.49	ND
9	52.1	2.43	30.42	10.67	4.38	ND
10	65.16	1.6	23.19	6.74	2.59	ND
11	41.54	1.81	39.06	15.81	1.78	ND
12	46.82	2.08	37.44	8.6	ND	3.19
Mean	59	2.6	29	7	2.3	
SD	9	1.5	6	4	1	
RSD	15%	57%	19%	58%	50%	
Sem	3	0.5	2	1	0.3	

ND: not detected; **SD**: standard deviation (n=12); **RSD**: relative standard deviation; **sem**: standard error of the mean.

Table A.5 *Average relative mass percentage composition of elements calculated from 12 repeat 16s scans on different areas of samples*

Sample	Result	Relative percentage mass (%)					
		Ta	Ag	Mn	Fe	Sb	Cu
100%-TaCap powder	Mean	59.5	2.6	28.7	6.5	2.3	3.2
	SD	8.9	1.5	5.6	3.8	1.1	3.2
	RSD	15%	57%	19%	58%	50%	100%
50%-TaCap powder	Mean	59.7	3.0	27.2	5.8	3.4	ND
	SD	7.8	0.8	5.3	3.9	1.6	
	RSD	13.1%	26.1%	19.4%	67.0%	47.1%	
25%-TaCap powder	Mean	60.74	2.79	29.66	6.57	ND	1.09
	SD	1.34	0.33	1.44	0.75		-
	RSD	2.2%	11.9%	4.9%	11.4%		-

B) Absolute composition – use of an internal standard

Quantitative Analysis by Inclusion of Metallic Zn internal standard – 1.1272 g of metallic zinc was added to 1.7242 g of 100%-TaCap powder and ground for 15 mins, giving a sample with Zn present at 39.5 wt% (*Figure A.4*) whose spectra obtained with 32s scan time is given in *Figure A.5*.
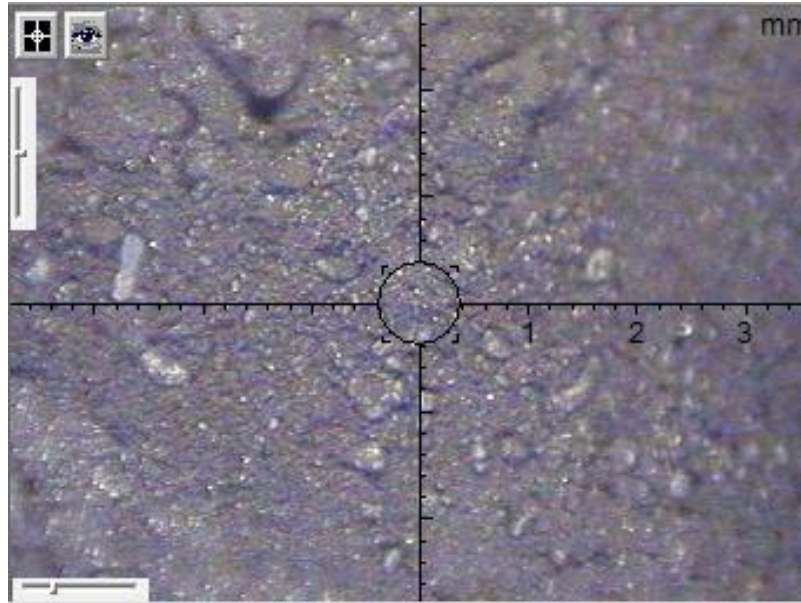
Figure A.4 Ground Ta capacitor powder containing 39.5 wt% metallic Zn
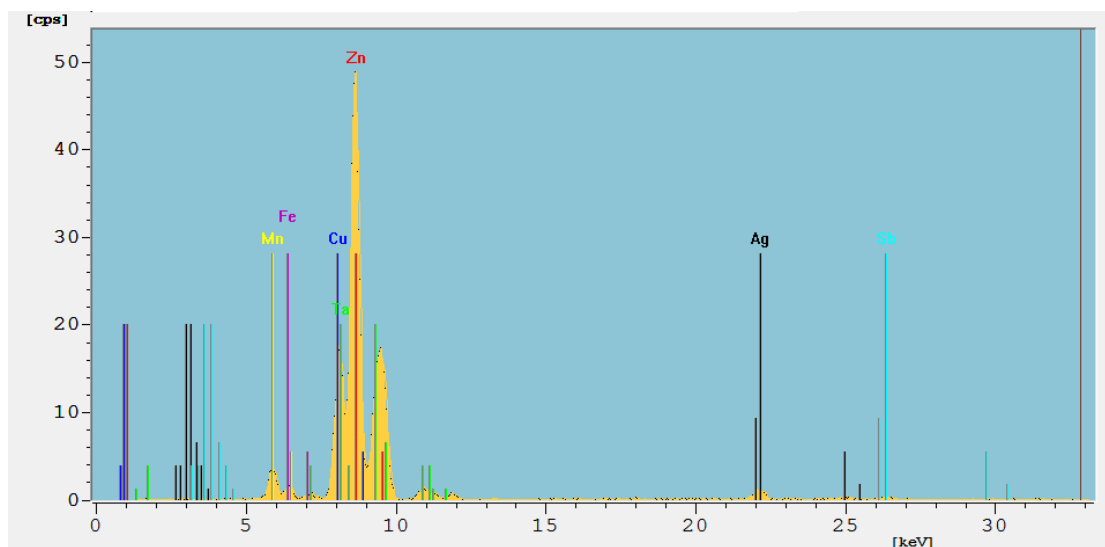
Figure A.5 X-ray emission spectrum of 35.9 wt%-Zn sample obtained with 32s scan time

12 areas of the powder were analysed using 32s scans (*Table A*.6). The standard deviation (SD) of results obtained for rel.% composition across all areas scanned are large (22-96%). The behaviour of metallic Zn, which is soft and ductile, during grinding may go some way to account for this. Close inspection of the 39.5wt%-Zn sample (*Figure A.**4***) revealed poor homogeneity, with large particles of Zn dispersed throughout the finer TaCap powder. The problem of beam size relative to particle size is worsened by this. More precise results may be obtained if a brittle salt of Zn with better grinding performance were used.

Table A.6 *rel.% of elements detected in 12 sample locations in 39.5% Zn sample using 32s scan times and calculated wt% of elements in the sample.*

Scan	Relative percentage masses (%)						
	Zn	**Cu**	**Ta**	**Mn**	**Ag**	**Fe**	**Sb**
1	44.44	5.97	36.77	9.57	1.06	1.69	0.51
2	45.33	2.73	38.1	9.82	1.68	1.64	0.7
3	68.96	2.21	20.39	6.38	0.81	1.01	0.25
4	11.56	1.75	49.95	22.17	6.5	4.76	3.31
5	38.97	6.29	40.49	10.54	1.26	1.68	0.77
6	25.02	13.98	45.71	11.02	1.3	2.23	0.74
7	48.33	6.79	32.35	9.4	1.02	1.7	0.41
8	38.54	5.7	40.54	11.49	1.46	1.62	0.65
9	43.88	4.2	37.79	10.46	1.41	1.58	0.69
10	52.74	1.73	33.02	9.1	1.33	1.47	0.62
11	52.71	1.27	32.6	9.88	1.37	1.51	0.67
12	10.07	1.58	51.05	22.62	6.52	5.56	2.6
mean rel.%	40	5	38	12	2.1	2.2	1.0
SD	17	3.6	8.4	5	2.1	1.4	0.9
RSD	43%	80%	22%	43%	96%	64%	95%
sem	5	1	3	2	0.6	0.4	0.3
Wt% in sample	39.5	4	38	12	2	2	1.0
% error	0.4%	27%	15%	18%	32%	23%	31%
Error	0.2	1	5	2	1	1	0.3
mass in sample	1.1272#	0.13	1.1	0.33	0.06	0.06	0.03
% error	0.03%	27%	15%	18%	32%	23%	31%
Error	0.0003	0.03	0.2	0.06	0.02	0.01	0.01
Wt% in 100%-TaCap powder		7	62	19	3	3.6	1.6
% error		27%	15%	18%	32%	23%	31%
Error		2	9	4	1	0.8	0.5

SD: standard deviation (n=12); **RSD**: relative standard deviation; **sem**: standard error of the mean; **% error** – error expressed as % of result.

It quickly became clear that while XRF is an excellent rapid qualitative and/or semi-quantitative method, much calibration and preliminary standardisation work would be required before XRF could be used as a reliable quantitative technique with a precision comparable to other methods, such as AAS. Therefore, the decision was taken to use XRF for rapid qualitative/semi-quantitative analysis only, and to use methods such as AAS and ICP-OES and/or ICP-MS for quantitative analysis. AAS analysis of 0.1 g samples of the powder (~5% of total sample mass) gives results with a RSD of ~5%. This reflects, in part at least, the fact that the larger sample sizes used in AAS are more representative of the overall sample composition than that imaged in a 1 mm diameter beam. XRF instruments with beam widths of 40 mm such as the PANalytical CubiX XRF are available and would be more suited to quantitative analysis of powder samples.

Glossary

Term	Definition
3rd generation, or printable photovoltaics (3GPV or PPV)	An emerging set of thin-film photovoltaic technologies which can be manufactured using printing and which includes dye-sensitized solar cells (DSSCs), organic PV (OPV) and perovskite solar cells.[238]
Cascading components and materials	"This involves a series of new applications for constituent materials/components of a product, each providing a fresh use and additional commercial benefit..
Eco-design	
EEE	"Any household or business item with circuitry or electrical components with power or battery supply".[6]
Industrial symbiosis	"An association between two or more industrial facilities or companies in which the wastes or by-products of one become the raw materials for another".[71]
Industrial Ecology[a]	"Industrial ecology can be best defined as the totality or the pattern of relationships between various industrial activities, their products, and the environment. Traditional ecological activities have focused on two time aspects of interactions between the industrial activities and the environment — the past and the present. Industrial ecology, a systems view of the environment, pertains to the future".[320]
LCA (lifecycle analysis)	A systematic set of procedures for compiling and examining the inputs and outputs of materials and energy and the associated environmental impacts directly attributable to the functioning of a product or service system throughout its life cycle.
Recycling	"process of recovering materials for the original purpose or for other purposes, excluding energy recovery"[47]
Refurbishment	"A process of returning a product to good working condition by replacing or repairing major components that are faulty or close to failure, and making 'cosmetic' changes to update the appearance of a product, such as cleaning, changing fabric, painting or refinishing."[47]
Remanufacturing	"A process of disassembly and recovery at the subassembly or component level. Functioning, reusable parts are taken out of a used product and rebuilt into a new one. This process includes quality assurance and potential enhancements or changes to the components."[47]
Reuse	"The use of a product again for the same purpose in its original form or with little enhancement or change".[47]
Urban mining	"the process of reclaiming compounds and elements from any kind of anthropogenic stocks, including buildings, infrastructure, industries, products (in and out of use), environmental media receiving anthropogenic emissions, etc. The stocked materials may represent a significant source of resources, with concentrations of elements often comparable to or exceeding natural stocks. As for natural ores, extraction and processing of anthropogenic stocks is necessary and the generation of an economic benefit is essential. For these reasons, urban mining originally focussed on electrical and electronic wastes (WEEE) which contain relatively high concentrations of expensive metals and rare earth elements."[119]
WEEE (e-waste)	"E-waste is a terms used to cover items of all types of electrical and electronic equipment (EEE) and its parts that have been discarded by the owner as waste without the intention for re-use".[6]

[a] there is no one definition of industrial ecology as a complex multi-disciplinary subject. For an excellent overview of the subject and further definitions see Garner and Keoleian[321]

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