Precious, strategic and toxic elements in electronic waste: bibliometric evaluation, proposition of reference material and direct analysis by laser-based techniques and fluorescence spectrometry

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'They say that knowledge is power. But knowledge is power only when given away; then it empowers. Knowledge retained is knowledge squandered.'

Professor A.T. Sparks, *Cultural Evolution*, 1948

Dedico esse trabalho a minha família, amigos e professores que me ajudaram e incentivaram durante todo o processo.

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LIST OF ACRONYMS

ABNT	Associação Brasileira de Normas Técnicas (Brazilian Association of Technical Standards)
ANN	Artificial neural network
BFRs	Brominated flame-retardants
CCD	Coupled charged device
CF	Calibration free
CFCs	Chlorofluorocarbons
CRM	Certified reference material
EDXRF	Energy dispersive X-ray spectrometry
EEE	Electrical and electronic equipment
EoL	End-of-life
ETAAS	Electrothermal atomic absorption spectrometry
EU	European Union
E-WASTE	Electronic waste
FAAS	Flame atomic absorption spectrometry
FECS	Federation of European Chemical Societies
GFAAS	Graphite furnace atomic absorption spectrometry
HCRCs	Hydrochlorofluorocarbons
HD	Hard disk
ICP-MS	Inductively coupled plasma mass spectrometry
ICP OES	Inductively coupled plasma optical emission spectrometry
IT	Information technology
IS	Internal standardization
ISO	International organization for standardization
IUPAC	International union of pure and applied chemistry
LA	Laser ablation
LA-ICP-MS	Laser ablation-inductively coupled plasma mass spectrometry

LA-ICP OES	Laser ablation-inductively coupled plasma optical emission spectrometry
LCD	Liquid crystal display
LED	Light emitting diodes
LIBS	Laser-induced breakdown spectroscopy
LOD	Limit of detection
MCR-ALS	Multivariate curve resolution alternating least squares
MEC	Multi-energy calibration
MLR	Multi linear regression
MMC	Matrix-matching calibration
Mt	Million metric tons
NIR	Near-infrared spectrometry
NIST	National institute of standards and technology
OP GSA	One-point gravimetric standard addition
OP MLC	One-point and multi-line calibration
PARAFAC	Parallel factor analysis
PC	Personal computer
PCA	Principal component analysis
PCB	Printed circuit board
PCR	Principal component regression
PLS	Partial least squares
PLSDA	Partial least squares discriminant analysis
P-XRF	Portable X-ray spectrometry
REE	Rare earth elements
RM	Reference material
SA	Standard addition
SRC	Slope ration calibration
SSC	Single-sample calibration
TP CT	Two-point calibration transfer

u_{bb}	Standard uncertainty associated with between-bottle variability
u_{char}	Standard uncertainty associated with a value assigned in a characterization study
u_{lts}	Standard uncertainty associated with long-term stability
u_{sts}	Standard uncertainty associated with short-term stability
U_{RM}	Expanded uncertainty associated with a property value of the RM
WDXRF	Wavelength dispersive X-ray spectrometry
WEEE	Waste electrical and electronic equipment
WoS	Web of science
XRF	X-ray spectroscopy

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RESUMO

ELEMENTOS PRECIOSOS, ESTRATÉGICOS E TÓXICOS EM RESÍDUOS ELETRÔNICOS: AVALIAÇÃO BIBLIOMÉTRICA, PROPOSIÇÃO DE MATERIAL DE REFERÊNCIA E ANÁLISE DIRETA POR TÉCNICAS BASEADAS EM LASER E ESPECTROMETRIA DE FLUORESCÊNCIA. Resíduos de equipamentos elétricos e eletrônicos estão entre os tipos de resíduos sólidos que mais crescem no mundo. Além disso, este é um fluxo de resíduo complexo quando se trata de reciclagem, devido à grande variedade de materiais valiosos e elementos tóxicos presentes em plásticos, metais, vidro, cerâmicas, etc. Nesse contexto, a análise química do resíduo eletrônico e assuntos que envolvem o manejo dessa matriz foram discutidos nessa tese: (1) inicialmente foi empregado recursos bibliométricos para avaliar os diferentes temas que envolvem o manejo do lixo eletrônico e a evolução da pesquisa mundial; (2) assim como, dado a falta e dificuldade de produção de materiais para assegurar a rastreabilidade de medições e validação de métodos analíticos, um candidato a material de referência de resíduo eletrônico foi produzido e avaliado seguindo as normas definidas pelas guias ISO 30-35; (3) por fim, diferentes técnicas de análise direta, tais como *laser-induced breakdown spectroscopy* (LIBS), *laser ablation inductively coupled plasma mass spectrometry* (LA-ICP-MS) e *X-ray spectrometry* (XRF) foram empregadas para desenvolvimento de procedimentos analíticos visando a determinação elementar em amostras de placas de circuito impresso (PCB) e telas de cristal líquido (LCD). A bibliometria mostrou-se como um recurso eficiente para analisar tópicos antigos, temas emergentes e avaliar o status atual da pesquisa sobre resíduos eletrônicos. Estudos envolvendo a análise de elementos críticos (e.g. In, Pd, terras raras) e desenvolvimento de materiais de referência para resíduo eletrônico foram identificados como lacunas da literatura atual, os quais foram abordados e discutidos nessa tese. Novas estratégias de calibração univariada (*multi-energy calibration*, MEC) e multivariada (fusão de dados usando regressão por mínimos quadrados parciais, PLS) foram propostas para análise direta dessas amostras (i.e. PCB e LCD), através da análise elementar e mapeamento químico da superfície das amostras. Considerando a aplicabilidade, vantagens e limitações de cada técnica analítica empregada, combinado a ferramentas quimiométricas

adequadas, foi possível propor novos métodos de análise de matrizes complexas como o resíduo eletrônico, que possibilitam minimizar ou mesmo eliminar possíveis interferências, com desempenho analítico semelhante ou superior às alternativas tradicionais existentes.

ABSTRACT

PRECIOUS, STRATEGIC AND TOXIC ELEMENTS IN ELECTRONIC WASTE: BIBLIOMETRIC EVALUATION, PROPOSITION OF REFERENCE MATERIAL AND DIRECT ANALYSIS BY LASER-BASED TECHNIQUES AND FLUORESCENCE SPECTROMETRY. Waste electrical and electronic equipment (WEEE) is among the fastest growing types of solid waste in the world. In addition, this is a complex waste stream when it comes to recycling, due to the large variety of valuable materials and toxic elements present in plastics, metals, glass, ceramics, etc. In this context, the chemical analysis of electronic waste and issues involving the management of this matrix were discussed in this thesis: (1) initially, bibliometric resources were used to evaluate the different topics involving the handling of electronic waste and the evolution of world research; (2) as well, given the lack and difficulty of producing materials to ensure the traceability of measurements and validation of analytical methods, an electronic waste reference material was produced and evaluated following all standards established by ISO guides 30 - 35; (3) finally, different techniques of direct analysis such as laser-induced breakdown spectroscopy (LIBS), laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) and X-ray spectrometry (XRF) were used to develop analytical methods for elementary determination in printed circuit board (PCB) and liquid crystal display (LCD) samples. Bibliometrics proved to be an efficient resource for analyzing past research topics, emerging research hotspots and assess the current status of electronic waste research. Studies involving the analysis of critical elements (e.g. In, Pd, rare earths) and the development of reference materials for e-waste have been identified as gaps in the current literature, which are addressed and discussed in this thesis. New univariate (multi-energy calibration, MEC) and multivariate (data fusion using partial least squares regression, PLS) calibration strategies have been proposed for direct analysis of e-waste samples (i.e. PCB and LCD), through elemental analysis and chemical mapping within the sample surfaces. Considering the applicability, advantages and limitations of each analytical technique used, combined with appropriate chemometric tools, it was possible to propose new methods for analyzing complex matrices such as e-waste, which make it possible to minimize or even eliminate possible

interferences, with analytical performance similar or superior to those existing traditional alternatives.

SUMMARY

Chapter 1

Introduction

1.1   What is electronic waste?

The advances in technology have brought benefits to society at various levels and areas of interest. Electrical and electronic equipment (EEE) are indispensable in modern societies and is enhancing living standards. After a certain life-time, which varies from product to product, EEE is disposed of, becoming a complex and chemically rich waste. The term electronic waste, or e-waste, is used for covering all end-of-life (EoL) products which are discarded by its owner as waste without the intent of re-use. E-waste is also referred as waste electrical and electronic equipment (WEEE), electronic scrap or EoL electronic equipment.[1,2]

This waste stream is directly linked to the consumption of EEE which increases annually by 2.5 million metric tons (Mt) with the global economic and technological development. In addition, the consistent advent of new designs and "smart" functions are causing the rapid obsolescence of many electronic items. The way in which we produce, consume, and dispose of electronic products has been unsustainable.[1]

In the period of 2016 to 2020, the global quantity of e-waste has increased more than 9.0 Mt, reaching the total of 53.6 Mt in 2019 distributed among Asia (24.9 Mt), Americas (13.1 Mt), Europe (12 Mt), Africa (2.9 Mt), and Oceania (0.7 Mt). China generated the highest e-waste quantity in the world (10.1 Mt), followed by the United States of America with 6.9 Mt. Brazil was the second largest producer of e-waste in the Americas in 2019 (2.1 Mt). E-waste is increasing at an alarming rate and the global generation is estimated to exceed 74 Mt in 2030.[1]

Given the wide range of products in the e-waste stream, the WEEE Directive enforced in the European Union Member States lists six general categories, which are representative of the e-waste collection streams in practice.[3] These categories are: (1) temperature exchange equipment, commonly referred to as cooling and freezing equipment; (2) screens and monitors; (3)

lamps; (4) large equipment, typical examples includes washing machines, clothes dryers, dish-washing machines, electric stoves, photovoltaic panels, etc.; (5) small equipment, such as vacuum cleaners, microwaves, toasters, electric kettles, calculators, radio sets, video cameras, small monitoring and control instruments, etc.; and (6) small IT and telecommunication equipment. This categorization is referred to similar function, comparable material composition, average weight, and similar end-of-life attributes of each EEE.[1,4]

1.2   Environmental implications in WEEE management

Most countries (e.g. Brazil) lack any e-waste treatment infrastructure, and waste management laws and enforcement. Less than half of all countries in the world are currently covered by an e-waste policy, legislation, or regulation.[1] Nevertheless, even countries that have developed waste management laws, does not always translate to a concrete action.[4] The recycling rate is still low and only 17.4% of the global quantity of e-waste generated in 2019 was documented to be collected and properly recycled.[1]

E-waste is usually regarded as a waste problem, which contains several toxic additives or hazardous substances, such as cadmium, mercury, brominated flame-retardants (BFRs), lead, beryllium, chromium hexavalent, and chlorofluorocarbons (CFCs), or hydrochlorofluorocarbons (HCFCs).[5] Moreover, the production of modern electronics requires the use of scarce and expensive resources (e.g. around 10% of total gold worldwide is used for their production).[3] The ever-increasing levels of e-waste, low collection/recycling rates, and non-environmentally sound disposal and treatment of the e-waste pose significant risks to both environment and human health.[6-8]

In most developing countries, a significant number of informally self-employed people are engaged in the collection and recycling of e-waste.[1] Recyclers burn, leach, and melt e-waste to convert it into secondary raw materials. In this scenario of "backyard recycling", the hazardous substances in e-waste can threaten human health where people who work under poor occupational exposure conditions are constantly exposed to toxic substances. Additionally, these people are indirectly exposed via food chain by contamination

of agricultural soils and other stages of human food chain either by inputs from informal recycling or through sub-standard disposal sites of e-waste.[9]

Another challenge is the lack of knowledge or information about the correct disposal of WEEE, as well as government incentives to make the management of e-waste more effective and controlled manner. Consumers often dispose of e-waste in normal waste bins with other types of household waste.[4] As a consequence, the final stage of these technologies is most likely incinerated or landfilled without proper material recycling. Neither option is regarded as an appropriate technique to treat e-waste, leading to major environmental risks in the significant contamination of soil, water and air of surrounding areas. Landfills leach toxins into the soil and contaminate groundwater, while incineration emits toxic gases into the atmosphere.[9,10]

Finally, many strategic and precious elements play a central role in the digital economy. These raw materials are essential for the production of a broad range of goods and applications used in everyday life. To address the growing concern of securing valuable raw materials from primary resources, the EU Commission lists 27 critical raw materials with a high supply-risk shortage and a high economic importance for the manufacturing industry.[11] Hence, to improve the environmental management of WEEE in a sustainable way and to enhance resource efficiency, the improvement of collection, treatment and recycling of electronics at the end of their life is essential.

1.3 The potential of e-waste recycling

In order to efficiently harvest resources from the WEEE, it is necessary to adopt circular economy approaches which aims at eliminating waste and minimizing the use of natural resource inputs.[12] Figure 1.1 shows a simplified circular economy which implies reusing, repairing, refurbishing, remanufacturing and recycling to create a closed-loop system, increasing the value of EEE when wasted, while reducing the environmental pressures. Towards a sustainable development through the circular economy, the recycling of WEEE is, thus, a relevant opportunity in both environmental and economic terms.[13]
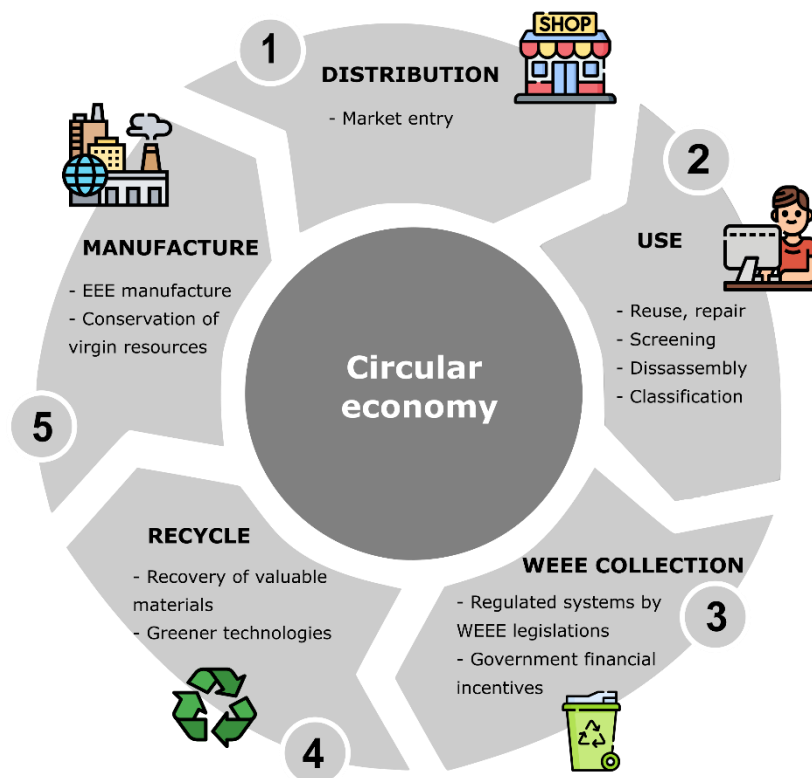
FIGURE 1.1 Circular economy system in a sustainable WEEE management.

From a material design perspective and chemical composition, EEE is very complex. Indeed, more than 60 elements from the periodic table can be found in electric and electronic appliances, and many of them are technically recoverable.[1] Then, in addition to hazardous compounds, the e-waste contains precious metals (e.g. gold, silver, copper, platinum, palladium, ruthenium, rhodium, iridium, and osmium), critical raw materials (e.g. cobalt, palladium, indium, germanium, bismuth, antimony, and rare earth elements, REE), and noncritical metals, such as aluminum and iron (known as base elements in EEE) of unquestionable industrial and technological importance.[14] Hence, the mine of e-waste should be also considered as an important source of raw materials. This waste is a promising secondary resource to maintain a circular economy, to reduce the pressure on primary or virgin resources and mitigate their material demand in a secure and sustainable way.[1,13]

In this context, e-waste has become an important source of resources that can be harnessed using methods or strategies at the reclamation of the target metals. This procedure is known today by the term "urban mining".[1,15] For instance, while one ton of ore contains approximately 5 grams of gold, one ton of

mobile phones or PCs may contain 280-400 grams of the same noble metal (up to 80-fold more).[1,16]

The recovery of materials, specially metals, have been extensively reported in the scientific literature. Different processes for recovering precious, critical and base metals are currently in use, such as physical-mechanical separation, hydrometallurgical and pyrometallurgical processes, among others.[17-19] Physical-mechanical separation includes selective methods of disassembly, crushing and physical separation (e.g. magnetic separation, Eddy current separation, airflow separation and electrostatic separation). Pyrometallurgical and hydrometallurgical technologies include smelting (i.e. high temperature furnace) and leaching processes (i.e. acid, mix-acids, alkali, organic acid leaching, etc.), respectively, for further extraction and recovery of pure metals.[17]

LI and XU (2010)[20] developed a technology using physical-mechanical processes for recovering metals from WEEE, which included a multiple grinding of the material, screening of material, multiple roller electrostatic separator, and dust precipitation. The authors reported an environmental friendly automatic line reaching 600 kg/hour and the recovery rate of Cu reached 95%. After separation, metallic and non-metallic components were completely reused.

Pyrometallurgy is the most used technology globally for recovering metals from WEEE.[21] Indeed, e-waste recycling has been dominated by pyrometallurgical routes in industrial-scale. Many recycling and e-waste co-processing facilities make use of pyrometallurgical processing, such as Glencore's Horne Smelter in Quebec, Canada, Boliden Ltd. Rönnskår Smelter in Skelleftehamn, Sweden, and Umicore in Belgium.[22] An application for pyrometallurgical process was the plant of Umicore integrated smelter and refinery. This procedure included the WEEE pretreatment (i.e. dismantling, shredding and physical processing) and then the precious metals operations were smelted in an Isa Smelt furnace. In this case, the e-waste is processed mainly focused on recovery of precious metals from WEEE including Ag, Au, Pt, Pd, Rh, Ru and Ir.[17,23] Another application was practiced at the Rönnskår Smelter, in which more than 100,000 t of WEEE were fed into Kaldo Furnace every year.

This process was implemented to recover elements such as Cu, Ag, Au, Pd, Ni, Se, Zn, etc.[17,24]

In recent years, extensive studies and practices have given a special attention to recycling metals from WEEE by hydrometallurgical technology.[25-27] Unlike the pyrometallurgical process, the hydrometallurgy process is more accurate, predictable and easier to control as well as produces no toxic gas, do not require a high temperature process and expensive instrumentation.[21] One disadvantage of these methods is that failure to recover single metals. This means, it is difficult to independently and efficiently separating the resulting mixture of metals (Al, Ag, Au, Cu, Fe, Sn, Pb, Zn, etc.) from WEEE.[17] SETHURAJAN et al. (2019)[28] reviewed the advances on hydrometallurgical processes for recycling and recovery of critical and precious elements from EoL electronic wastes. Different types of WEEE were discussed such as spent PCBs[29], spent LCDs[30], spent fluorescent lamps[31], spent light emitting diodes (LEDs)[32], spent batteries[33], etc. CASTRO and PEREIRA-FILHO (2018)[34] also investigated the feasibility of an analytical procedure for the characterization of magnets from hard disks (HDs). A set of 50 HD samples were used for the determination of REEs and other elements (e.g. Al, Cu, Fe, Ni, Zn), after acid leaching using diluted HNO_3. For instance, high concentration of Nd were determined in these samples, ranging from 16 to 26% w/w. Interesting concentration levels of strategic elements were determined in the HD samples, and the recycling of these residues can be an important source of raw material for the future production of new technologies.

However, even with many developments in e-waste management, a huge amount of recyclable raw materials is still wasted and undocumented.[1] As discussed earlier, the effective recycling rate of most WEEE is still very low in practice and can be improved by better collection, pretreatment, and chemical inspection/characterization of the e-waste stream.

1.4   Analytical Method Development in WEEE management

Undoubtedly, the WEEE is a challenging waste stream as well as a powerful economic and technological source due to the countless chemical elements can be found in this type of waste. Therefore, the correct management

and recycling from WEEE is an important way to recover materials and achieve sustainability conditions. To this end, greater efforts must be made towards implementation of new technologies that can be environmentally friendly, economy feasible and widely available.[35,36]

Nowadays, it is well known that analytical procedures play a key role in environmental monitoring.[37,38] In fact, the development of fast and reliable methods with reasonable costs and sensitivity, can help in the correct handling of the e-waste. Considering these facts, it is important to use analytical techniques that combine these requirements with little or no sample preparation, such as laser-induced breakdown spectroscopy (LIBS), Raman spectrometry, near-infrared spectrometry (NIR), X-ray fluorescence spectroscopy (XRF), and laser ablation-inductively coupled plasma-mass spectrometry (LA-ICP-MS).[39] The ability to perform direct, fast and multi-elemental analysis make these techniques applicable to many different types of samples. Due to the outstanding advantages of these spectroscopy techniques, such monitoring provides a rapid return of the chemical information while minimizing errors, costs, time, treatment of samples, use of hazardous reagents and generation of waste associated with traditional laboratory-based analyses.[40]

1.5   The purpose and outline of this PhD thesis

Therefore, the main goal of this thesis was proposing analytical methods to obtain chemical information about valuable/critical metals (e.g. Au, Ag, In), base metals (e.g. Al, Cu, Fe, Ni) and hazardous elements (e.g. Cd, Cr, Pb) in PCB and LCD samples using different spectroanalytical techniques such as LA-ICP-MS, LIBS, XRF, and ICP OES. In addition, some specific goals were:

- ✓ Scientific literature analysis about WEEE management through bibliometric indicators;
- ✓ Development of analytical methods for characterization and direct determination of Ag, Al, As, Au, Ba, Cr, Cu, Fe, Ni, Pb, Sb, Si, Sn and Zn in PCB samples;
- ✓ Development of analytical methods for direct determination of In content in LCD screens using LIBS;

- ✓ Data fusion of analytical signals from LIBS and XRF, and exploratory analysis employing LA-ICP-MS and ICP OES in proposing analytical methods for PCB analysis, and;

- ✓ Use of chemometric approaches to design or select optimal measurement procedures and experiments, and to provide maximum relevant chemical information by analyzing chemical data.

This thesis consists of 6 chapters. The present chapter 1 briefly introduces the global e-waste scenario and the development of analytical methods for characterization of the WEEE stream. Chapter 2 focus on bibliometric analysis of the scientific literature regarding to e-waste studies. Chapter 3 is about the proposition of a certified reference material for chemical monitoring of e-waste samples. Chapter 4 is concerned with the proposition of calibration methods for WEEE analysis, first for direct determination of In content in LCD samples using LIBS, and then in the chemical inspection and elemental determination of Cu in PCB samples using laser-based techniques (LA-ICP-MS and LIBS) and XRF. Finally, chapters 5 and 6 are concerned with conclusion and references, respectively.

Chapter 2

Bibliometric analysis of the scientific literature

2.1 Bibliometrics – an overview

For many years, issues about recycling and handling the e-waste have been one of the main topics on the agenda of researchers. In the early 2000s, technological advances and rapid innovation in electronic products were significant indicators of the evolution in the quality of research in this area. As well, this perspective has continued to evolve exponentially over the years to the present day.[41]

Articles, books and other media of communication are considered the main indicators of research and the most important sources for supporting in subsequent academic studies.[42] After publication, these researches studies are used by other scientists for their own studies and cited as references. The citation of one article by another is characteristic of scientific publications, and the number of publication and citation are interesting to study as they reflect the countable aspects of "research quality" and scholarly performance.[43,44]

The evaluation of quality and quantity of publications can be done using a set of statistical and mathematical indices to measure the relative importance of a particular article or a specific journal, as well as the connectivity among scientific fields, research organizations, authors, etc.[45] The methods utilized in this measurement are well known as bibliometrics, in which its analysis is carried out by special software using specified algorithms.[46] According to most historical references, initial systematic development using bibliometric indicators was reported by D.J.D. Price and Eugene Garfield, as founders.[47,48] To date, many studies have been conducted after the 1950s and bibliometrics still hold a privileged position among the various statistics of science. This is one of the few subfields focusing on the output side of research.[47]

Bibliometrics is an important tool for analyzing the scientific literature in which the state of the art of a given theme in a given period of time can be observed and explored.[49] The main bibliometric indicators can be divided into three classes: (1) quantity indicators measuring the productivity of a particular

researcher, team or organization; (2) performance indicators measure the quality of a journal, researcher, or research group; and (3) structural indicators measure connections among publications, authors, or research fields.[44] All quantity and performance (i.e. quality) indicators are based on information obtained from citation indexes. For this purpose, the Thomson Reuters' Web of Science (WoS) database is recognized as an authoritative citation index for citation analysis. WoS is a multidisciplinary resource that indexes selected publications from over 20,000 scientific journals worldwide in sciences, social sciences, arts, and humanities.[50] It covers the majority of significant scientific results, as well other online databases also contain citation information such as Google Scholar, Scopus, Science Direct, SciELO, etc. Currently, neither database is complete and accurate, covering all publications and citation indexes for bibliometric indicator calculation. The user should keep in mind that databases have flaws and limitations such as lack of journals/documents not indexed, duplications and errors.[44]

In respect with the structural indicators, it can be performed by bibliometric maps to describe how specific disciplines, scientific domains, or research fields are conceptually, intellectually, and socially structured.[51,52] The general workflow in a bibliometric mapping analysis has different steps: data retrieval (i.e. online database), preprocessing, network extraction, normalization, mapping, analysis and visualization.[52] That is, the data input is retrieved using an online database, and the further steps are performed by software tools specifically developed for bibliometric mapping purpose. Some examples of these software are Bibexcel,[53] CiteSpace II,[54] Network Workbench Tool,[55] VOSViewer,[56] among others. At the end of this process, the analyst has to interpret and obtain some conclusions from the results. For more details in bibliometric analysis, please watch the posted videos in the Prof. Edenir's channel on YouTube: https://www.youtube.com/playlist?list=PL4CuftF4l_fCc9t1xoQSaYOUq-UBz_2VD

Therefore, given the large quantity of information already available in WEEE management and its constant growth, there is a high demand from scientists to synthesize data to reveal previously unknown information into this scientific field. It is in this context that bibliometrics can contribute to the

advancement of science, demonstrating the current state of research, its directions and generating unprecedented information.[57,58]

2.1.1 Past and emerging topics related to electronic waste management: top countries, trends, and perspectives, Environmental Science and Pollution Research 26 (2019) 17135–17151.

RESEARCH ARTICLE

Past and emerging topics related to electronic waste management: top countries, trends, and perspectives

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Abstract

A bibliometric analysis was performed to assess historical and recent research trends regarding e-waste studies from 1998 to 2018. Documents related to e-waste were identified from the Clarivate Analytics Web of Science© (WoS) database, and a total of 3311 academic articles was retrieved. The analysis was performed from four main aspects: (1) publication activity by year, by WoS category, and by geographic distribution; (2) journals; (3) most-cited papers; and (4) top 10 countries and author keyword analysis. The number of publications concerning e-waste issues has increased substantially over the last 20 years, especially in the environmental science category, and more than a third of the publications were produced in China (1181 records). *Waste Management* and *Environmental Science & Technology* were the most sought-after journals for disseminating the results. Studies related to "e-waste flow analysis," "recycling," "recovery of precious metals," and "risk assessment of recycling areas" have been the most common for several years. The analysis of keywords suggested that there are many topics on electronic waste and that each country has presented a different focus of research. Overall, the bibliometric analysis proved to be an efficient tool with which to monitor historical and current research trends and to evaluate the sheer volume of currently existing scientific literature on e-waste topics.

Introduction

Since the year 1990, electronic devices have changed and revolutionized people's lives worldwide (Kumar and Dixit 2018). The market demand for the production of electric and electronic equipment (EEE) is continuously increasing, and in recent decades, electronic waste (e-waste) has grown significantly as a result of several trends, including that (i) many people today have more than one electronic device, especially

those dedicated to communication or information technology and (ii) the replacement intervals of these devices, such as cell phones, computers, and tablets, are decreasing. The rapid progress of technology regularly provides more advanced devices and equipment. In this sense, information and communication technology (ICT) instruments are becoming more affordable, and users change their devices more often to keep up with technological improvements (Baldé et al. 2017; Heacock et al. 2016).

Therefore, a widely used approach for estimating the flow of national and global e-waste is based on the total EEE put on the market. The high rate of obsolescence of product categories, the amount of e-waste officially collected and recycled, and other determinations help to monitor the total generation of e-waste. According to the United Nations University (UNU) 2017 report, the estimated global e-waste generated was approximately 45 million metric tons (Mt) in 2016. The amount of e-waste worldwide is rising much faster than any other form of waste, and it is expected to exceed 52 Mt in 2021 (Baldé et al. 2017; Ilankoon et al. 2018).

The global information society has grown very quickly due to advantages related to communication, transport systems,

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mobile networks and services, delivery service facilities, etc. (Baldé et al. 2015). Present trends suggest that the generation of e-waste will increase substantially over the next few years, and comprehensive studies aimed at understanding information and current trends in e-waste research are needed (Ilankoon et al. 2018).

Parallel to various problems related to electronic waste, the management of e-waste has become a research topic over the last two decades (Widmer et al. 2005; Kiddee et al. 2013). However, given the sheer volume of documents available in the scientific literature and the growth of published studies in many research fields, it is difficult to provide a comprehensive and systematic overview of this information. Currently, due to progress in the development of new technologies, it is common to observe more attention being paid to computerized methods and tools for assessing relevant information stored or indexed in large databases (Van Eck and Waltman 2010). In this context, bibliometric methods have been used in qualitative and quantitative approaches to organizing, monitoring, describing, and evaluating documents from the scientific literature (Zupic and Cater 2015).

Bibliometrics is a tool by which state-of-the-art science and technology can be observed through the general production of scientific literature (Okubo 1997). Its analysis involves the measurement of scientific progress in a given field over time, helping to explain the social, intellectual, and conceptual structure through bibliographic networks (Batagelj and Cerinsek 2013) and making it possible to examine the performances of countries, co-words, co-citations or co-authors, and most trending topics, among other attributes. The results are presented in various forms (e.g., maps) to provide an overview of the relationships among participants and expand the means of analysis of a certain topic (Okubo 1997).

In bibliometrics, there are two main ways to explore scientific literature data: performance analysis and scientific maps (Noyons et al. 1999). The first approach is based on the productivity impacts and citations of scientific journals, evaluated through popular metrics such as the h index (author-level metric) (Hirsch 2005) and the journal impact factor (Garfield 1972). In the second approach, bibliometric maps show structural and dynamic aspects by visually representing scientific literature based on bibliometric data (Börner et al. 2003).

Thus, this study combines citation analysis and bibliometric maps to evaluate the scientific literature covering topics related to electronic waste from 1998 to 2018. Currently, there is a lack of studies on the systematic evaluation of electronic waste topics in the scientific literature. In this sense, the goal of this paper was to reflect the bibliometric analysis of the scientific literature and generate indicators for "e-waste" topics through the Web of Science© (WoS) database. Moreover, the relations of these indicators to trends that involve the central theme e-waste for the most influential countries in the management of electronic waste are also discussed.

Method

Data retrieval

The dataset used in this research was downloaded from the online database Science Citation Index Expanded (SCI-E) in Clarivate Analytics' ISI - Web of Science© (https://webofknowledge.com/) on February 9, 2019. This citation index is usually assessed by academics for bibliometric studies (Milanez et al. 2013; Li et al. 2018; Romanelli et al. 2018), and it has extensive and multidisciplinary coverage of bibliographic data concerning major international and regional scientific journals around the world (Garfield 2006, 2007). In addition, it has been described as the world's leading database of science and technology journals, with a rigorous selection process (Jiupeng et al. 2012). Articles and reviews were predominantly used for further analysis because these publications represent the majority of document types that included entire research ideas and results (Ho et al. 2010).

The first step of this research was to define the set of terms related to the central subject "electronic waste." Search expressions consisted of applying these terms to the "Topic" field, which seeks publications by searching their article titles, abstracts, author keywords, and WoS-assigned keywords, called "Keywords Plus" (Boudry et al. 2018). The application of Boolean operators and quotation marks was the key factor in selecting the final dataset (Ştirbu et al. 2015). In total, 3311 publications were retrieved for the time span of 1998–2018.

The term "international collaboration network" was designated to describe the number of co-authored publications among countries, organizations. and universities in the last 20 years. Articles originating from England, Scotland, North Ireland, and Wales were all considered to be from the UK, and articles from Hong Kong were included under the heading of China (Fu et al. 2013; Zhang et al. 2010). Impact factors (IFs) were taken from the Journal Citation Reports (JCR) published in 2018. The assessment involved the following information obtained from the collected samples: (1) publication activity—by year, by WoS category, and by geographic distribution; (2) main journals—top 20; (3) most-cited papers—in the last 20 years and in the last 5 years; and (4) performance by country—the top 10 countries and author keyword analysis. The synthesis of the systematic literature review employed in this study is presented in Fig. 1.

Data analyses

All analyses were performed using the "Analyze Results" tool provided by Web of Science, with the support of MS Excel (v. 2016) in performing calculations and creating charts and tables (indicator visualization). Bibliometric mapping of author keywords was based on co-occurrence analysis performed using VOSviewer software (version 1.6.8; www.vosviewer.com) to
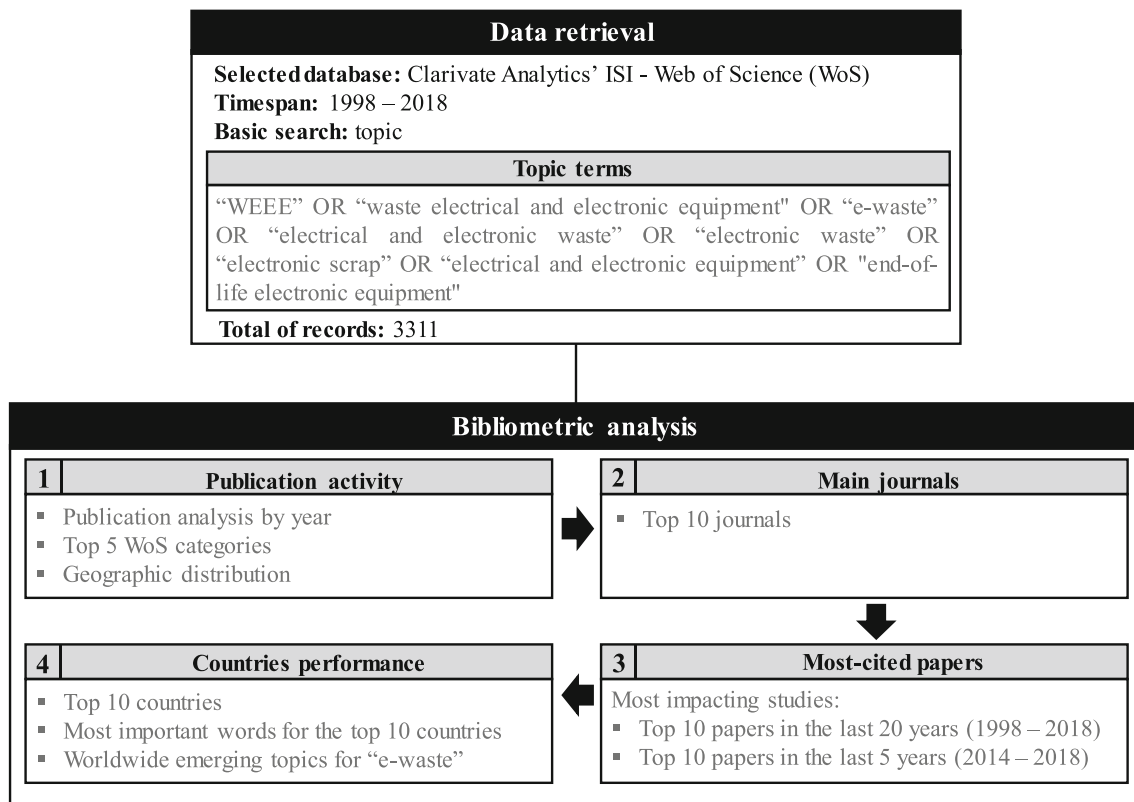
Fig. 1 Process of the systematic literature review

visualize and understand how the main 50 terms are organized regarding the central concept, electronic waste. Repeated words (i.e., search terms, repeated author keywords) and meaningless words (also called "stop words") were not taken into account. VOSviewer uses clustering algorithms based on the strengths of the connections among items to help in the analysis of the network (Van Eck and Waltman 2010). Finally, the geographic distribution of the most productive countries was analyzed with the support of ArcGIS® (v. 10.5) according to the number of publications used to categorize the mapping classes.

Results and discussion

International scientific productivity

Previous studies that used bibliometric analyses of the topic of environmentally friendly electronic waste have indicated that from 1980 to 2016, the subject of electronic waste was an important topic on the international agenda (Durmusoglu 2016). Waste management, recycling, raw material recovery, elemental analysis, and material flow analysis were considered the main emerging topics in the scientific literature and in e-waste statistics (Durmusoglu 2016). Figure 2 shows the evolution of the number of publications on electronic waste in relation to five main WoS categories over the last two decades.

In general, the analysis of Fig. 2 reveals three major moments in the development of scientific research on e-waste worldwide. From 1998 to 2004, there were fewer than 16 publications/year on average, which is a relatively small number, and the WoS categories cannot be highlighted. However, from 2005 to 2012, there was a linear increase in the number of publications, and the average over this time span exceeded 118 publications/year, with the main categories being environmental science and environmental engineering. From 2007 to 2012, the number of publications increased at a rate of approximately 22% papers/year. More recently (2013 to 2018), the average number of publications was greater than 370 publication/year, and the tendency in the main WoS categories remained the same. The number of publications reached a peak in 2013 (280 papers), at approximately 100 more papers than in the previous year (186 papers). In general, the research topics from 1998 to 2018 were primarily in the environmental science and environmental engineering WoS categories. The total of 2061 academic papers in environmental science comprised 62% of the papers retrieved among more than 100 subject categories. More than one third of the publications (34% of the total records) were in the field of environmental engineering, followed by green sustainable science and technology (10% of the total records) and by chemical engineering and multidisciplinary chemistry, with 8% and 6% of the total records, respectively. The category of green sustainable science and technology appeared as an emerging topic after
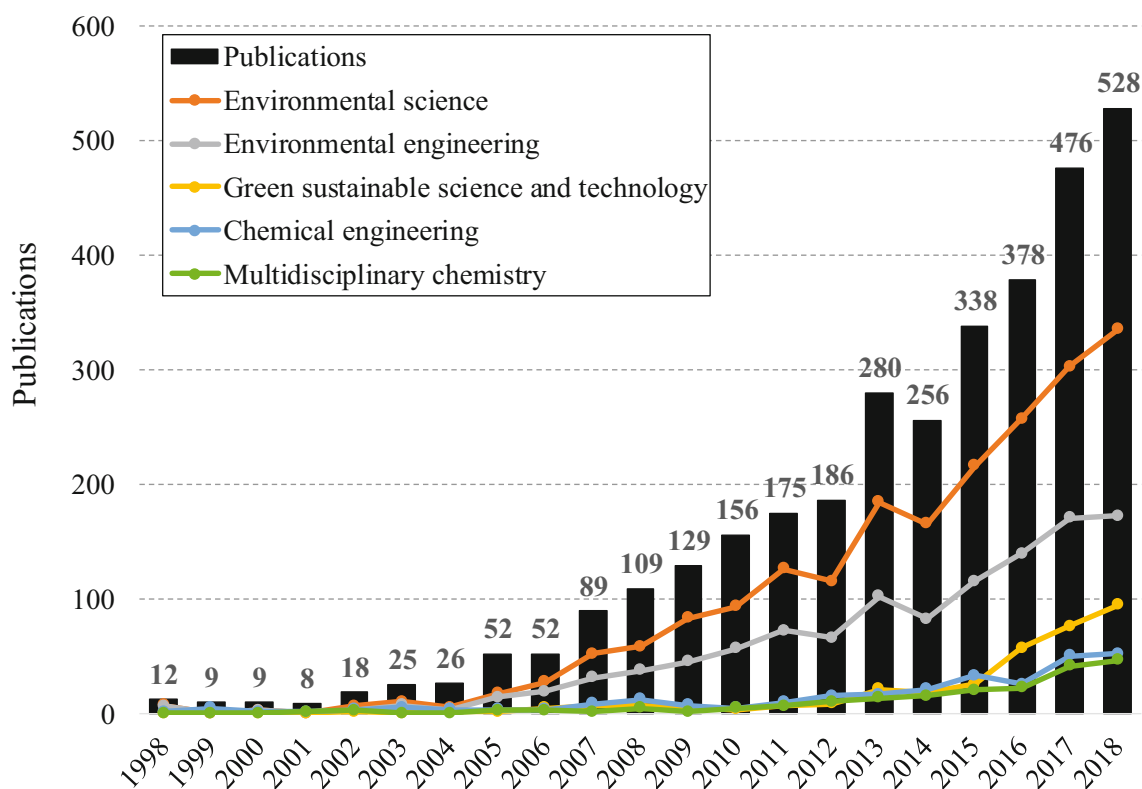
Fig. 2 Total number of publications from the Web of Science (WoS) online database involving the topic "electronic waste" from 1998 to 2018 and their association with the growth trends of the top five main WoS categories

2015, as did chemical engineering and multidisciplinary chemistry.

The increasing number of e-waste studies related to environmental implications in a global scenario may be associated with the main issues posed by e-waste over the last 20 years (Lundgren 2012):

(i) The large amount generated due to rapid obsolescence;
(ii) Hazardous materials and adverse health and environmental problems;
(iii) Complex and expensive e-waste treatment that imposes many challenges on the recycling industry;
(iv) A general lack of labor regulations (standards and rights), legislation, or enforcement surrounding it; and
(v) A general lack of information and financial incentives to cover the costs of correct e-waste management in a responsible way.

E-waste research has been addressed in 91 different countries worldwide. Figure 3 shows the most productive countries in terms of the number of publications. China (PRC), the USA, India (IND), Germany (GER), Japan (JPN), the UK, Australia (AUS), Italy (ITA), Brazil (BRA), and South Korea (KOR) are the top 10 countries that have produced the most publications over the last 20 years. More than 35% of the total number of published academic papers were produced in China (1181

records) or in partnership with this country. Three other Asian countries with some of the highest numbers of papers published were India (202 records), Japan (166 records), and South Korea (99 records). In total, 1648 of the published papers were from Asian countries, corresponding to approximately 50% of the total number of academic papers retrieved. The USA produced 398 documents dedicated to electronic waste research in the last 20 years, which is the second largest number and approximately 12% of the total. The other countries in the ranking also presented significant numbers of publications, varying from 99 (South Korea) to 184 papers (Germany).

Description of the main scientific journals

This topic discusses how the main journals related to e-waste research are organized in terms of the number of publications (ranking). Table 1 shows the top 10 journals that have published the most studies on e-waste topics in the last 20 years. These journals represent more than 40% of all publications. The number of citations indicates the total number of references cited for all items found in the organized dataset. This is the total sum of citations, including self-citations, which corresponds to the total number of articles cited from 1998 to 2018 in the WoS citation report. Overall, the retrieved papers were published in more than 500 different journals; however,
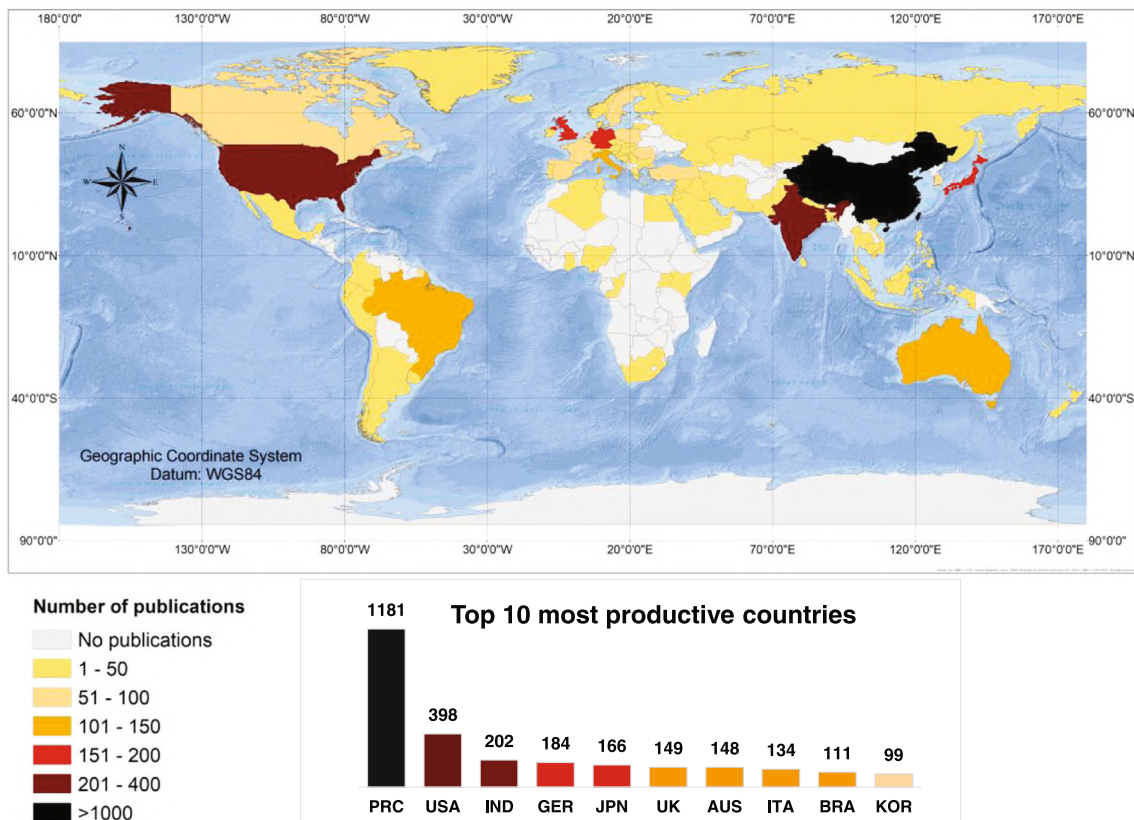
Fig. 3 Global country performances according to the total number of publications on e-waste topics. PRC = People's Republic of China, USA = United States, IND = India, GER = Germany, JPN = Japan, UK = United Kingdom, AUS = Australia, ITA = Italy, BRA = Brazil, KOR = South Korea

most journals (approximately 98%) have published fewer than 88 papers in the last two decades.

Waste Management is the most popular journal for researchers in the field of electronic waste, with 281 publications. The sum of citations was 6592, and 43 papers had effectively 43 citations or more (see the *h*-index). The second-most influential journal is the *Journal of Cleaner Production*,

which published 178 papers (5.4% of the total records). Though *Waste Management* has the highest number of publications, this journal does not have the highest impact factor among the journals listed in Table 1. Importantly, *Environmental Science & Technology* is the most-cited journal, with 7159 citations. This journal has the highest *h* index (51) and impact factor (6.653), as well as the third place in the

Table 1 Top 10 journals ranked by the total number of papers published (1998–2018)

Rank	Journal	NP[a]	NC[b]	*h*-index[c]	2017 journal impact factor
1	*Waste Management*	281	6592	43	4.723
2	*Journal of Cleaner Production*	178	2879	29	5.651
3	*Environmental Science & Technology*	156	7159	51	6.653
4	*Resources, Conservation and Recycling*	143	3522	32	5.120
5	*Environmental Science and Pollution Research*	116	1173	18	2.800
6	*Science of the Total Environment*	115	3698	34	4.610
7	*Chemosphere*	109	3176	32	4.427
8	*Journal of Hazardous Materials*	99	5062	35	6.434
9	*Waste Management & Research*	95	1540	20	1.631
10	*Environmental Pollution*	88	2660	27	4.358

[a] Number of publications

[b] Number of citations

[c] *h* index for these publications

number of publications (156 papers published), followed in this category by *Resources Conservation and Recycling* (143) and *Environmental Science and Pollution Research* (116). In addition, other less-represented journals published significant numbers of papers (see details in Table 1).

Description of the most impactful papers

Citation analysis in bibliometrics studies has been established as an indicator of a paper's quality and contribution to a specific field (Garfield 1979). Citation measurements demonstrate the main contribution from an individual work. Therefore, the most impactful papers were assessed, and the 10 most-cited papers are presented in Table 2. These papers have influenced many related studies, as evidenced by their number of citations. The most-cited paper (636 citations), entitled "Metallurgical recovery of metals from electronic waste: a review", was published in the *Journal of Hazardous Materials* in 2008. This journal was sixth in the ranking (Table 1). In general, the analysis of the most-cited papers revealed that there is no close relationship between the most-cited articles and the most influential journals (see Table 1). It must be emphasized that the longer a scientific article is indexed, the higher the probability that it will be cited. Items

that have been recently published and have many citations may indicate new perspectives in the field (Okubo 1997).

Four studies have assessed global trends in the production and recycling of electronic waste. Cui and Zhang (2008) presented an overview of the state of the art in the recovery of metals (especially precious metals) from electronic waste by metallurgical processes, including through pyrometallurgical, hydrometallurgical, and biometallurgical processing. These authors highlighted two important points: (i) samples of electronic scrap from cell phones and printed circuit boards (PCBs) are composed of a large amount of precious metals and (ii) the recycling of electronic waste is essential for the recovery of valuable elements. Robinson (2009) assessed the present and future production of electronic waste associated with potential environmental contaminants and recycling. The author also emphasized that e-waste may contain valuable metals (e.g., Cu and platinum groups); hazardous materials and potentially toxic elements (Cd, Hg, Ni, Pb, and Sb); polybrominated diphenyl ethers (PBDEs); polychlorinated biphenyls (PCBs); dioxins; furans; polycyclic aromatic hydrocarbons (PAHs); polyhalogenated aromatic hydrocarbons (PHAHs); and hydrogen chloride. In this context, several papers have noted the importance of the prior characterization of e-waste before the recycling process. Cui and Forssberg (2003) highlighted that waste electrical and electronic

Table 2 Ten most-cited papers in the last 20 years (1998–2018)

Rank	Authors	Countries	Title	Journal	Year	NC
1	Cui, J.R. and Zhang, L.F.	NOR	Metallurgical recovery of metals from electronic waste: a review	*Journal of hazardous materials*	2008	636
2	Robinson, B.H.	NZL	E-waste: an assessment of global production and environmental impacts	*Science of the total environment*	2009	603
3	Cui, J.R. and Forssberg, E.	SWE	Mechanical recycling of waste electric and electronic equipment: a review	*Journal of hazardous materials*	2003	499
4	Wong, M.H. et al.	PRC and USA	Export of toxic chemicals—a review of the case of uncontrolled electronic-waste recycling	*Environmental pollution*	2007	433
5	Leung, A.O.W. et al.	PRC and USA	Spatial distribution of polybrominated diphenyl ethers and polychlorinated dibenzo-p-dioxins and dibenzofurans in soil and combusted residue at Guiyu, an electronic waste recycling site in southeast China	*Environmental science & technology*	2007	364
6	Ongondo, F.O. et al.	UK	How are WEEE doing? A global review of the management of electrical and electronic wastes	*Waste management*	2011	338
7	Wilford, B.H. et al.	CAN and UK	Polybrominated diphenyl ethers in indoor dust in Ottawa, Canada: Implications for sources and exposure	*Environmental science & technology*	2005	284
8	Fu, J. et al.	PRC	High levels of heavy metals in rice (*Oryza sativa* L.) from a typical E-waste recycling area in southeas China and its potential risk to human health	*Chemosphere*	2008	280
9	Huo, X. et al.	PRC	Elevated blood lead levels of children in Guiyu, an electronic waste recycling town in China	*Environmental health perspectives*	2007	267
10	Bi, X. et al.	UK and PRC	Exposure of electronics dismantling workers to polybrominated diphenyl ethers, polychlorinated biphenyls, and organochlorine pesticides in South China	*Environmental science & technology*	2007	262

NOR Norway, *NZL* New Zealand, *SWE* Sweden, *PRC* People's Republic of China, *USA* United States, *UK* United Kingdom, *CAN* Canada, *NC* number of citations

equipment (WEEE) is significantly heterogeneous and complex regarding its composition, size, and shape of components. Furthermore, the mechanical/physical processing of WEEE is considered an indispensable process that provides improvements to a recycling system. A global review of e-waste management and a critical discussion of the generation, treatment, prevention, and regulation of WEEE in various countries and regions was reported by Ongondo et al. (2011).

Among the 10 most-cited papers in the last 20 years, there are five studies that have evaluated the presence of organic pollutants and potentially toxic elements in different environmental regions of Southeast China (Bi et al. 2007; Fu et al. 2008; Huo et al. 2007; Leung et al. 2007; Wong et al. 2007). Four papers have addressed studies in the Guiyu region (Bi et al. 2007; Huo et al. 2007; Leung et al. 2007; Wong et al. 2007), which has become an intensive artisanal e-waste recycling site in China. Persistent organic pollutants, such as flame retardants (PBDEs), organochlorine pesticides (OCPs), polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/Fs), PAHs, and polychlorinated biphenyls, were analyzed in the air, soil, and combusted residue samples of Guiyu (Bi et al. 2007; Leung et al. 2007; Wong et al. 2007). High lead levels in the blood of children in Guiyu were also detected (Huo et al. 2007). Approximately 165 children from Guiyu were found to have lead concentrations ranging from 4.4 to 32.7 μg/dL. Taizhou in Zhejiang Province is another typical e-waste recycling region in China that was the subject of a study. The authors who developed this study investigated 10 potentially toxic elements (As, Ba, Cd, Co, Cr, Cu, Hg, Mn, Ni, and Pb) in rice samples (Fu et al. 2008). Finally, Wilford et al. (2005) evaluated indoor air PDBE levels in Ottawa, Canada. From the total concentration, an average of 42% BDE209 (the major component of the deca-mix PBDE product) was found in all analyzed samples.

More recent publications with a high number of citations may indicate an innovation or new perspective contained in the article (Okubo 1997). Considering the increasing number of publications between 2014 and 2018 (see Fig. 1), a brief analysis was conducted of the 10 most-cited papers published in the last 5 years (see details in Table 3) to verify the recent trends on e-waste research and the study foci.

In the last 5 years, concerns about nonmetallic fraction recycling (e.g., plastic, glass, and PCB fractions) (Wang et al. 2014), estimates of the global transport (export and import) of the amount of e-waste generated around the world (Breivik et al. 2014), and the use of recycled plastics (rABS) for multifunctional nanocomposites preparation (Li et al. 2017b) have become prominent issues in the academic literature or have drawn wide attention and research interest, which suggests a new trend in e-waste studies. Most studies in recent years with a higher number of citations have maintained the context previously observed, including risk assessments for human and environmental exposure to e-waste recycling

regions (Abbasi et al. 2015; Law et al. 2014; Song and Li 2014; Zhang et al. 2014), the state of the art of different WEEE streams (Cucchiella et al. 2015), and PCB recycling (Akcil et al. 2015; Ghosh et al. 2015)

In general, the most impactful papers in this study were published in journals that have the highest number of publications on e-waste (Table 1). *Environmental Science & Technology* is the most frequently cited journal (Table 1) and has published the most impactful articles in recent years (Tables 2 and 3). China, which has an important influence on the academic literature concerning electronic waste, conducted most of the studies on this topic.

Research emphases: author keyword analyses

Author keyword analysis can offer information on research trends (Zhi and Ji 2012). Garfield (1990) reported that the statistical analysis of keyword searches successfully indicates future science directions. Bibliometric analysis using author keywords was demonstrated by Chiu and Ho (2007).

The statistical analysis of author keywords revealed that 6357 different author keywords have been used from 1998 to 2018. Among them, 1454 (23%) appeared two times, 761 (12%) appeared three times, and 485 (7%) appeared four times or more, probably suggesting a great diversity of research foci (Chen et al. 2014; Chuang et al. 2007). A bibliometric mapping analyses was performed for the top 50 most influential author keywords in the theme. Figure 4 shows one network, wherein the size of the node is proportional to the number of publications and the thickness of the edges and the colors indicate to which cluster the item belongs. The cluster information is particularly useful in providing an overview of the assignment of items to clusters and the way in which these clusters of items are related to each other. The most frequent terms were e-waste, recycling, WEEE, electronic waste, and PBDEs, which presented 515, 367, 278, 222, and 102 occurrences, respectively. Table 4 shows which author keyword belongs to each cluster shown in Fig. 4 and the number of occurrences of each term.

The cluster analysis of Fig. 4 reveals that these terms are central to the topic of e-waste management and link the other fields derived from this topic. The terms were divided into clusters according to the co-occurrence and association of the terms in the literature. In cluster 1 (green), the subjects of "risk assessment to the environment and humans after exposure to persistent organic pollutants such as flame retardants (PBDEs), PCDDs/Fs, PAHs, polychlorinated biphenyls and heavy metals" were the primary focus of research. Cluster 2 (red) shows study concepts focused on "leaching/bioleaching of printed circuit boards for recovery of valuable metals (e.g., copper and gold)". According to the terms of cluster 3 (blue), the research foci were related to the "assessment of the life

Table 3 Top 10 most-cited papers published in the last 5 years (2014–2018)

Rank	Authors	Countries	Title	Journal	Year	NC
1	Law, R.J. et al.	UK, BEL, NOR, EGY, CAN, AUS and JPN	Levels and trends of PBDEs and HBCDs in the global environment: Status at the end of 2012	*Environment international*	2014	190
2	Cucchiella, F. et al.	ITA and UK	Recycling of WEEEs: an economic assessment of present and future e-waste streams	*Renewable & sustainable energy reviews*	2015	136
3	Ghosh, B. et al.	IND	Waste printed circuit boards recycling: an extensive assessment of current status	*Journal of cleaner production*	2015	127
4	Akcil, A. et al.	TU and IND	Precious metal recovery from waste printed circuit boards using cyanide and non-cyanide lixiviants—a review	*Waste management*	2015	96
5	Wang, R.X. and Xu, Z.M.	PRC	Recycling of non-metallic fractions from waste electrical and electronic equipment (WEEE): a review	*Waste management*	2014	94
6	Breivik, K. et al.	NOR, CAN and UK	Tracking the global generation and exports of e-waste. Do existing estimates add up?	*Environmental science & technology*	2014	92
7	Abbasi, G. et al.	CAN, CHE and USA	Stocks and flows of PBDEs in products from use to waste in the U.S. and Canada from 1970 to 2020	*Environmental science & technology*	2015	81
8	Song, Q.B. and Li, J.H.	PRC	A systematic review of the human body burden of e-waste exposure in China	*Environment international*	2014	81
9	Li, Y. et al.	PRC and USA	Reparation of recycled acrylonitrile-butadiene-styrene by pyromellitic dianhydride: reparation performance evaluation and property analysis	*Polymer*	2017	80
10	Zhang, Q. et al.	PRC	Risk assessment of polychlorinated biphenyls and heavy metals in soils of an abandoned e-waste site in China	*Environmental Pollution*	2014	77

UK United Kingdom, *BEL* Belgium, *NOR* Norway, *EGY* Egypt, *CAN* Canada, *AUS* Australia, *JPN* Japan, *ITA* Italy, *IND* India, *TU* Turkey, *PRC* People's Republic of China, *CHE* Switzerland, *USA* United States, *NC* number of citations

cycle and reuse of e-waste". Topics in "heavy metals/flame retardants and their health risks" were highlighted in cluster 4 (yellow). In cluster 5 (purple), studies were basically focused on issues associated with the "reverse logistics for the life cycle of electronic waste and extended producer responsibility (EPR)". This last topic is an emerging research field in several countries, especially in developing countries (Ikhlayel 2018; Kiddee et al. 2013). Several associated strategies currently used in these countries, such as life cycle assessments (LCA), material flow analysis (MFA), multicriteria analysis (MCA), and EPR, were developed to manage e-waste mainly in developed countries (Kiddee et al. 2013). Extended

producer responsibility is a good approach to solving the growing e-waste problems. If manufacturers take back items collected by retailers or local governments, there are two important aspects that must be highlighted: (i) the correct management and safe destruction of end-of-life (EoL) electronic goods and (ii) the recovery of materials that can be reused in the production of new electronics (Kiddee et al. 2013).

The present study adopted a more limited search criterion because a systematic review of general research topics is limited in addressing the most relevant trends in the academic literature. Therefore, the bibliometric mapping of the top 50 author keywords was performed through co-occurrence
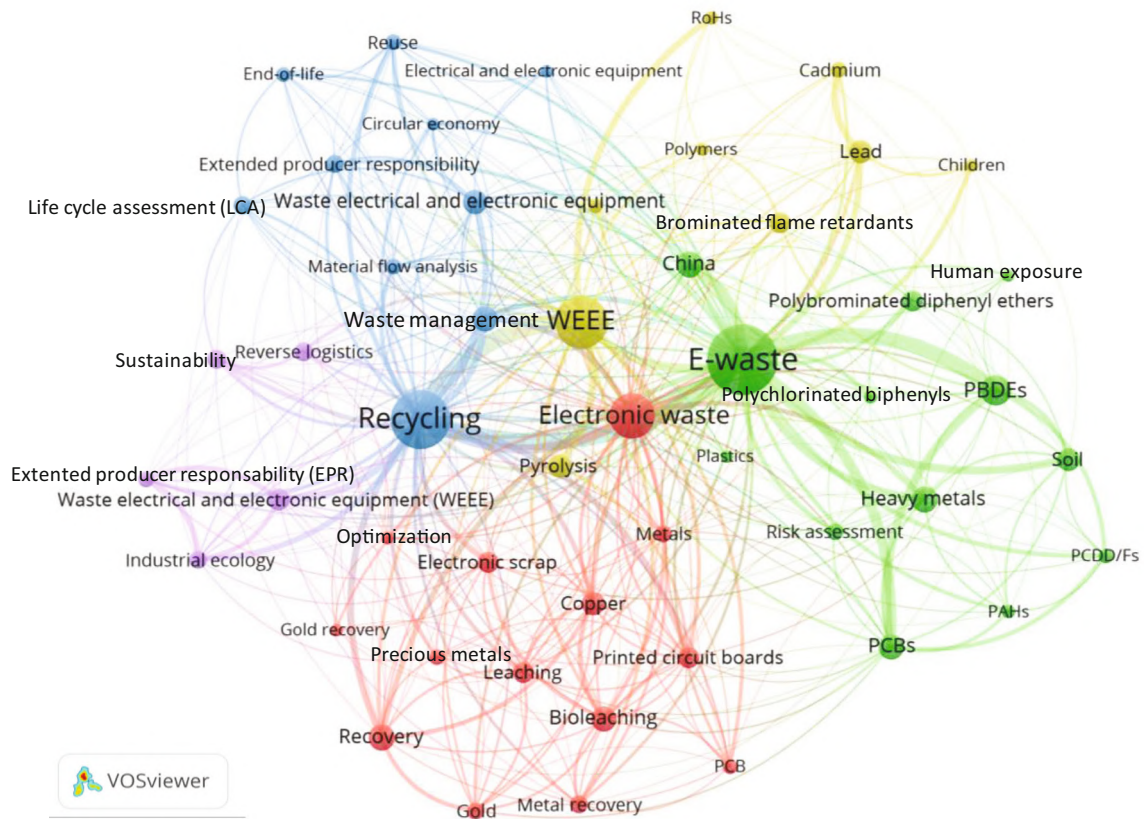
Fig. 4 Bibliometric mapping of the 50 most important author keywords

analysis for the top 10 countries (see Supplementary material for detailed information, Appendix A. Figs. 1S–10S). This approach was applied to identify, among other main words, emerging research fields in employment for the most influential countries in e-waste management.

Table 5 shows the top 10 countries, the total number of articles published in the e-waste field, and the 10 most important author keywords (highest occurrence number) among the papers from each country. These results indicate the most important topics in each country after discounting repeated words that were search terms (e-waste, electronic waste, WEEE, and waste electrical and electronic equipment) or that were terms common to all evaluated datasets, such as recycling, e-waste recycling, flame retardants (PBDEs), and persistent organic pollutants (i.e., polychlorinated biphenyls, PBBs, PCDD/Fs and PAHs).

China

For many decades, China has played a role of paramount importance in global waste management. In addition to being a world power in the production of new technologies, it contributes the most critical scenario of WEEE generation in the world. China has the most e-waste generation indexes in the world and plays a primary function in global e-waste

management, including in the manufacturing, refurbishment, reuse, and recycling of e-waste (Baldé et al. 2017). According to the most recent monitoring of the electronic waste stream reported in 2017, most e-waste is generated in Asia. This region was responsible for 18.2 Mt of e-waste, of which 7.2 Mt was from China (Baldé et al. 2017).

A few studies indicate that more than half of the e-waste collected for recycling in developed countries is sent to developing countries for processing or final disposal (Sthiannopkao and Wong 2013). China is generally considered the largest importer and recycler of e-waste globally and has become the leading destination, among other sites such as India and African countries, due to the cheap labor in several regions for informal dismantling and recycling activities (Breivik et al. 2014). Thus, it is not surprising that China is the top country for publishing and research in the e-waste field.

Informal e-waste processing is common in some regions of China. Almost 80% of families in Southeast China work in e-waste recycling (Bi et al. 2007). Guiyu (GY), Qingyuan (QY), Taizhou (TZ), and a set of other cities in China have large regions of e-waste processing (Wang et al. 2011). In this context, the keyword "China" mostly appears in relation to "heavy metals" and "contamination by flame retardants (PBDEs) and persistent organic pollutants (e.g., polychlorinated biphenyls, PBBs, PCDD/Fs and PAHs)",

Table 4 Clusters of the network visualization map produced using the 50 most important author keywords (Fig. 4)

Rank	Cluster 1 (green)	OC[a]	Rank	Cluster 3 (blue)	OC[a]
1	e-waste	515	2	recycling	367
5	PBDEs	102	11	waste management	69
6	heavy metals	85	12	waste electrical and electronic equipment	69
7	China	79	25	circular economy	39
10	PCBs	70	28	extended producer responsibility	37
17	soil	58	29	life cycle assessment (LCA)	35
21	polybrominated diphenyl ethers	47	32	reuse	33
34	risk assessment	32	37	end-of-life	26
40	polychlorinated biphenyls	24	38	material flow analysis	25
41	human exposure	24	44	electrical and electronic equipment	22
42	PCDD/Fs	22			
43	PAHs	22	**Rank**	**Cluster 4 (yellow)**	**OC[a]**
50	plastics	17	3	WEEE	278
Rank	**Cluster 2 (red)**	**OC[a]**	13	pyrolysis	69
4	electronic waste	222	15	lead	60
8	recovery	77	20	brominated flame retardants	49
9	bioleaching	77	31	cadmium	34
16	copper	58	45	RoHs	21
18	printed circuit boards	57	47	children	18
19	leaching	54	48	polymers	18
23	electronic scrap	45			
26	gold	38	**Rank**	**Cluster 5 (purple)**	**OC[a]**
27	metals	38	14	waste electrical and electronic equipment (WEEE)	61
30	metal recovery	34	22	sustainability	47
35	precious metals	31	24	reverse logistics	41
39	PCB	24	33	industrial ecology	33
46	optimization	19	36	extended producer responsibility (EPR)	27
49	gold recovery	17			

OC occurrences

which have been the focus of research in this country in recent years. The "assessment of risk to human health" (especially to children and expectant mothers) of hazardous materials is frequently reported in the scientific literature. The "bioleaching efficiency of metals" from waste printed circuit boards is a topic with less occurrence in the papers under study, which can be found among the subjects of the most recently published papers from China (see Table 5).

USA

For the USA, the author keyword analysis identified research terms such as "extended producer responsibility (EPR)," "industrial ecology," "reverse logistics," and "product take-back" in combination with potentially hazardous elements, i.e., "heavy metals" (Table 5). Currently, problems related to

environmental issues have also become an important topic of discussion and have gained attention from policy makers. Faced with an increase in the amount of e-waste, several state governments have revised their policies and implemented post-consumer responsibilities for producers. The main result of this project was the guidance manual for governments that was published in 2001 (OECD 2016). In this guide, the EPR program sets the key role in the management of products. Since then, over the last decade, there has been a substantial increase in the implementation of and interest in EPR programs (Kaffine and O'Reilly 2013). USA estimation studies (Electronics Take Back Coalition 2014; US EPA 2016) reported that electronic products recycling improved by 10% (0.2 Mt) in 2000 to 37.8% (1.3 Mt) and 41.7% (1.4 Mt) in 2013 and 2014. Currently, the USA is ranked second in e-waste generation around the world (6.3 Mt), and the recycling

Table 5   Top 10 countries and the 10 most important words in each country according to the total author keywords

Rank	Country	NP	10 most recurrent words
1	PRC	1181	China, soil, heavy metals, lead, risk assessment, bioaccumulation, cadmium, human exposure, children, bioleaching
2	USA	398	Lead, extended producer responsibility (EPR), industrial ecology, cadmium, reverse logistics, waste management, material flow analysis, environment, heavy metals, product take-back
3	IND	202	Bioleaching, gold, printed circuit boards (PCBs), leaching, sustainability, reverse logistics, waste management, pyrolysis, heavy metals, separation
4	GER	184	Industrial ecology, pyrolysis, RoHS, critical metals, rare earth elements, material flow analysis, precious metals, resource recovery, polymer recycling, X ray fluorescence, reference material
5	JPN	166	Recovery, Vietnam, Ghana, population balance model, steam gasification, gold, precious metals, rare metal, hexabromocyclododecanes (HBCDs), indium
6	UK	149	Industrial ecology, reuse, pyrolysis, circular economy, EPR, sustainability, life cycle assessment (LCA), environment, product take-back, plastic
7	AUS	148	Phytoremediation, sustainability, bioleaching, leaching risk, heavy metals, nanoparticles, pyrolysis, chelator, soil, copper
8	ITA	134	Pyrolysis, circular economy, life cycle assessment, yttrium, hydrometallurgy, rare earths, waste printed circuit boards (WPCBs), leaching, indium, mobile phones
9	BRA	111	Printed circuit boards (PCBs), copper, reverse logistic, mobile phones, mechanical processing, polymers, characterization, leaching, laser-induced breakdown spectroscopy (LIBS), chemometrics
10	KOR	99	Bioleaching, moderate thermophiles, hydrophilization, tin, toxicity potential, electronic scrap, environmental impact, metal recovery, sustainability, copper

PRC People's Republic of China, *USA* United States, *IND* India, *GER* Germany, *JPN* Japan, *UK* United Kingdom, *AUS* Australia, *ITA* Italy, *BRA* Brazil, *KOR* South Korea, *NP* number of publications

of WEEE still has a long way to go. Electronics are difficult to recycle, and the complex structures and physical designs make recycling challenging.

India

In the author keywords analysis for terms associated with India, many scientists have been studied "leaching processes and recovery of valuable metals from electronic waste". "Printed circuit boards (PCBs)" have been the subject of several works over the last 20 years. This is not surprising because valuable substances are in PCBs, making PCB waste an economically attractive urban ore for recycling (Ghosh et al. 2015).

"Bioleaching" is also a process that has been explored for many years concerning metal extraction from ores. On the other hand, the use of microbiological processes for the extraction of copper and valuable elements from e-waste has been less explored/investigated until present day (Cui and Zhang 2008).

Germany

The most important topics among the published studies of German researchers and collaborators cited economically relevant metals, such as Cu and Au ("precious metals"); "critical metals", such as Ga, Ge, In, and Pd; and "rare earths" (Castro and Pereira-Filho 2018). The context of these elements is related to the worldwide supply of raw materials for industrial sectors that are vulnerable due to diminishing natural reserves and political conflicts in countries that exploit such resources (Zhang et al. 2017). To enable a continuous and sustainable supply, studies of "resource recovery" from secondary sources have been increasing and offer promising potential. However, although WEEE contains precious metals and important nonmetallic fractions (polymers), it also contains hazardous substances. The term "RoHS" (restriction of hazardous substances) is highly associated with the use of brominated substances as flame retardants in polymers, such as PBB and PBDE, which are limited in European countries by Directive 2011/65/EU (EC 2011).

In addition, emerging separation technologies are discussed in the literature to improve recycling results. The processes can be combined with spectroscopic techniques, such as near-infrared (NIR) spectroscopy and "X ray fluorescence" (XRF). "Reference materials" can be used to validate and evaluate the accuracy of developed methods. However, among publications reporting the use or preparation of reference materials, most studies are related to polymer analysis (Mnim Altwaiq et al. 2003; Pohlein et al. 2009; Roth et al. 2015). Presently, there is a lack of certified reference materials (CRM) to be used as quality control samples or standards for WEEE in laboratories that perform analyses of these samples.

Japan

Japan has conducted studies on environmental issues primarily associated with chemical contamination in Asian countries. Due to activities in e-waste recycling, studies have investigated whether chemical pollutants, including halogenated flame retardants and "hexabromocyclododecanes (HBCDs)", have spread to other countries in the region. In Asia, particularly in China, activities primarily related to the recycling of electronic waste and damage to the environment by flame retardants and persistent organic pollutants have been extensively reported, as mentioned before; however, there is little relevant information on Asian countries that surround this region, such as Japan, South Korea, Vietnam, and India (Li et al. 2017a). In addition, concern for other developing countries, such as Ghana, has emerged in recent years and appears as an author keyword in Japanese studies. Accra (Ghana) has a large informal e-waste recycling center, and studies on environmental exposure to chemicals/substances emitted from e-waste recycling sites and their effects on human health have been reported (Tokumaru et al. 2017; Tue et al. 2017).

In addition to the recycling and correct handling of electronic waste, monitoring the amount of a particular e-waste stream is essential for many sectors, but it is not simple. Faced with a large amount of e-waste generated annually and a wide variety of complex materials found in this waste, it is difficult to monitor the flow of e-waste. In addition, some countries do not have official statistics on this type of waste. The "population balance model (PBM)" based on the WEEE generated has been used to understand e-waste production estimates. In addition, the amount of critical raw materials (e.g., the "indium" content in LCD monitors) in WEEE has also been projected using the PBM (Yamasue et al. 2007).

UK

The most highlighted words in studies from the UK are related to sustainable e-waste recycling, which is important not only for e-waste treatment and to avoid "environmental impacts" but also for the recovery of valuable elements. These are essential points for manufacturers engaging in programs such as "reverse logistics, industrial ecology, and product take-back projects in a sustainable practice". Producers that expand their businesses and enter into product recovery projects are seeking, among other goals, to generate profits for their company by replacing raw material inputs (through the recycling and recovery of valuable materials) or inserting themselves into new segments in the market by using reprocessed products ("reuse, remanufacturing, and reconditioning") (Stindt and Sahamie 2014). "Extended producer responsibility (EPR)" has also captured the attention of most European contributors following the introduction of EU directives. Producers with economic incentives to reduce the environmental impact of their products have implemented the directives

of EPR, and 34% of the incentives cover electronics (Kaffine and O'Reilly 2013).

Australia

For Australia, the author keywords analysis highlighted terms such as "phytoremediation, sustainability and leaching risk", which can be associated with "heavy metals, soil, and copper". The decontamination of soil in regions that have suffered environmental impacts from an e-waste recycling site has been recently reported (Luo et al. 2017a, b).

In addition, novel approaches to synthesizing different types of "nanoparticles" using electronic waste were proposed in several recent studies. Among them, the synthesis of silicon carbide (SiC) nanoparticles using electronic-waste compact discs (CDs) (Rajarao et al. 2014), the use of spent waste batteries for the synthesis of manganese oxide (MnO) and zinc oxide (ZnO) nanoparticles (Farzana et al. 2018), a green route by which to synthesize Pr^{3+}/Dy^{3+}-doped Nd_2O_3 nanoparticles from Nd–Fe–B magnets (Maroufi et al. 2018), and the direct conversion of waste PCBs into a homogenous nanostructured alloy (Cu_{79}–Zn_{13}–Fe_3–Sn_3–Ni_1) (Nekouei et al. 2018) can be highlighted.

Italy

"Pyrolysis" (the main author keyword addressed to Italy) is a process traditionally used for metal recovery from electronic waste equipment; however, the main challenges of this process are dehalogenation, avoidance of the emission of highly toxic pollutants (i.e., PBDEs, PBDD/Fs, PAHs, polychlorinated biphenyls, and heavy metals) and the preparation, accumulation and separation of metals in the recycling process (Barontini and Cozzani 2006). In recent decades, greater attention to "hydrometallurgical" processes based on the leaching of a variety of elements has been reported (Cui and Zhang 2008; Tuncuka et al. 2012).

Compared to pyrometallurgical processes, hydrometallurgical methods are more accurate, more predictable, and easier to control (Andrews et al. 2000). For "leaching," various agents can be used, including cyanide, halide, thiourea, and thiosulfate, which is followed by a recovery process using methods such as cementation, solvent extraction, adsorption onto activated carbon, and ion exchange (Cui and Zhang 2008). Due to the increasing demand for critical elements, current applications include the "recovery of critical materials like indium, yttrium, and rare earths, among other materials less exploited" (Dodson et al. 2015; Innocenzi et al. 2014; Venkatesan et al. 2018; Andrade et al. 2019).

Other important terms highlighted in papers from Italian research were "circular economy (EC)" and "life cycle assessment (LCA)". The recycling of e-waste is one of the measures that helps to maintain the economic model based on resource optimization while promoting the use of waste as a resource.

EC is a regenerative system in which the consumption of raw material input and the generation of residues are minimized through measures such as e-waste maintenance, repair, reuse, remanufacturing, refurbishing, and recycling. To achieve models that are economically and environmentally sustainable, the LCA method can be useful to support the analysis of the impacts and benefits associated with recycling and bring significant gains to the regenerative system.

Brazil

Brazil has reported studies mainly related to "printed circuit boards". PCBs are one of the components of electronic waste of which the reuse and recycling has not been effectively solved. However, there is extensive literature on PCB recycling (Marques et al. 2013). The composition of these materials is very rich and complex due to the diversity of materials used, and in general, a PCB board is composed of 40 wt% metals, 30 wt% plastic, and 30 wt% ceramic. It is reported that approximately one third of the weight of PCBs is "copper," which is recoverable by chemical methods (Marques et al. 2013), and if a suitable treatment and recovery process is applied, waste PCBs might serve as a secondary copper source.

However, in Brazil, the recovery processing of metals contained in PCBs, among other electronic wastes, has primarily been developed by foreign companies (Europe, Asia, and North America) (Neto et al. 2017). The main barrier for Brazilian producers in adopting WEEE reverse logistics for recycling and reuse is the lack of technology to handle PCBs. Currently, the main recycling activities involve "polymers" (Aquino and Pereira-Filho 2015), which require simpler technology (Neto et al. 2017). In this context, the recycling of PCBs is a relatively new opportunity for Brazil in terms of processes related to the extraction and reuse of raw materials (precious metals).

In addition, topics in "e-waste characterization, chemical analysis by laser-induced breakdown spectroscopy (LIBS), and chemometrics" have emerged as a common trend in the field of e-waste research in recent years (Costa et al. 2018). LIBS is an emerging technique in analytical chemistry and has demonstrated great potential in different applications. In this sense, several researchers have proposed methods applying the LIBS technique to the analysis of different materials in electronic waste, such as polymers (Costa et al. 2017a, b), flame retardants and hazardous elements (Stepputat and Noll 2003; Sperança et al. 2018), PCBs (Carvalho et al. 2015), rare earth elements in magnets (Martin et al. 2015), and scraps of mobile phones (Aquino et al. 2015), among other applications (Aguirre et al. 2013; Aquino et al. 2016). Chemometrics has been frequently reported along with LIBS applications, as it is often better for data analysis when extracting and visualizing the information inherent in chemical data by the application of

suitable mathematical and statistical methods. In addition, experimental design methods for the planning and performance of experiments to obtain data containing the maximum amount information can also be performed (Wold 1991).

South Korea

In South Korean studies, the most commonly occurring author keyword was "bioleaching" (see Table 5). As discussed previously, most hydrometallurgy techniques for e-waste metal recovery involve cyanide and halide leaching of valuable elements (Zupic and Cater 2015). However, bioleaching has been reported as an environmentally friendly technique for recovering metals from primary and secondary metal sources. The use of microorganisms for metal extraction offers a number of advantages compared to conventional methods, including low operating cost (an economic method), lower generation of waste, and high efficiency in detoxifying effluents (Cui and Zhang 2008). Bioleaching using "moderate thermophilic bacteria" for the maximal extraction of metals from electronic scrap has been frequently reported in the published articles under study (Ilyas et al. 2013, 2014; Xia et al. 2017).

Regarding the nonmetallic fraction, different techniques for separating polymers have been developed, such as electrostatic separation, gravitational separation, selective dissolution, and automated sorter systems based on laser scanning (e.g., LIBS (Costa et al. 2017a), Raman (Sommer and Rich 2001)) and infrared or x-ray spectroscopy (Schlummer 2014). In addition, the froth flotation technique has received attention as an alternative method due its efficiency in separating a mix of waste polymers having similar characteristics, such as density, surface hydrophobicity, and dielectric constant (Wang et al. 2014). Recently, several studies have shown progress in selective surface "hydrophilization of plastics" to allow the separation of different polymers (Mallampati et al. 2017; Truc and Lee 2017).

Conclusions and future directions

Over the last two decades, much has been developed for and learned about the management of electronic waste. A general review of the body of literature on e-waste reveals that rapid development concerning this subject has occurred primarily during the past decade, when more than 100 articles were published per year. On the other hand, we must recognize that due to the large amount of e-waste generated each year and the complexity of e-waste, this research topic still has a long way to go.

Waste Management is the most sought-after journal among researchers, and *Environmental Science & Technology* contains the papers with the highest number of citations. In general, the most impactful papers have assessed global reviews

of e-waste management, generation, treatment, regulations of WEEE, value recycling, and risk assessment for human and environmental exposure to e-waste recycling regions. In addition, among the total number of articles published between 1998 and 2018 (3311 records), the most active country, with more than one third of the publications (1181 records), was China (PRC). This finding may be linked to China having the highest indexes of e-waste generation and playing a key role in global e-waste management, including the manufacturing, refurbishment, reuse, and recycling of e-waste.

Given the sheer volume of scientific literature, bibliometric mapping was a powerful tool for studying the connections between and occurrences of the most influential terms in the electronic waste domain. The most important research focuses were on "leaching/bioleaching and recovery of valuable metals," "environmental and human risks after exposure to hazardous materials," "assessment of the life cycle, reverse logistics and reuse of e-waste," and "extended producer responsibility (EPR)."

Developing countries are beginning to catch up on issues once touched upon by the most influential countries in the field of e-waste, and they are beginning to no longer see electronic waste as a solid waste but as a "source of resources". After individual analysis of the author keywords in the top 10 countries, it was observed that some countries presented concerns related to waste management (the USA, IND, and UK, for example). Other countries, such as China and Japan, mainly presented studies about the environmental impact. Germany and Brazil were the only two countries that presented author keywords related to analytical techniques for waste characterization (X ray fluorescence and laser-induced breakdown spectroscopy).

Search topics such as "printed circuit boards," "leaching and recovery of precious metals," "recycling," "environmental and human damages in recycling areas," "EPR programs," and "life cycle assessment" began to enter the agenda of researchers in recent years, and they are current topics of research in different countries. In addition, emerging separation technologies to help in the recycling process are discussed in the scientific literature. These processes can be combined with analytical techniques, such as near-infrared (NIR) spectroscopy, X ray fluorescence (XRF) spectrometry, and laser-induced breakdown spectroscopy (LIBS).

Finally, the results and analyses of emerging topics in e-waste research suggest that future studies should be devoted to (i) critical materials (e.g., In, Ga, Pd, and rare earth elements) due to their scarcity and demand each year; (ii) electronic devices that have a short lifespan and are an important source of valuable materials (e.g., mobile phones, tablets, and laptops); (iii) the establishment of directives to restrict toxic elements in e-waste, especially in developing countries that have not implemented such policies; and (iv) certified reference materials (CRMs), as there is presently a lack of

comprehensive reference samples for WEEE. In addition, other specific topics may appear upon a more in-depth search of more advanced studies on each topic.

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2.A Appendix

Supplementary material

Fig. 1S. Bibliometric mapping of the top 50 author keywords from People's Republic of China.

Fig. 2S. Bibliometric mapping of the top 50 author keywords from United States.

Fig. 3S. Bibliometric mapping of the top 50 author keywords from India.

Fig. 4S. Bibliometric mapping of the top 50 author keywords from Germany.

Fig. 5S. Bibliometric mapping of the top 50 author keywords from Japan.

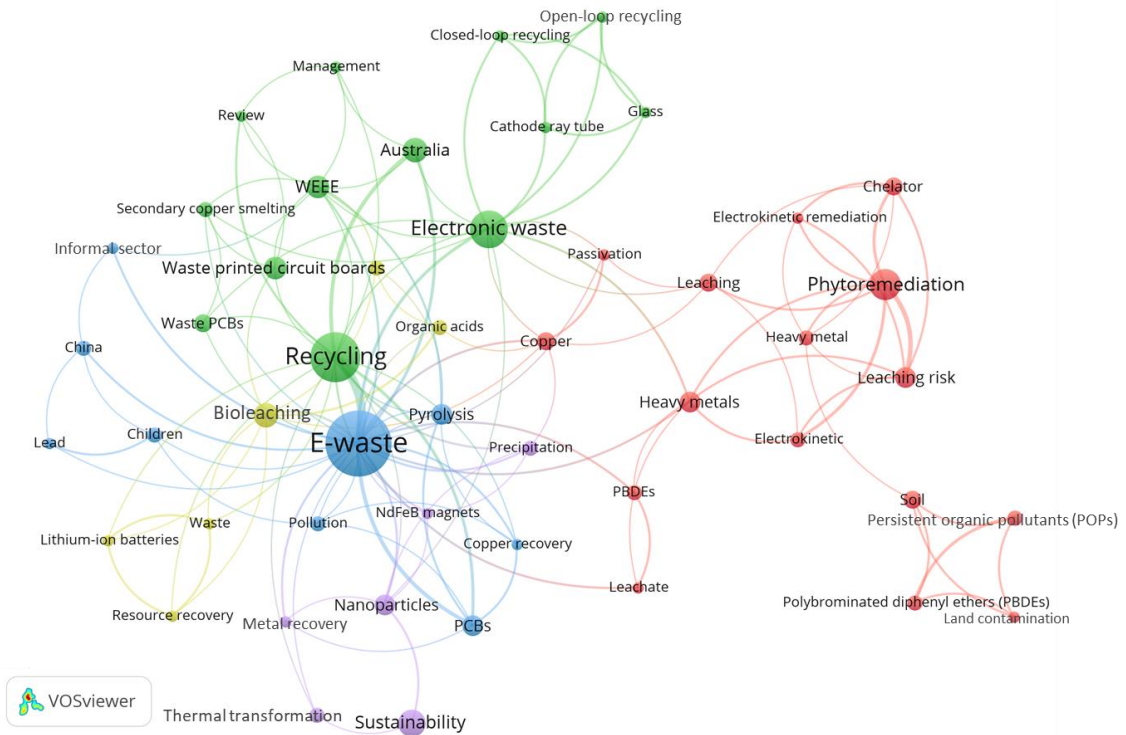**Fig. 6S.** Bibliometric mapping of the top 50 author keywords from United Kingdom.

Fig. 7S. Bibliometric mapping of the top 50 author keywords from Australia.
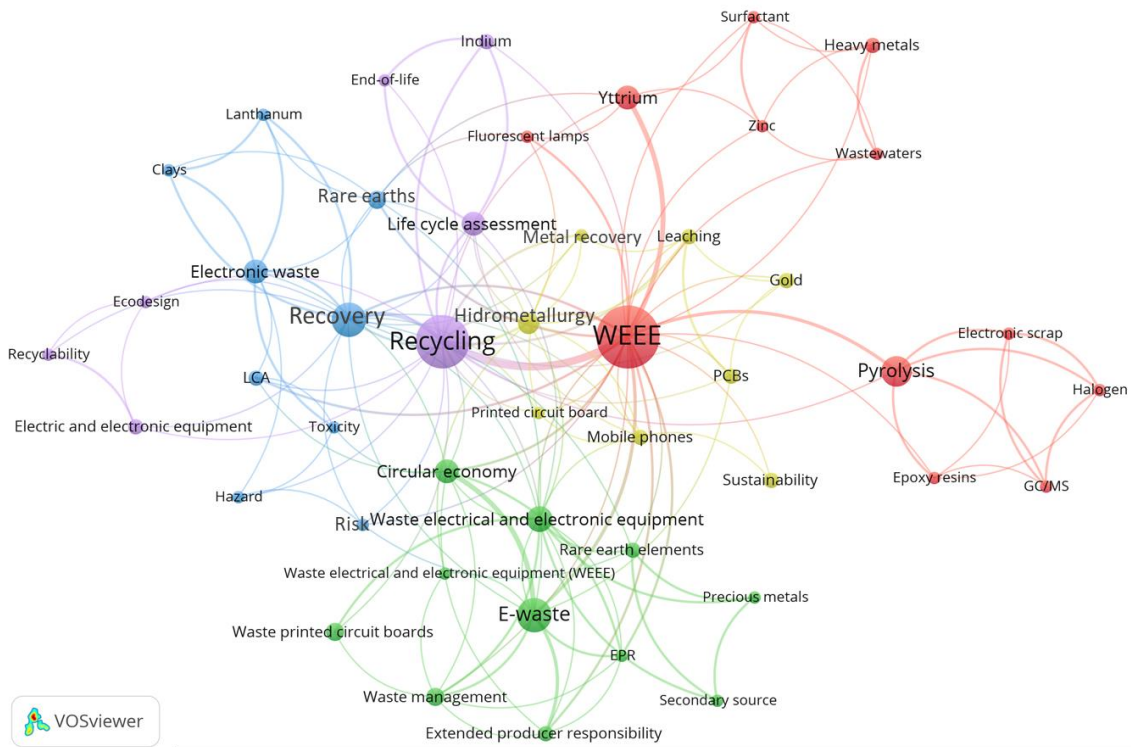

Fig. 8S. Bibliometric mapping of the top 50 author keywords from Italy.
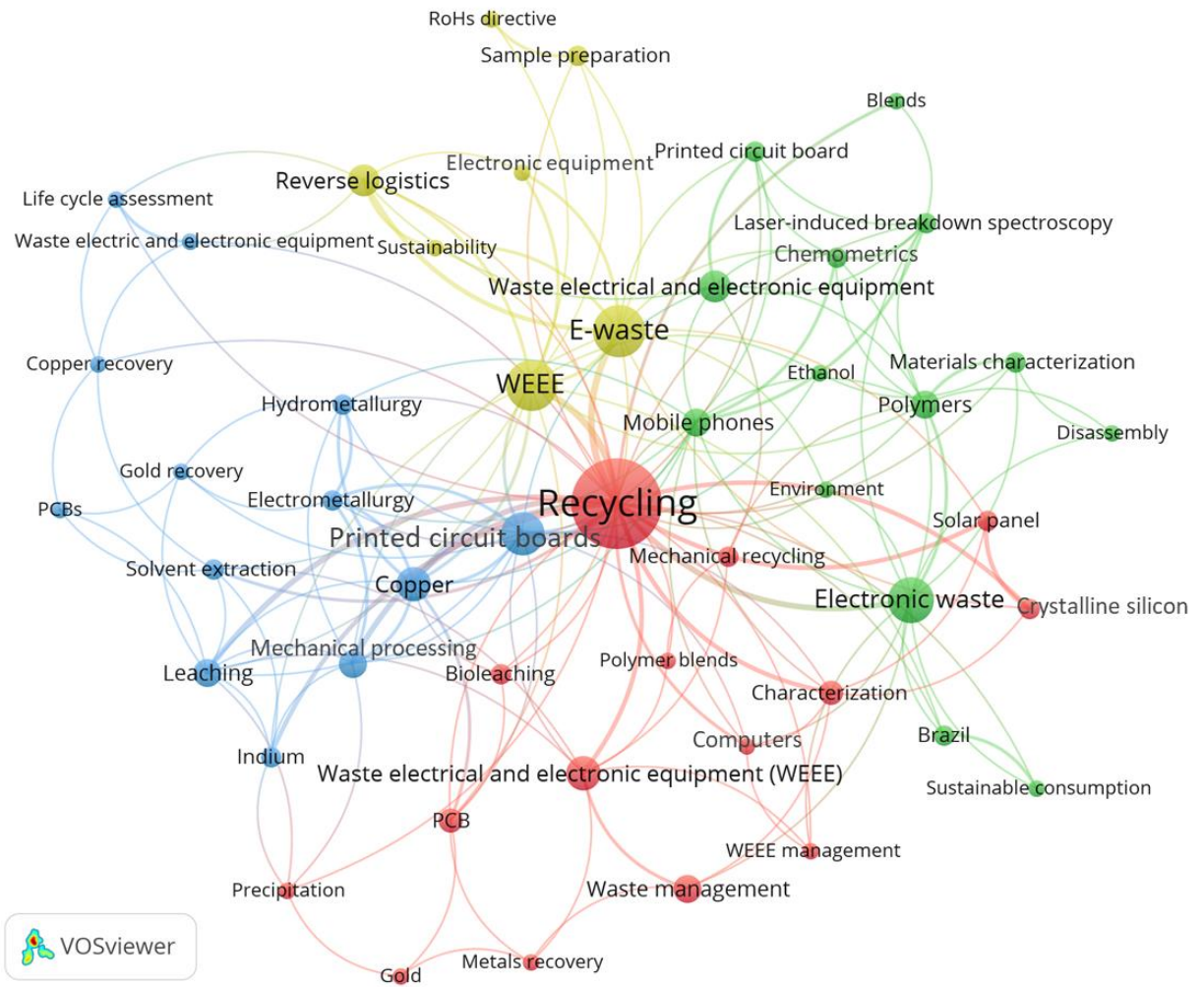
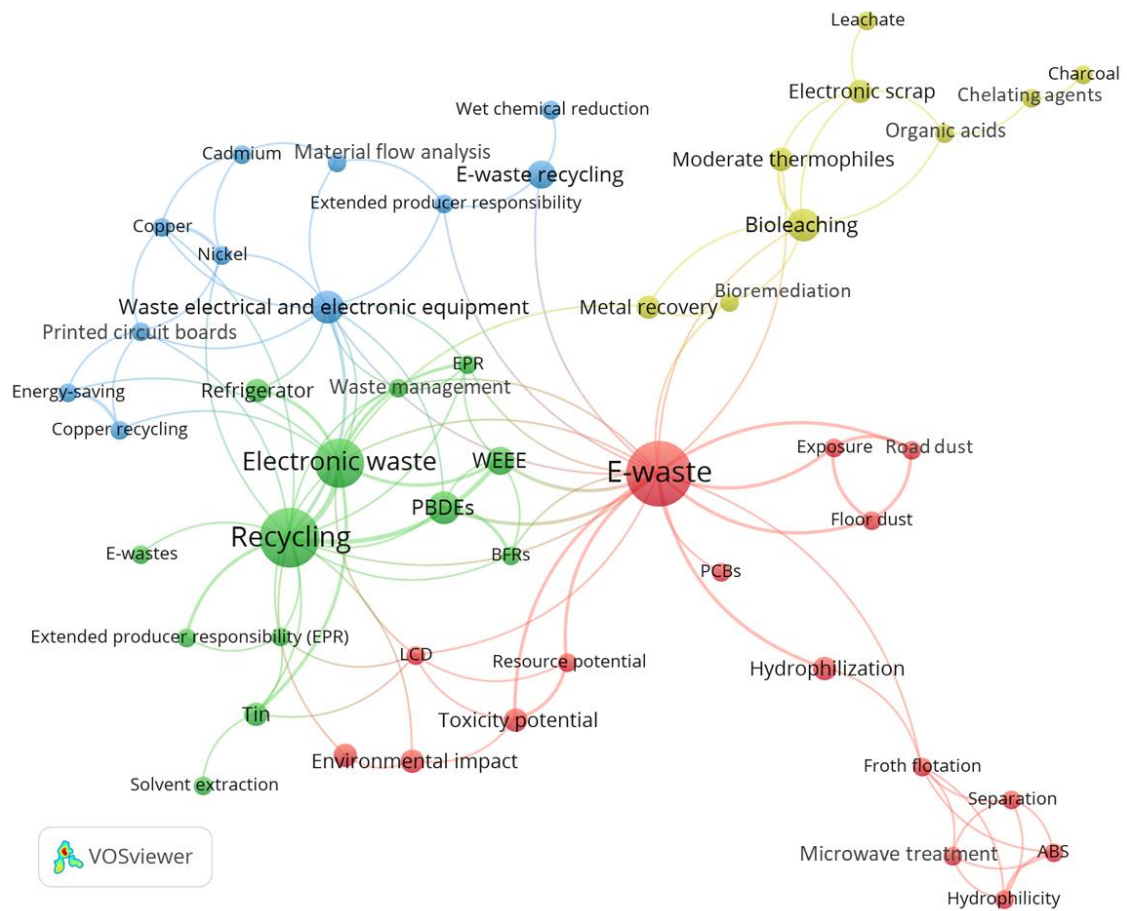**Fig. 9S.** Bibliometric mapping of the top 50 author keywords from Brazil.

Fig. 10S. Bibliometric mapping of the top 50 author keywords from South Korea.

Chapter 3

Reference material for chemical analysis of WEEE

3.1 The role of reference materials in analytical chemistry

The constant demand on guarantee the quality of a measurement obtained through analytical tests is today one of the main requirements in laboratories. The results obtained in these tests are essential for decision-making in several areas such as in industries, health and the environment. Unreliable results carry a high risk of incorrect decisions and may lead to higher costs, health risks and illegal practices.[59,60]

It is well known that analytical chemistry as a branch of chemistry play a fundamental support in the science of measurement in general. As proposed by the Federation of European Chemical Societies (FECS)[61] in 1993 and later adopted by the International Union of Pure and Applied Chemistry (IUPAC), analytical chemistry is defined as:

"… a scientific discipline which develops and applies methods, instruments and strategies to obtain information on the composition and nature of matter in space and time, as well as on the value of these measurements, i.e. their uncertainty, validation and/or traceability to fundamental standards".

The impact of analytical chemistry on the economy and society is of increasing importance, and quality of the measurement results must be more and more rigorously guaranteed if the ensuing beneficial effects are to be fully exploited.[62] In this framework, there are many parameters that contribute to obtaining reliable and comparable measurement results, such as the competence of the analyst or laboratory, routine checks of accuracy and precision, validation of analytical methods for the accreditation of laboratories and the use of reference materials (RMs), especially certified reference materials (CRMs), which are very important tools and the basis for verifying analytical measurement results.[63,64]

Reference materials and CRMs are the materials characterized to an acceptable standard in terms of homogeneity and stability, with respect to one or more of whose property values, for which traceability and values of uncertainty at

a stated level of confidence are established.[65] These materials are widely used to check the quality and metrological traceability of products, to validate analytical measurement methods, or for the calibration of instruments. The need for reliability of analytical data of chemical analysis largely depends on the reference materials used in analysis. Hence, many analytical methods rely heavily on the use of a RM with known composition/concentration for quantitation purposes.[59,65]

In Brazil, the acquisition of these materials is mainly by importing international products at high costs. In fact, the complexity of the preparation and characterization of materials makes the final price of the product is high.[66] Besides the cost it is not always possible to have a similar reference material matrix to the sample under study or concentration levels of the same order of magnitude. Thus, the field of technology for the production of RMs in Brazil represents a strategic breakthrough for putting the country in a position to provide specific materials to their own needs.

The production of RMs/CRMs is based on requirements posed by the International Organization for Standardization (ISO), and adopted by the Brazilian Association of Technical Standards (ABNT) in Brazil. The procedures for the development are well established in the ISO Guides 30–35, especially by the ISO Guide 35 (Reference materials – Guidance for characterization and assessment of homogeneity and stability) and ISO 17034 (General requirements for the competence of reference material producers).[67,68] In summary, the production of a RM involves the following main steps:

- Definition of the matrix, the properties to be characterized and their desired levels, and the target uncertainty (for CRMs);
- Acquisition of the material;
- Design of a preparation procedure;
- Selection of measurement procedures appropriate for characterization, homogeneity and stability studies;
- Material preparation, i.e. sampling, crushing for reduction of particle size, sieving, homogenization, packaging;
- Assessment of homogeneity and stability;
- Characterization of the reference material;

- Combination of all results for evaluation of the measurement uncertainties of certified values;
- Certification report.

The assignment of property values must be estimated using adequate statistic calculations and the uncertainty contributions to the homogeneity study (u_{bb}), stability tests (i.e. short- and long-term stability, u_{sts} and u_{lts}), and characterization of the material (u_{char}).[67] Figure 3.1 provides a schematic outline of the main tests and their uncertainty associated for the RM production/certification.
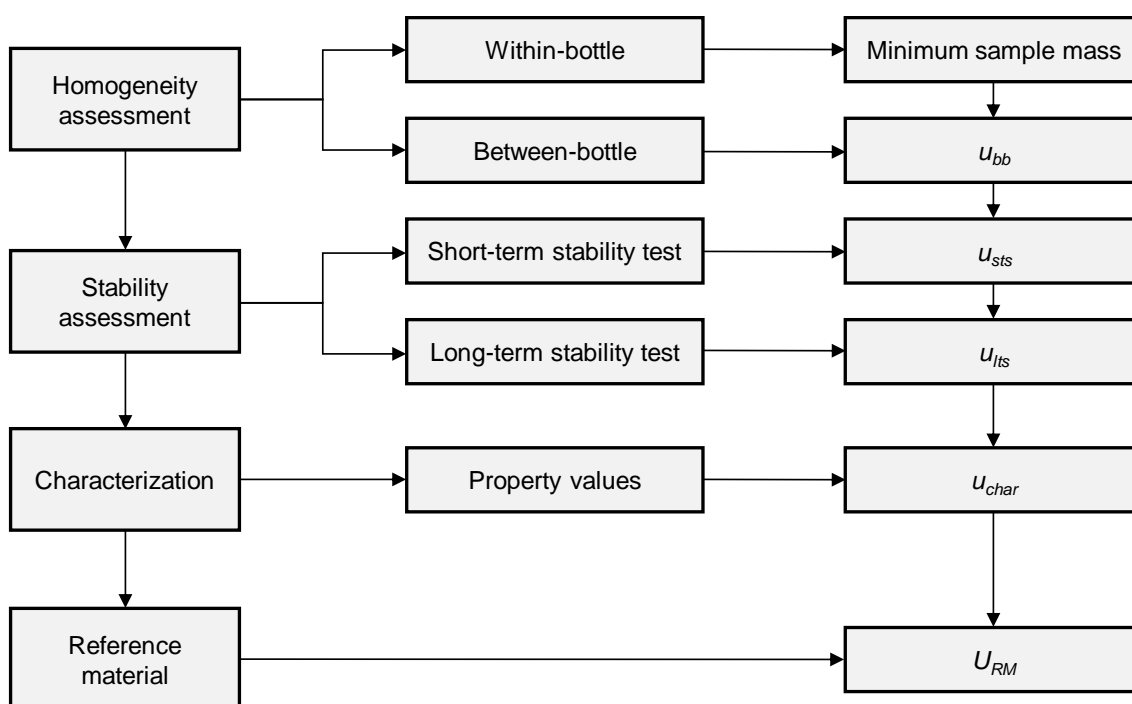
FIGURE 3.1 Main tests for the production of a reference material and estimation of measurement uncertainty (U_{RM}).

Undoubtedly, RMs/CRMs are fundamental for the science of measurement in general (including direct solid sampling analysis) and for analytical chemistry in particular. However, there are no materials available to meet the demands in all sectors, mainly in electronic waste and technological materials monitoring, in which it lacks materials and studies to ensure the attainment and maintenance of reliable results.[41,69]

Considering the need for the availability of reference materials in Brazil and the ever-increasing importance of studies focused on the WEEE

management in the country, the demand for the production of electronic waste RMs is evident, mainly to assist in obtaining reliable analytical results for chemical inspection and determining the composition of this type of waste stream. Therefore, in this chapter was proposed and discussed the production of a new RM using waste PCB samples. The results present complementary information from two studies:

3.1.1 Proposition of electronic waste as a reference material – part 1: sample preparation, characterization and chemometric evaluation

3.1.2 Proposition of electronic waste as a reference material – part 2: homogeneity, stability, characterization, and uncertainties.

Finally, the appendix includes extra information about the validation of the obtained results in this study. To this end, the concentrations reported from one laboratory in the collaborative trial were used. This results were reported after the given deadline for the interlaboratory comparisons, then this laboratory was not included in the estimated mass fraction and associated uncertainty (U_{RM}) to the RM of electronic waste.

3.1.1 Proposition of electronic waste as a reference material – part 1: sample preparation, characterization and chemometric evaluation, Journal Analytical Atomic Spectrometry 34 (2019) 2394.

Proposition of electronic waste as a reference material – part 1: sample preparation, characterization and chemometric evaluation†

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Electronic waste (e-waste) is attracting increasing interest in industry, politics, academic centers, and initiatives worldwide. Because of its complex composition of precious and hazardous substances, new technologies are often required to process e-waste in order to maximize resource recovery and minimize possible harm to humans and the environment. Printed circuit boards (PCBs) are present in most electronic products and currently comprise a significant fraction of e-waste. In this study, a reference material (RM) for inorganic constituents in PCB samples was prepared and leaching procedures for its characterization were developed. Full factorial design and principal component analysis (PCA) were applied to evaluate five different types of acidic solvents (aqua regia, inverted aqua regia, aqua regia 50% v/v, 7 mol L^{-1} HNO_3 + H_2O_2, and 14 mol L^{-1} HNO_3) in sample leaching by microwave radiation and inductively coupled plasma optical emission spectrometry (ICP OES) for the determination of Ag, Al, As, Au, Ba, Cr, Cu, Fe, Ni, Pb, Sb, Si, Sn, and Zn. Diluted aqua regia provided high leaching efficiency and the best results for these elements. The optimal conditions for further experiments were fixed for 0.1 g of sample and 10 mL of acid mixture. The PCB material was also submitted to nondestructive testing by instrumental neutron activation analysis (INAA) and a paired *t*-test was applied to compare the results obtained by microwave radiation and INAA. A minimum mass study was carried out and 100 mg was established as the minimum sample mass for further studies in agreement with the optimal conditions fixed for the sample mass after optimization.

Introduction

The technological advances in the last few decades have facilitated the fast growth of the electrical and electronic equipment (EEE) industry, leading to the manufacturing of increasingly advanced products. This intense production and consumption of high-tech products has led to a decrease of the lifetime of EEE, generating large amounts of waste electrical and electronic equipment (WEEE).[1] It is estimated that by 2021 more than 52 million metric tons of WEEE will be generated worldwide.[2]

WEEE has a heterogeneous composition, with large fractions of metals such as aluminum, copper and iron, plastics and fiberglass. More than 60 elements may be found in WEEE,[3] such as rare earth elements (REEs),[4] platinum group elements (PGEs), indium[5] that presents strategic importance from the

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economic point of view, halogens from flame retardants used in the plastics of EEE,[6,7] with contaminants and some noble elements present at higher concentration than in the ores used for the manufacturing of EEE.[8,9]

Printed circuit boards (PCBs) are key parts of electronic products and main components of WEEE. PCBs are made of a copper-clad laminate with glass-reinforced epoxy resin and different metals, including precious ones such as Ag, Au, Pd and Pt, other elements such as Cu, Fe, Sn and Pb used to solder different PCB components, and potential toxic elements, such as As, Cd, Cr, and Hg.[10,11] The complex composition of PCBs hampers the recycling processes that are important not only for avoiding environmental pollution but also for the recovery of elements that can be reused in the manufacture of components for new EEE.[12]

The analysis of PCBs is not an easy task due their complexity and heterogeneity. Several treatment steps such as dismantling, crushing and sieving are required for the reduction of particle size, improvement of the homogeneity of the material and the precision of the results in the sample analysis.[13,14] Another important step is the sample leaching procedure using inorganic acids for the elemental analysis. According to the EN 62321 guidelines, two leaching procedures can be used for the

determination of Cd, Hg and Pb in electrical products: the first involves leaching with aqua regia in an open vessel under reflux conditions and the second involves the use of HNO_3, H_2O_2 and HBF_4 in a closed vessel, assisted by microwave radiation.[15] In addition to these mixtures used for the leaching of the PCB samples, other studies reported the use of aqua regia and H_2O_2, H_2SO_4 and HNO_3, HNO_3 and HF, and $HNO_3 : HCl$ in the 1 : 5 ratio. Most of these procedures involve the use of concentrated acid wherein sample residues remain after leaching.[13,16–18]

In this context, chemometric tools such as experimental design and principal component analysis (PCA) can be used as strategies in the selection of the ideal conditions for PCB sample leaching and further element determination.[19] PCA helps to reduce the dimension of the original dataset and assists in the pattern recognition, allowing the determination of the conditions that favor the achievement of precise and accurate results for all analytes simultaneously.[20,21]

The complex composition of WEEE combined with the difficulties of sample leaching and the lack of certified reference material (CRM) for PCBs has made the analysis of this material challenging. Therefore, this study describes the preparation of a RM for PCB samples and the development of an analytical method for the determination of Ag, Al, As, Au, Ba, Cr, Cu, Fe, Ni, Pb, Sb, Si, Sn, and Zn by inductively coupled plasma optical emission spectrometry (ICP OES). A full factorial design and PCA were used to evaluate five different acid solutions for PCB leaching. Instrumental neutron activation analysis (INAA) was used for direct solid sample analysis and the obtained results were compared to those obtained by ICP OES.

Materials and methods

Reagents, analytical solutions, and samples

High purity water (18.2 MΩ cm, Milli-Q®, Millipore Corp., Bedford, MA, USA) was used to prepare all solutions. Microwave-assisted acid leaching experiments were conducted using HNO_3 (Neon, Suzano, SP, Brazil) and HCl (Qhemis, Indaiatuba, SP, Brazil) previously purified using a subboiling distillation system, model BSB-939-IR (Distillacid, Berghof, Germany), and 30% m m^{-1} H_2O_2 (Synth, Diadema, SP, Brazil). Monoelement stock solutions (Ag, Al, As, Au, Ba, Cr, Cu, Fe, Ni, Pb, Sb, Si, Sn, and Zn) containing 1000 mg L^{-1} (Merck, Darmstadt, Germany) of analyte were properly diluted to obtain multielement calibration solutions for ICP OES.

A sample composed of twelve PCB pieces from spent computers (10 units) and telephone boards (2 units) was prepared. The computer PCBs consisted of four laptop boards and six desktop boards. A diverse set of PCBs was acquired with respect to the functionality, year of manufacture, and manufacturer. The weight of all PCBs combined was 4.72 kg.

Instrumentation

The PCBs were ground using a toothed roll crusher (FT/150, Fragmaq, São Paulo, Brazil), hammer mill (FC-7, Astecma, Brazil), stainless steel knife mill (MA 630/1, Marconi, Brazil), and vibrating cup mill (PULVERISETTE 9, Fritsch, Germany).

After grinding, the material was homogenized in a "Y"-shaped polytetrafluorethylene-coated bowl (201/5 MO, Marconi, Brazil). Grain size distribution was determined using laser diffraction particle sizing by wet dispersion (ANALYSETTE 22 MicroTec Plus, Fritsch, Germany).

Sample leaching was carried out using a microwave system (UltraWAVE™, Milestone, Italy) with a high-pressure single reaction chamber (SRC) equipped with 5 vials of PTFE/TFM (internal volume of 40 mL). This system consists of a stainless steel SRC (1 L) covered with a 900 mL TFM liner that was sealed and pressurized with nitrogen (White Martins, São Paulo, Brazil) to 40 bars prior to heating. The PCB samples were leached under 1500 W and at a maximum temperature and pressure of 240 °C and 100 bar, respectively.

An inductively coupled plasma optical emission spectrometer (iCAP 7000 model, Thermo Fisher, Madison, USA) and instrumental neutron activation analysis (INAA) were used for determination of all the analytes. In the ICP OES analysis, the gas for plasma generation, nebulization and auxiliary was 99.996% argon (White Martins-Praxair, Sertãozinho, SP, Brazil) and instrumental operating conditions are summarized in Table 1.

For INAA, triplicate portions (100 mg) of the samples ($n = 7$) were directly weighed in high purity polyethylene vials and placed into aluminum containers. NiCr wires with a known composition were added between the vials as neutron flux monitors. Irradiation was carried out in the IEA-R1 nuclear research reactor (Nuclear and Energy Research Institute – National Nuclear Energy Commission, IPEN/CNEN, São Paulo, Brazil), within a thermal neutron flux of 8.4×10^{12} cm^{-2} s^{-1} for 4 h. The induced activity was measured twice by gamma-ray spectrometry, after the approximate decay times of 10 and 20 days, using a high purity Ge detector with 50% relative efficiency (GEM50P4, ORTEC, Oak Ridge, USA). The results and respective expanded uncertainties were obtained by the k_0-method applied using in-house software (Quantu).

Preparation of the reference material

The PCB samples (4.72 kg) were processed as follows: (1) manual separation to remove some components (heat sinks, batteries, and fans); (2) crushing using a toothed roll crusher, obtaining particles size ranging from 10 to 12 mm; the comminution process was performed using a (3) hammer mill followed by a (4) knife mill and a vibrating cup mill; (5) homogenization using a "Y"-shaped blender/homogenizer. Approximately 4.2 kg of the sample was placed into a homogenizer and mixed for 20 min. This procedure was repeated three times to ensure the homogeneity of the sample. Then, the material was placed in 104 previously demineralized polypropylene bottles (around 50 g each) and labeled. Details of each step and mass losses during the grinding process of the PCB samples are shown in Fig. 1.

The residual moisture was measured from the following experiment: three bottles were chosen randomly and approximately 1 g of sample taken from each bottle was dried in an oven for 24 hours at 105 °C. Then, the three portions were

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Table 1   Instrumental parameters for ICP OES analysis

Instrumental parameter	Operational condition
Integration time (s)	15 and 5 s for low and high wavelengths, respectively
RF applied power (kW)	1.15
Coolant gas flow rate (L min^{-1})	12.0
Auxiliary gas flow rate (L min^{-1})	0.50
Nebulizer gas flow rate (L min^{-1})	0.70
Sample introduction flow rate (mL min^{-1})	2.10
Nebulizer	Concentric
Spray chamber	Cyclonic
Analyte and wavelength (nm)	Ag I 328.068[a], Al I 308.215[a], As I 189.042[a], Au I 242.795[a], Ba II 455.403[b], Cr II 284.325[a], Cu I 327.396[a], Fe II 259.940[a], Ni II 231.604[a], Pb I 216.999[a], Sb I 217.581[a], Si I 212.412[a], Sn I 283.999[a], and Zn I 213.856[a]

[a] Axial viewing mode. [b] Radial viewing mode.
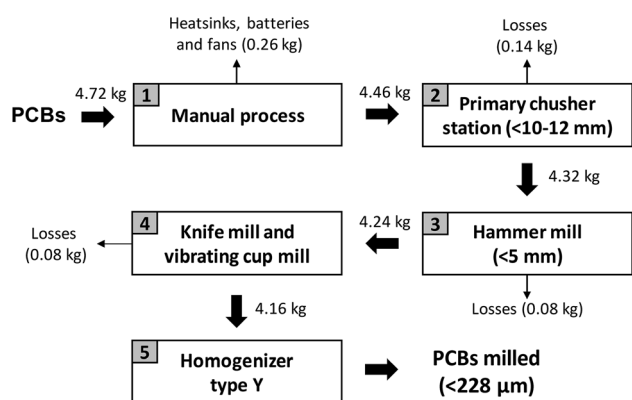

Fig. 1   Grinding sequence of the PCB units.

Table 2   Full factorial design experiments evaluated for concentrated aqua regia, inverted aqua regia, aqua regia 50% (v/v), nitric acid 14 mol L^{-1} and nitric acid 7 mol L^{-1}

Experiment	Sample mass (g)		Reagent volume (mL)	
	Real	Coded	Real	Coded
1	0.100	−1	8	−1
2	0.500	1	8	−1
3	0.100	−1	12	1
4	0.500	1	12	1
5	0.300	0	10	0
6	0.300	0	10	0
7	0.300	0	10	0

placed in a desiccator until reaching room temperature and after this, they were weighted again. The residual moisture was obtained from the difference between the initial and final mass.

Sample leaching procedure

Five acid mixtures were evaluated for the leaching of the elements from the PCB samples as follows: (1) concentrated aqua regia (AR), (2) inverted aqua regia (ARI), (3) aqua regia 50% v/v (AR 50% v/v), (4) 7 mol L^{-1} HNO$_3$ + H$_2$O$_2$ (HNO$_3$ 50% v/v) diluted with water, and (5) 14 mol L^{-1} HNO$_3$ (concentrated). A full factorial design at two levels [(2^2 + central point, 7 experiments)] was employed to assess the effects of the sample mass and acid volume on the PCB acid leaching. These experiments were repeated for all the mixtures mentioned above and a total of 45 experiments [(5 × 7) + 10 blanks] were performed.

The sample mass was varied from 0.100 (lower level, −1) to 0.500 g (higher level, +1) and reagent volume was varied between 8 (lower level, −1) and 12 mL (higher level, +1). In addition, experiments under the intermediate conditions (central point, 0) were performed using 0.300 g of sample and 10 mL of acid. Further details regarding the experimental design for leaching of PCB samples are given in Table 2.

The PCB sample mass (0.100–0.500 g) was accurately weighed directly into the PTFE/TFM vessels, and the reagent (8–

12 mL) was added. The microwave system equipped with a high-pressure single reaction chamber (SRC) allows processing samples of different masses with different acids within the same run and at the same temperature and pressure. The microwave heating program consisted of a temperature ramp up to 240 °C for 15 min, holding at 240 °C for 20 min, and cooling to room temperature for 10 min.

At the final step of the leaching, the solutions were quantitatively transferred to polypropylene tubes that were then filled up to 50 mL with ultrapure water. Then, the supernatant was separated for elemental determination of As and Au and two-fold diluted for Ag, Ba, Cr, Ni, Pb, Sb, and Zn determination, and four-fold diluted for Al, Cu, Fe, Si, and Sn determination. Multielement calibration solutions were prepared from stock standard solutions (1000 mg L^{-1}) by subsequent dilutions with aqua regia, inverted aqua regia or HNO$_3$ 1% v/v prior to ICP OES measurements. To evaluate the accuracy of the proposed method, analyte recovery tests were carried out for acid leaching, adding volumes of the standard solution to obtain the desired concentration of each analyte.

Minimum sample mass study

According to ISO Guide 35,[22] during the preparation of the candidate reference material (RM), it is important to carry out

the study on a minimum sample mass to ensure that the minimum portion of the sample will be representative during the analysis. Therefore, one bottle of RM was randomly selected and three sample masses were tested, *i.e.*, 100, 300 and 500 mg, in triplicate. The relative standard deviation (RSD) of the results obtained was used to evaluate the repeatability of the method and analysis of variance (ANOVA) was used to evaluate the results.

Results and discussion

Particles size distribution

Due to the diverse and complex nature of PCB residues, sample grinding was the most critical step in the preparation of the RM. According to Gerbase and Oliveira,[23] the average composition of a printed circuit board is 28% metals, 19% plastic, 4% bromine and 49% glass and oxide ceramic materials. The variety of PCBs, structures and electronic components connected to PCBs make it difficult to obtain a material with adequate homogeneity. The initial crushing of the PCBs into 10–12 mm particles was essential for the further comminution process (see Fig. 1, step 2). Fig. 2 shows the particle size distribution profile, indicating that after the completion of the entire grinding process, 90% of the particles had a size of less than 228 μm. The residual moisture was used for sample mass correction to dry mass. Three bottles were randomly selected for this study and approximately 1 g of dry sample of each one was used, resulting in a residual moisture of 0.41% ± 0.10%.

Acid leaching conditions

Initially, the experimental conditions for acid leaching (sample mass and acid volume) by microwave assistance were optimized using a full factorial design (2^2 + central point) for each acid mixture. The goal of these experiments was to establish the optimal conditions for acid leaching of PCB samples. In the evaluation of the variables, the desirability function was calculated to cover the concentration values for all analytes
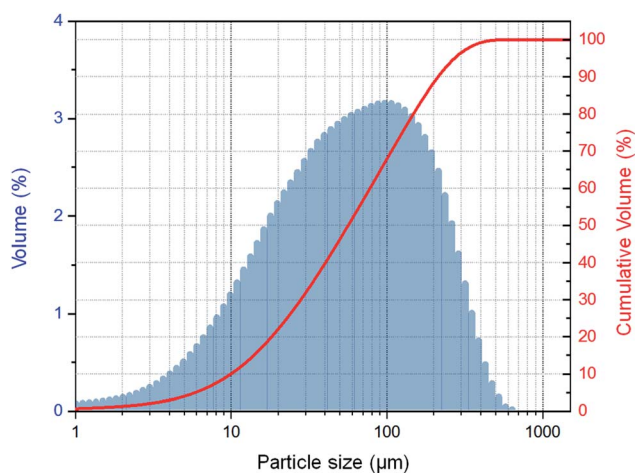
simultaneously (Ag, Al, As, Au, Ba, Cr, Cu, Fe, Ni, Pb, Sb, Si, Sn, and Zn). In this case, the concentrations obtained after ICP OES determinations (Table S1 in the ESI†) were converted to individual desirability (d_i) values coded from 0 (undesired response, lowest concentration) to 1 (desired response, highest concentration). Therefore, the individual desirability of each analyte was combined into a single response (D, global desirability). Then, the data matrix (**X**) was organized into 35 rows (the experiments) and 15 columns (d_i for each analyte and D), autoscaled and subjected to PCA using the Pirouette (Infometrix, Bothell, WA, USA) software package (version 4.5 rev. 1). Microsoft Excel was used for data processing and evaluation (see Table S2 in the ESI†).

The score and loading plots from the PCA are shown in Fig. 3. The explained variance due to the first and second principal components (PC1 and PC2) was 64% (44% for PC1 and 20% for PC2). The experiments using AR (purple circle) and AR 50% v/v (green circle) were positively correlated with most elements for the loadings of PC1 (except Ba and Zn). In addition, the highest values of D (black circle, highest concentrations for most analytes) were obtained from experiments 1c–7c evaluated for AR 50% v/v (see Table S2†). PC1 explains the greater variance of the data in the PCA and separated the experiments according to the highest concentrations of the analytes. As observed in Fig. 3, the use of diluted aqua regia was the best condition, leading to high scores for PC1. In the next step, these values of PC1 scores were used to calculate linear models and to find the optimal conditions for the PCB sample leaching.

Five linear models were calculated using the scores from the PC1 data (one for each reagent), and a 3D surface was shown. Fig. 4 shows the surface for AR 50% v/v, where the highest desirability values (D) were observed. The best results were

Fig. 2 Particle size distribution for the sample after the milling process.
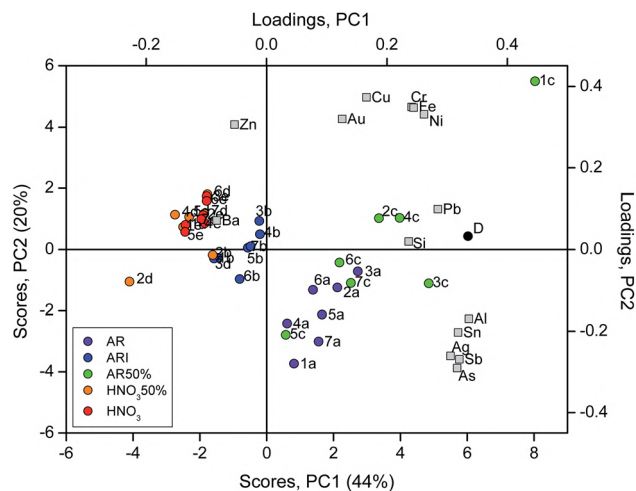
Fig. 3 Scores and loadings for PCA obtained using d_i (14 values of individual desirability) and D (global desirability) calculated for the concentrations determined after the leaching of the samples: concentrated aqua regia (AR, experiments 1a–7a), inverted aqua regia (ARI; experiments 1b–7b), aqua regia 50% v/v (AR 50% v/v; 1c–7c experiments), 7 mol L^{-1} HNO$_3$ + H$_2$O$_2$ (HNO$_3$ 50% v/v; experiments 1d–7d), and 14 mol L^{-1} HNO$_3$ (HNO$_3$; experiments 1e–7e).

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Fig. 4   Response surface for the PC1 data for the microwave-assisted leaching of the sample using aqua regia 50% v/v.

obtained using low sample mass for any volume of reagent. The optimal conditions for further experiments were fixed as follows: 0.100 g of sample and 10 mL of acid mixture (intermediate condition). The linear models for the other acid mixtures are presented in the ESI (Fig. S1–S4†).

Aqua regia (diluted or not) provided better leaching due to production of nitrosyl chloride (NOCl) and molecular chlorine (Cl) (see eqn (1)), which have high oxidizing power and are very reactive.[24]

$$HNO_3 + 3HCl \rightarrow NOCl + 2Cl + 2H_2O \qquad (1)$$
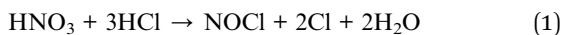
However, in the case of ARI (mixture of HNO_3 and HCl, 3 : 1 v/v, respectively), this reaction is incomplete and chloride ions remain free in solution. The chloride ions in the ARI solution complexed with metal ions (especially with Ag^+) forming insoluble compounds. The Ag concentrations determined for the full factorial design experiments are given in Table S1 in the ESI.†

Since the Ag ions were precipitated as silver chlorides in the presence of ARI, it became difficult to determine Ag by ICP OES. Due to the lower oxidizing power of HNO_3 and HNO_3 50% v/v 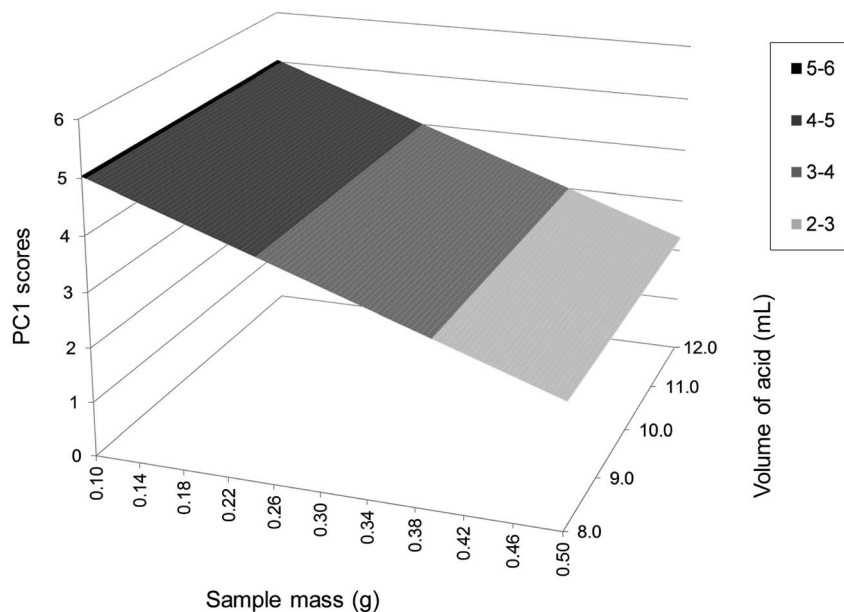leading to low Ag leaching it was also not possible to determine Ag using these reagents (see Table S1 for details†). From Fig. 3, it is observed that the experiments performed with ARI, HNO_3 50% v/v and HNO_3 led to negative scores for PC1 and were inversely correlated with D that led to positive loadings values for PC1. HNO_3 is a strong acid and a powerful oxidizing agent for most elements, but not for noble metals (i.e., Ag) and elements that are passivated in the presence of concentrated HNO_3 (e.g., As, Al, Cr, Fe, and Sb).[24]

Table 3   Concentrations determined (mean ± standard deviation, $n = 3$) for Ag, Al, As, Au, Ba, Cr, Cu, Fe, Ni, Pb, Sb, Si, Sn, and Zn using ICP OES for different mass fractions

Element (% m m^{-1})	100 mg	RSD (%)	300 mg	RSD (%)	500 mg	RSD (%)	p-Value
Ag	0.09 ± 0.01	11	0.034 ± 0.005	15	0.018 ± 0.002	11	0.000025
Al	6.3 ± 0.5	8	5.9 ± 0.7	11	4.1 ± 0.3	8	0.0025
As (mg kg^{-1})	32 ± 2	5	36 ± 2	5	34 ± 1	4	0.089
Au (mg kg^{-1})	146 ± 54	37	116 ± 46	39	111 ± 20	18	0.5145
Ba	0.58 ± 0.04	6	0.61 ± 0.03	5	0.65 ± 0.02	4	0.1072
Cr	0.41 ± 0.02	5	0.6 ± 0.1	17	0.39 ± 0.08	22	0.0194
Cu	14.6 ± 0.3	2	19 ± 3	15	22 ± 4	20	0.0522
Fe	7.7 ± 0.5	6	8 ± 1	14	10 ± 3	28	0.3333
Ni	0.46 ± 0.02	4	0.57 ± 0.03	6	0.43 ± 0.06	15	0.0070
Pb	1.28 ± 0.06	5	1.17 ± 0.03	3	1.29 ± 0.09	7	0.1182
Sb	0.80 ± 0.06	8	0.6 ± 0.1	19	0.39 ± 0.03	7	0.0016
Si	4.3 ± 0.6	14	1.5 ± 0.1	8	0.84 ± 0.02	2	0.000049
Sn	4.4 ± 0.6	14	4.9 ± 0.8	17	4.5 ± 0.4	9	0.6173
Zn	2.45 ± 0.05	2	3.2 ± 0.3	11	2.3 ± 0.4	19	0.0079

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Minimum sample mass study

A minimum sample mass study was carried out using 100, 300 and 500 mg of the PCB sample for determination of the mass fraction of Ag, Al, As, Au, Ba, Cr, Cu, Fe, Ni, Pb, Sb, Si, Sn, and Zn, using triplicate values, and the results are presented in Table 3. According to ISO Guide 35,[22] ANOVA was applied considering the 95% confidence level, and for As, Au, Ba, Cu, Fe, Pb, and Sn, no significant difference was observed among the results ($p > 0.05$; $F_{calculated} < F_{critical}$). In most cases, RSD values increased with the increase of the evaluated mass and therefore 100 mg was established as the minimum sample mass for further studies. This result agrees with the optimal condition fixed for the sample mass after optimization of this condition in the acid leaching conditions section.

Acid leaching and ICP OES analysis

After defining the best acid solution and the condition for leaching 14 elements, three samples were randomly selected from the RM prepared and analyzed in triplicate. The samples were subjected to acid leaching using diluted aqua regia (50% v/ v) in the microwave system employed. Hydrometallurgical processes with aqua regia are mainly used for recycling the metallic fraction from PCBs where the leaching of metals is profitable (particularly for precious metals).[25,26] One of the aims of the present study was to develop a method for acid leaching and simultaneous determination of several elements including toxic elements (As, Cd, Cr, and Pb), precious metals (Au and Ag), and economically strategic elements (*i.e.*, Cu) as already carried out in several studies reported in the literature.[26]

In addition, due to the incomplete digestion, the samples were also analyzed by INAA. Table 4 shows the concentration determined by ICP OES and INAA methods. According to acid leaching and ICP OES analysis, the lowest concentration

determined was found for As (34 mg kg^{-1}), whereas the highest concentration was observed for Cu (12%). The relative standard deviation (RSD) of the analyte concentration values was lower than 10%, except for Ag, Au, Cr and Sn. A paired *t*-test was applied to compare the results for acid leaching under microwave radiation and the INAA method for each analyte. In Table 4, the values with the same letter in the row are statistically similar and those with different letters are significantly different according to the *t*-test with the 95% confidence level. Only for Sn, no significant difference was observed. Nevertheless, for Ag, Au, Cr, Fe, Sb, Sn, and Zn, the results for the leaching procedure were within the range of concentration values obtained by INAA.

Tests of analyte recovery were performed to assess the accuracy of the method. Table 5 shows the recoveries calculated

Table 5 Analyte recovery experiments for microwave acid leaching

Analyte (mg kg^{-1})	Added	Determined ± standard deviation	Recovery (%)
Ag	6	5.3 ± 0.1	89
Al	60	58.9 ± 0.6	98
As	9	8.2 ± 0.6	91
Au	1	0.91 ± 0.01	91
Ba	10	10.3 ± 0.7	103
Cr	10	8.8 ± 0.4	88
Cu	100	87.1 ± 0.8	87
Fe	60	60 ± 2	100
Ni	10	8.4 ± 0.5	84
Pb	20	17 ± 1	87
Sb	10	10 ± 1	101
Si	40	36.4 ± 0.5	91
Sn	40	37.0 ± 0.4	93
Zn	30	25 ± 2	85

Table 4 Comparison of the concentrations (% m m^{-1}) determined by INAA and ICP OES after PCB samples subjected to leaching using aqua regia 50% (v/v) and microwave oven assistance[a]

Analyte (% m m^{-1})	ICP OES mean ± standard deviation	INAA Mean ± standard deviation	Range (relative expanded uncertainty)
Ag	0.09 ± 0.01a	0.08 ± 0.01b	0.07 (6.0%)–0.11 (9.4%)
Al	5.5 ± 0.3	—	—
As (mg kg^{-1})	34 ± 2	—	—
Au (mg kg^{-1})	106 ± 39b	179 ± 50a	98 (7.2%)–274 (12%)
Ba	0.62 ± 0.03b	0.73 ± 0.07a	0.57 (17%)–0.85 (18%)
Cr	0.28 ± 0.04b	0.37 ± 0.07a	0.28 (11%)–0.53 (6.2%)
Cu	12.2 ± 0.9	—	—
Fe	5.3 ± 0.4a	5.3 ± 1.5b	3.9 (5.8%)–9.5 (10%)
Ni	0.37 ± 0.03	—	—
Pb	1.16 ± 0.08	—	—
Sb	0.56 ± 0.02b	0.58 ± 0.06a	0.40 (6.8%)–0.65 (7.0%)
Si	3.2 ± 0.2	—	—
Sn	3.8 ± 0.5a	3.5 ± 0.3a	3.1 (26%)–3.9 (12%)
Zn	2.1 ± 0.2a	1.8 ± 0.4b	1.3 (5.6%)–2.6 (5.2%)

a — not determined.

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for all elements added to leach the PCB samples. The recoveries varied from 84% for Ni to 103% for Ba. For all of the analytes, the recovery values are acceptable and ranged from 80 to 120%, demonstrating that the method was effective for determination of the analytes by ICP OES.

Since there is no CRM available for printed circuit boards (or similar electronic waste) and the composition of such electronic waste is diverse and complex, it is very difficult to verify the element concentrations in the material. Optimization of the best acid reagent and microwave radiation at high temperature (240 °C) have been explored to leach the investigated elements as much as possible. It can be inferred that this developed procedure was effective for acid leaching of the PCB samples and to obtain reliable results.

Conclusion

The first part of this study describes an analytical procedure for the preparation of a RM of electronic waste to be used in laboratories that perform analysis of these samples. The procedure of grinding the samples was the most difficult and laborious part of this study. The grinding stages of PCBs demonstrate the difficulty of obtaining a homogeneous set of samples of electronic waste. The combination of design of experiments (DoE) and PCA analysis was essential to select the best type of acid and optimize the leaching conditions for the characterization of the candidate certified reference material. The acid leaching procedure using diluted aqua regia (AR 50% v/v) and microwave radiation for the determination of 14 elements in PCB samples was developed in this study. The use of a direct solid sample analysis method (INAA) also indicated that the leaching procedure is adequate for determining Ag, Au, Cr, Fe, Sb, Sn and Zn. The present study is a pioneering effort in the development of a RM for PCBs. Despite the difficulties faced by the grinding process and characterization of these materials, the results presented point out that it is possible to develop a RM for complex samples such as electronic waste. These results are important during the uncertainty determination of the concentrations of the analytes in the RM, presented by the authors in part 2, to meet the demand of the scientific community for quality assurance of the results obtained in WEEE analysis.

Conflicts of interest

There are no conflicts of interest to declare.

List of acronyms

ANOVA	Analysis of variance
AR	Aqua regia
ARI	Inverted aqua regia
CRM	Certified reference material
D	Desirability values
d_i	Individual desirability
DoE	Design of experiments

EEE	Electrical and electronic equipment
ICP	Inductively coupled plasma optical emission
OES	spectrometry
INAA	Instrumental neutron activation analysis
ISO	International organization for standardization
LOQ	Limit of quantification
PCA	Principal component analysis
PCB	Printed circuit boards
PGE	Platinum group elements
PTFE	Polytetrafluoroethylene
REE	Rare earth elements
RM	Reference material
RSD	Relative standard deviation
SRC	Single reaction chamber
WEEE	Waste electrical and electronic equipment

Acknowledgements

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3.1.2 Proposition of electronic waste as a reference material – part 2: homogeneity, stability, characterization, and uncertainties, Journal Analytical Atomic Spectrometry 34 (2019) 2402.

PAPER

Proposition of electronic waste as a reference material – part 2: homogeneity, stability, characterization, and uncertainties†

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In many cases involving the management of technological materials, such as electronic waste, characterization is performed to determine the precise elemental composition, as well as to detect harmful elements and substances. However, this is hampered by the lack of suitable reference materials for electronic waste. In the present study, a newly developed reference material for electronic waste according to the requirements imposed by ISO Guides 30–35 is discussed. Homogeneity, stability and characterization studies were performed using microwave-assisted acid leaching (aqua regia 50% v/v) and inductively coupled plasma optical emission spectrometry (ICP OES) for determination of Ag, Al, As, Au, Ba, Cr, Cu, Fe, Ni, Pb, Sb, Si, Sn, and Zn. One-way analysis of variance (ANOVA) at the 95% confidence level and linear regression were used as statistical parameters to obtain the uncertainty contributions to characterization (u_{char}), between-bottle homogeneity (u_{bb}), and short-term (u_{sts}) and long-term (u_{lts}) stability tests. The results from the collaborative trial allowed the estimated mass fraction and associated uncertainty (U_{RM}) to be obtained for each element monitored.

Introduction

The rapid growth in the consumption of materials, energy, and other resources for the production of electrical and electronic equipment (EEE) is becoming increasingly unsustainable.[1] The production of electronic devices such as computers, cell phones, and TVs has increased dramatically in recent times. In addition to the benefits of modern technology, there is growing concern about the negative impacts that the industry and its products are having on both society and the environment.[2,3] The production and final disposal of electronic waste (e-waste) is a challenge given its complexity. Obsolete electronic material is a difficult waste to handle and dispose-off due to its diverse composition of polymers, oxides, glass, wood, metals (including precious and toxic elements) and hazardous substances.[4]

Measuring e-waste composition is an important step towards its correct management. The comprehensive investigation of the elemental composition of e-waste benefits a set of sectors including practices of policies, manufacturing, reuse, refurbishment, and recycling.[4] In this case, obtaining traceable and reliable results for analytical methods of analysis is a critical challenge.[5,6] Among the different quality management systems,

reference materials (RMs) and certified reference materials (CRMs) are always emphasized to ensure the attainment and maintenance of reliable results, such as for method validation, uncertainty estimation and quality control.[7]

Over the years, interest in RMs/CRMs has grown, and a significant production of RMs (certified or not) would be required to meet the growing demand.[8] On the other hand, many laboratories still see CRM as an expensive product, which in most cases prevents its purchase and subsequent use.[9] Although the importance of using RMs/CRMs has been recognized for many years,[10,11] the academic literature and the current market lack studies on the production of reference materials for e-waste.

This study presents complementary information from Part 1, where the feasibility of RM production using printed circuit board (PCB) samples was evaluated. Part 1 showed the preparation of e-waste as a quality control material, and leaching procedure development (using aqua regia 50% v/v) for its characterization was accomplished. A full factorial design and principal component analysis (PCA) were applied to assess five different types of acidic solvents in sample leaching by microwave radiation. Considering the previous study presented in Part 1, the present paper (Part 2) describes four essential steps in the development of RMs: characterization, homogeneity, stability and uncertainty evaluation.[7] The electronic waste material was prepared meeting the minimum quality requirements imposed by ISO Guides 30–35.[12,13] Statistical treatment of data was applied to evaluate the homogeneity and stability results and the contribution of uncertainty for both processes

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was estimated. Therefore, from the collaborative trial, consensus values were obtained for the RM covering a wider range of precious and hazardous elements in electronic waste.

Materials and methods

Assessment of homogeneity

A homogeneity study is required for certification of a material to ensure that the batch of candidate materials (bottles) is sufficiently homogeneous. In this way, variations for both between and within bottles are included as uncertainty in the final consensus value for RM. Homogeneity testing was carried out according to ISO Guide 35,[13] considering two types of homogeneities: between-bottle and within-bottle. For between-bottle homogeneity assessment, ten bottles were randomly chosen, and 100 mg were analyzed in triplicate by ICP OES for determination of Ag, Al, As, Au, Ba, Cr, Cu, Fe, Ni, Pb, Sb, Si, Sn, and Zn. For the within-bottle homogeneity, ten subsamples were analyzed from one bottle randomly selected. For both tests, ANOVA at the 95% significance level ($\alpha = 0.05$) was used to evaluate the results and the F test was applied to verify the homogeneity. The uncertainty associated with the between-bottle inhomogeneity of the material (u_{bb}) was estimated as reported in ISO Guide 35,[13] using eqn (1):

$$s_{bb}^2 = \frac{MS_{among} - MS_{within}}{n_0} \quad (1)$$

where $u_{bb} = s_{bb}$ (between-bottle standard deviation); MS_{among} and MS_{within} are the mean squares for between- and within-bottle variability, respectively, from a one-way ANOVA; and n_0 the number of replicates. If the method repeatability was not sufficiently good ($MS_{among} < MS_{within}$), eqn (2) was applied as an alternative to estimate the uncertainty contributions (u_{bb}^*) from possible heterogeneity:

$$u_{bb}^* = \frac{\sqrt{MS_{within}}}{n} \sqrt[4]{\frac{2}{\nu MS_{within}}} \quad (2)$$

where MS_{within} is the mean square deviation within-bottle; n is the number of replicate subsamples per bottle; and νMS_{within} is the degree of freedom within-bottle.

Short- and long-term stability study

The stability testing also represents a crucial process for certifying reference materials. Reference materials should be sufficiently stable to ensure the property values for the storage expected lifetime of the material.[14] There are two types of stability studies to be considered: (i) short-term stability (e.g. stability of the material under extreme transport conditions) and (ii) long-term stability (e.g. stability of the material under long storage conditions, or shelf-life).[13,14] For the first study, 3 bottles were randomly selected and subjected for a short time to high temperatures and humidity. The bottles chosen were placed inside a glass container filled with water and kept in a conventional oven for 4 weeks, at a controlled temperature of 38 °C ± 2 °C and 99% ± 1% relative humidity. The samples were analyzed in triplicate before and at the end of the experiment for determination of the elements. Long-term stability

was performed using 3 bottles randomly selected and stored at room temperature (25 °C). The samples were analyzed in triplicate at the beginning of the experiment and monitored periodically, every two months, for 8 months (5 analyses). For these studies the property values were monitored over time under a single set of storage conditions, and the stability was evaluated using ANOVA and linear regression (univariate linear model) to estimate the rates of change and significant differences over time according to ISO Guide 35.[13] The regression parameters can be calculated using the following equations (eqn (3)–(7)):

$$b_1 = \frac{\sum_{i=1}^{n}(x_i - \bar{x})(y_i - \bar{y})}{\sum_{i=1}^{n}(x_i - \bar{x})^2} \quad (3)$$

$$b_0 = \bar{y} - b_1\bar{x} \quad (4)$$

$$s(b_1) = \frac{s}{\sqrt{\sum_{i=1}^{n}(x_i - \bar{x})^2}} \quad (5)$$

$$s^2 = \frac{\sum_{i=1}^{n}(y_i - b_0 - b_1 x_i)^2}{n - 2} \quad (6)$$

$$s(b_0) = s(b_1)\sqrt{\frac{\sum_{i=1}^{n}x^2}{n}} \quad (7)$$

where b_1 and b_0 are the slope and intercept, respectively; x corresponds to the time of experiment and y to the analyte mass fraction; and $s(b_1)$ and $s(b_0)$ are the standard errors in b_1 and b_0, respectively.

Characterization of the electronic waste material

For characterization of the prepared material, an interlaboratory study using many participants was performed. A bottle of the material was provided to 31 laboratories selected based on demonstrated competence for analysis and that agreed to participate in the collaborative trial. Along with the reference material, instructions for the correct sample storage, elements to be determined, the number of independent replicates for each analyte ($n = 6$), and one analytical procedure suggested for sample preparation (if applied) were documented (see more details in Part 1). Outlying results (atypical values from the observed and measured results) were identified by the Grubbs test[15,16] at the 95% confidence level to remove individual replicates among bottle averages. The Cochran test was performed at the 95% confidence level and the z-score was calculated to evaluate interlaboratory variations (reproducibility problems) for each analyte and laboratory.

Estimation of measurement uncertainty

The measurement uncertainty with a property value of the reference material was provided by the combination of each

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Element (% m m^{-1})	p-Value	u_{bb}
Ag (mg kg^{-1})	0.082	16.06
Al	0.015	0.16
As (mg kg^{-1})	0.0082	1.05
Au (mg kg^{-1})	0.87	17.91
Ba	0.030	0.01
Cr	0.43	0.11
Cu	0.017	1.12
Fe	0.16	0.51
Ni	0.28	0.04
Pb	0.00032	0.03
Sb	0.0087	0.02
Si	0.11	0.13
Sn	0.24	0.22
Zn	0.016	0.14

individual uncertainty associated with characterization (u_{char}), between-bottle homogeneity (u_{bb}), and short-term (u_{sts}) and long-term (u_{lts}) stability studies. The combined uncertainty (U_{RM}) for the electronic waste material was calculated according to ISO Guide 35 (ref. 13) as shown in eqn (8) by the square root of the quadratic sum of each measured uncertainty, with coverage factor $k = 2$ for the 95% confidence level.

$$U_{RM} = k\sqrt{u_{char}^2 + u_{bb}^2 + u_{sts}^2 + u_{lts}^2} \qquad (8)$$

Results and discussion

Homogeneity study

During the RM preparation, the homogeneity study is an important step associated with size and distribution of the
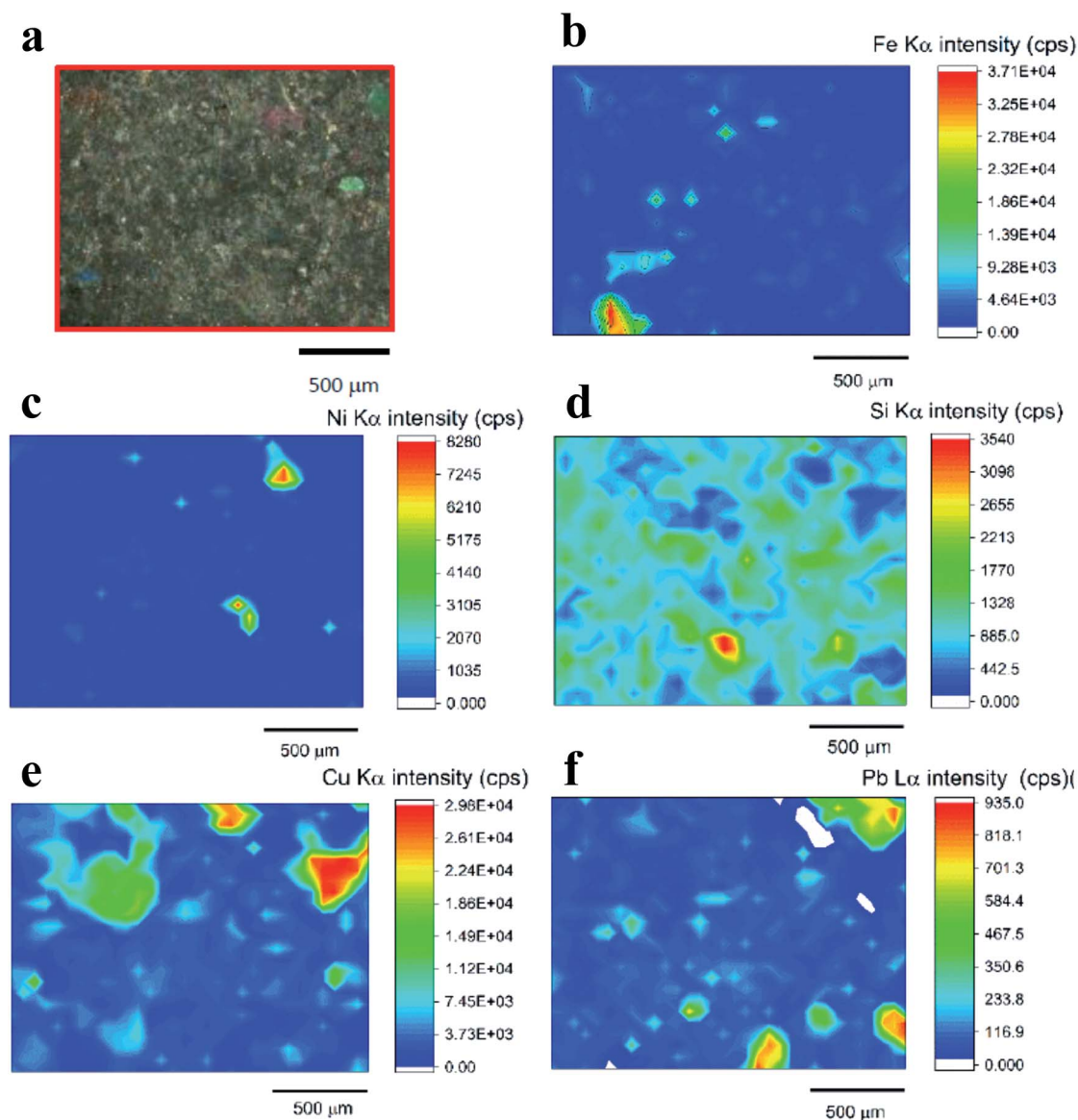

Fig. 1 Examples of elemental distribution for the RM of electronic waste obtained by X-ray fluorescence analysis. Mapped area in the sample (a), and chemical mapping images for Fe (b), Ni (c), Si (d), Cu (e), and Pb (f).

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Table 2 Statistical parameters obtained by ANOVA and estimated uncertainty for the short-term study (u_{sts})

Element (% m m^{-1})	p-Value	u_{sts}
Ag (mg kg^{-1})	0.071	49
Al	0.00019	0.3
As (mg kg^{-1})	0.11	1.4
Au (mg kg^{-1})	0.58	17
Ba	0.28	0.02
Cr	0.13	0.05
Cu	0.00015	0.6
Fe	0.13	0.5
Ni	0.81	0.03
Pb	0.22	0.05
Sb	0.0010	49
Si	0.03	0.3
Sn	0.061	1.4
Zn	0.092	17

particles in the sample and therefore it was considered during uncertainly determination in association with the concentration of each analyte in the minimum sample mass used for

analysis. To evaluate the between-bottle homogeneity, one-way ANOVA at the 95% significance level ($\alpha = 0.05$) was applied. Table S1 in the ESI† shows the results and no statistical differences for the concentrations of Ag, Au, Cr, Fe, Ni, Si, and Sn were observed. On the other hand, significant variations were found for Al, As, Ba, Cu, Pb, Sb, and Zn. The statistical parameters for ANOVA and uncertainty calculated using eqn (1) and (2), as discussed before, are shown in Table 1.

In order to obtain more details about the homogeneity of the sample, a microanalysis by X-ray fluorescence (Orbis PC Micro-XRF Analyzer, EDAX model) was performed. For this purpose, direct analysis of the sample was carried out with a pellet (15 mm diameter) obtained using 500 mg of the sample after pressing under 10 tons for 5 min. The chemical mapping (32 × 25 mm matrix) on the pellet surface was made for Cu, Fe, Ni, Si, and Pb. Fig. 1 shows the region of the mapped area (Fig. 1a), as well as the distribution maps of the corresponding elements (Fig. 1b–f). The chemical mapping for Fe, Ni, and Si, which did not present significant differences in the homogeneity testing, shows small particles distributed on the sample surface (Fig. 1b–d), while for
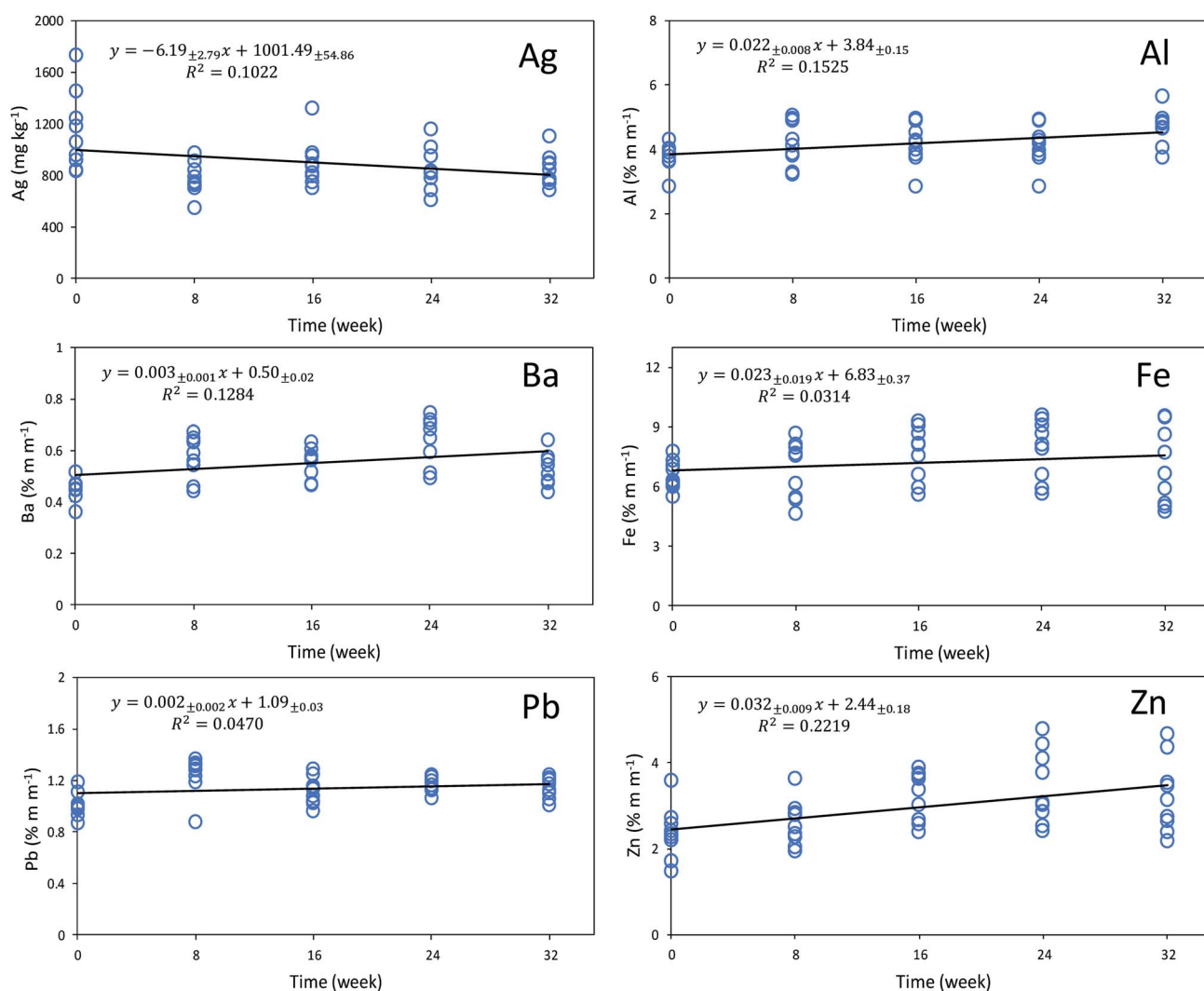

Fig. 2 Regression models for long-term stability testing.

Table 3 Results for the *t* test obtained for ICP OES analysis and estimated uncertainty for the long-term stability study (u_{lts})

Element (% m m^{-1})	$|b_1|$	$t_{0.95,n-2} \times s(b_1)$	u_{lts}
Ag (mg kg^{-1})	0.0041	0.0083	90
Al	0.14	0.18	0.3
As (mg kg^{-1})	1.59	2.12	1.6
Au (mg kg^{-1})	1.38	10.44	19
Ba	0.019	0.035	0.04
Cr	0.0017	0.026	0.06
Cu	0.11	0.10	2.2
Fe	0.15	0.26	0.6
Ni	0.026	0.025	0.04
Pb	0.016	0.057	0.05
Sb	0.020	0.017	0.04
Si	0.13	0.23	0.17
Sn	0.012	0.25	0.3
Zn	0.22	0.16	0.30

Cu and Fe (Fig. 1e and f), particles with a high heterogeneous distribution were observed (particles ≥ 500 μm).

Short- and long-term stability study

After RM production, it is common to transport the material to the location of use, as well as to store it for extended periods by RM users, at the RM producer's premises or by distributors. Since it is not possible to predict all changes that may occur in the material after preparation, the stability testing can introduce in the final consensus value significant differences that may be observed at the time of the application of the RM. In this evaluation, the part of the electronic waste material, the instability effects of the prepared material under adverse transport

conditions and changes in elemental composition during storage were taken into account.

For assessment of short-term stability, 3 bottles were subjected to high temperature and relative humidity conditions for 4 weeks. In the beginning and after this period the samples were prepared (acid extraction using aqua regia 50% v/v) and analyzed by ICP OES. ANOVA at the 95% confidence level was performed on the data to evaluate the short-term stability of the RM. The results of ANOVA are shown in Table S2 in the ESI.† It is possible to observe that Ag, As, Au, Ba, Cr, Fe, Ni, Pb, Sn, and Zn presented no significant differences and can be considered stable over the evaluated period. Except for Al, Cu, Sb, and Si, $F_{calculated} > F_{critical}$ that an instability was observed probably related to inhomogeneity of the material or instability of the measurement system, such as equipment or calibration. Table 2 shows some statistical parameters from ANOVA and the uncertainty calculated using the linear regression analysis for the short-term stability of the RM. The uncertainty was estimated from the standard error of the univariate liner model multiplied by the time of analysis, that is, 4 weeks.

The results for the long-term stability study to estimate the uncertainty related to the shelf-life of the RM were also analyzed by one-way ANOVA at the 95% significance level ($\alpha = 0.05$) and linear regression. Calculated *F* values smaller than the critical *F* value (2.21) were obtained for Ag, As, Au, Ba, Cr, Fe, Ni, Pb, Si, Sn, Zn, and the opposite results were obtained for Al, Cu, and Sb, which presented instability over the 32 weeks (8 months) they were monitored. The statistical parameters obtained by ANOVA are shown in Table S3 in the ESI.†

The univariate linear models obtained for Ag, Al, Ba, Fe, Pb, and Zn are shown in Fig. 2. The regression plots for the other elements monitored are depicted in Fig. S1 in the ESI.† In this case, the statistically significant changes for regression

Table 4 Procedures for reference values obtained by the laboratories during the interlaboratory comparison[a]

Element	AR 50% (v/v) and MWAE	AR 50% (v/v) and DB	AR and MWAE	AR and DB	AR and SB	AR and UB	HNO$_3$ and HClO$_4$ (3 : 1 v/v), and DG	Analytical technique
Ag	X	X	X	X		X		ICP OES, ICP-MS, INAA
Al	X		X	X	X	X		ICP OES, HR-CS FAAS
As	X	X				X		ICP OES, HG-AAS
Au	X		X			X		ICP OES, ICP-MS, INAA
Ba	X	X		X	X	X		ICP OES, ICP-MS, INAA
Cr	X	X	X	X		X		ICP OES, ICP-MS, HR-CS FAAS, INAA
Cu	X	X	X	X	X	X	X	FAAS, ICP OES, HR-CS FAAS
Fe	X		X	X	X	X	X	FAAS, ICP OES, HR-CS FAAS, INAA
Ni	X	X	X	X	X	X		ICP OES, ICP-MS, HR-CS FAAS
Pb	X	X	X	X	X	X		ICP OES, ICP-MS, HR-CS FAAS
Sb	X	X	X	X		X		ICP OES, ICP-MS, HR-CS FAAS, INAA
Si	X					X		ICP OES
Sn	X	X	X	X	X	X		ICP OES, ICP-MS, HR-CS FAAS, INAA
Zn	X	X	X	X	X	X	X	FAAS, ICP OES, ICP-MS, HR-CS FAAS, INAA

[a] AR: aqua regia; MWAE: microwave-assisted extraction; DB: digester block; SB: sand bath; UB: ultrasonic bath.

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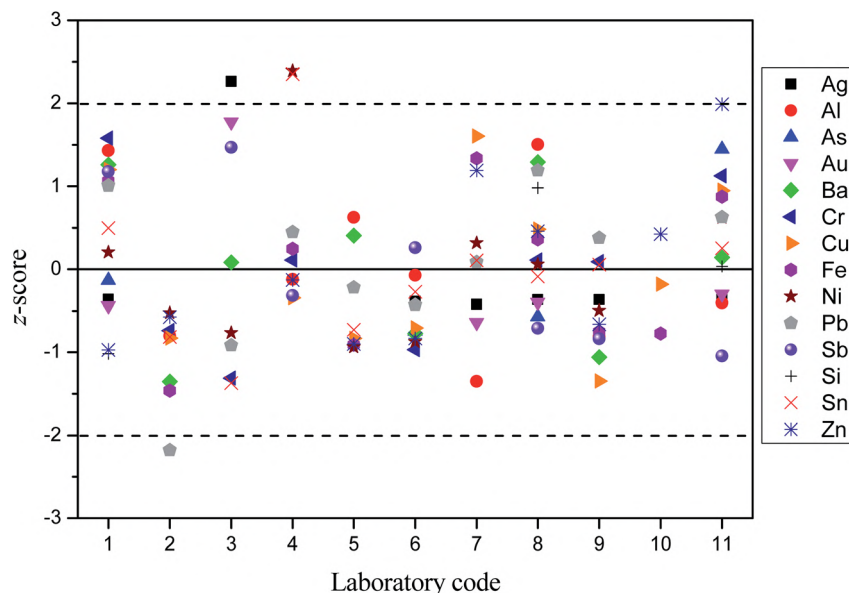This journal is © The Royal Society of Chemistry 2019

Fig. 3 z-Scores plot for the results from laboratories participating in the collaborative trial for comparison of the mass fraction of the elements monitored.

assumptions as discussed in the Materials and methods (eqn (3)–(7)) were evaluated by a t-test with the two-tailed critical value of Student's t for $n-2$ degrees of freedom at the 95% level of confidence. The t statistics for the absolute value of the slope, $|b_1|$, can be calculated using eqn (9):

$$t_{b_1} = \frac{|b_1|}{s(b_1)} \quad (9)$$

and if the slope, $|b_1|$, is smaller than the product of t factor ($t_{0.95,n-2}$) with standard error in b_1, $s(b_1)$, it means that no instability was observed for the elemental testing. Table 3 shows the statistical parameters calculated and the estimated uncertainty for the long-term stability study by the standard deviation of regression multiplied by the shelf-life of the experiment (32 weeks).

Interlaboratory comparison

After characterization of the reference material through the collaborative trial, the consensus values for the electronic waste material were estimated using the results provided by the participating laboratories. A bottle was sent to each laboratory with 14 elements to be monitored (Ag, Al, As, Au, Ba, Cr, Cu, Fe, Ni, Pb, Sb, Si, Sn, and Zn) and one method of acid extraction: aqua regia (50% v/v) and microwave oven assistance, with a maximum temperature of 240 °C for 45 min. Prior to sending samples to each laboratory, this method was developed and validated (see Part 1). A total of 11 laboratories reported results, varying according to the elements determined, that is, 3 (Si) to 10 (Cu, Ni, Pb, Sn, and Zn) results applying different analytical techniques: flame atomic absorption spectrometry (FAAS), hydride generation atomic absorption spectrometry (HG-AAS), inductively coupled plasma optical emission spectrometry (ICP OES), inductively coupled plasma mass spectrometry (ICP-MS), high-resolution continuum source flame atomic

absorption spectrometry (HR-CS FAAS), and instrumental neutron activation analysis (INAA). Table 4 summarizes the sample preparation procedures and analytical techniques applied in the collaborative trial.

According to ISO/IEC 17043:2010,[17] the collaborative trial involves the use of interlaboratory comparisons to determine the performance of each laboratory. In order to qualify the results, the z-scores, commonly used in proficiency tests to assess the performance of participants according to ISO Guide 35, were calculated.[13] This index represents a measure of the relative deviation of the laboratory result from the value designated in the study. The Grubbs test at the 95% confidence level was previously applied to identify and eliminate outliers of the results from each laboratory. If the z-score values are closer to

Table 5 Estimation of standard uncertainties of characterization (u_{char}), between-bottle homogeneity (u_{bb}), short-term stability (u_{sts}), long-term stability (u_{lts}), and associated uncertainty (U_{RM}), where $k = 2$ (for the 95% confidence level) for the mass fraction of each element in the reference material of electronic waste

Element (% m m^{-1})	u_{char}	u_{bb}	u_{sts}	u_{lts}	U_{RM}
Ag (mg kg^{-1})	11.87	16.06	48.89	89.60	208.01
Al	0.35	0.16	0.28	0.25	1.08
As (mg kg^{-1})	4.77	1.05	1.42	1.64	10.69
Au (mg kg^{-1})	16.43	17.91	17.08	19.04	70.56
Ba	0.04	0.01	0.02	0.04	0.13
Cr	0.03	0.11	0.05	0.06	0.28
Cu	1.33	1.12	0.61	2.16	5.67
Fe	0.38	0.51	0.52	0.62	2.05
Ni	0.04	0.04	0.03	0.04	0.15
Pb	0.07	0.03	0.05	0.05	0.20
Sb	0.06	0.02	0.03	0.04	0.15
Si	0.03	0.13	0.18	0.17	0.57
Sn	0.22	0.22	0.22	0.30	0.97
Zn	0.03	0.14	0.14	0.30	0.71

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zero, better will be the reported results. Laboratory measurements within the limit of $|z| \pm 2$ were considered acceptable, and z-score results within the range $3 < |z| < 3$ were considered questionable and unsatisfactory, and not included in the final concentration calculated. Fig. 3 shows the z-score values for each laboratory and for the elements monitored.

Applying the z-scores, it was possible to visualize the presence of reproducibility problems (interlaboratory variation) for some elements and laboratories that presented results that are extreme and, therefore, can be eliminated. For instance, results

of Pb for laboratory 2, Ag for laboratory 3, and Ni and Zn for laboratory 4 were considered anomalous data and removed from the original set. In addition, the Cochran test to evaluate the homogeneity of variances was applied after removing outliers by the Grubbs test and z-score.

Estimated mass fraction and associated uncertainty

To assess the standard uncertainties of a specific RM, all factors that could contribute significantly to the associated uncertainty in the property values of the material must be included. In principle, according to ISO Guide 35,[13] the value of a certified property for the RM can be affected by the characterization process, by actual variations between bottles (heterogeneity), changes during transportation and changes over time (shelf-life) and during subsequent storage. Assuming all these sources of variation, the associated uncertainty for the property value of the RM can be expressed by eqn (6), as discussed before in the Experimental section. Table 5 shows the values of standard uncertainty for characterization (u_{char}), between-bottle homogeneity (u_{bb}), short-term stability (u_{sts}), long-term stability (u_{lts}), and expanded uncertainty (U_{RM}).

Assignment of property values for each analyte was obtained by averaging the consensus values reported by the laboratories participating in the collaborative trial. The mass fraction and relative expanded uncertainty for all elements monitored are shown in Table 6. The calculated uncertainties imply greater reliability on the validation process of a measurement result, and the designated value presented with its uncertainty allows the use of the reference material candidate as a quality material

Table 6 Mass fraction of each element for electronic waste material and relative associated uncertainty with coverage factor $k = 2$ for the 95% confidence level

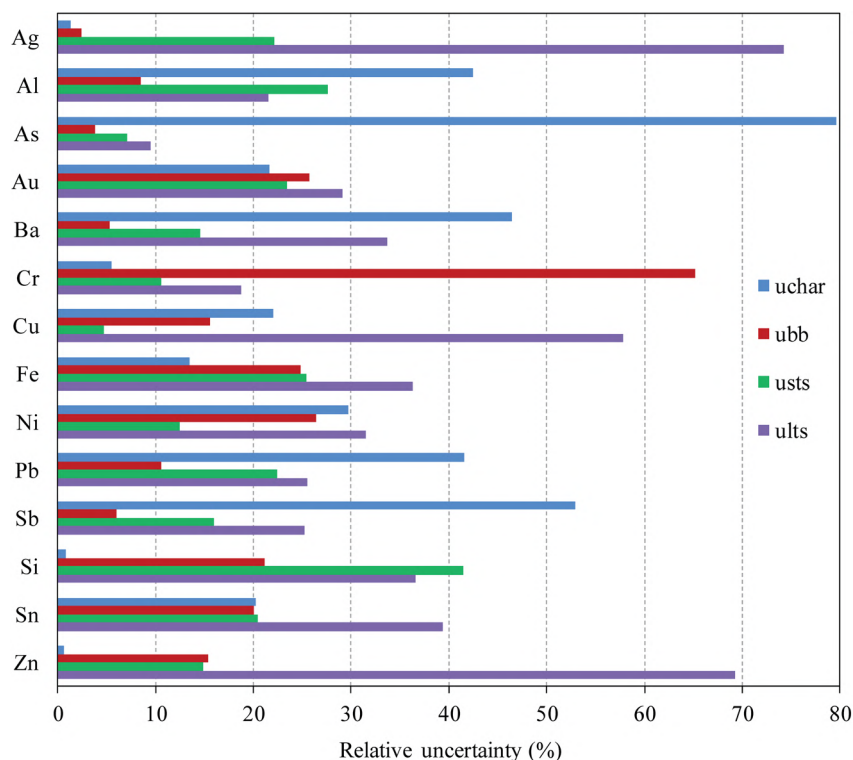| Element (% m m^{-1})	Mass fraction $\pm$ U_{RM}	U_{RM} (%)
Ag (mg kg^{-1})	880.04 $\pm$ 208.01	24
Al	4.80 $\pm$ 1.08	22
As (mg kg^{-1})	28.62 $\pm$ 10.69	37
Au (mg kg^{-1})	236.55 $\pm$ 70.56	30
Ba	0.50 $\pm$ 0.13	26
Cr	0.29 $\pm$ 0.28	96
Cu	14.08 $\pm$ 5.67	40
Fe	3.92 $\pm$ 2.05	52
Ni	0.42 $\pm$ 0.15	36
Pb	1.19 $\pm$ 0.20	17
Sb	0.45 $\pm$ 0.15	33
Si	1.45 $\pm$ 0.57	39
Sn	2.85 $\pm$ 0.97	34
Zn	1.36 $\pm$ 0.71	52

Fig. 4 Relative contribution of each component to the combined uncertainty for the elements monitored.

for assessment of the accuracy and/or precision of an analytical method.

By analyzing the uncertainty results, it is possible to point out the factors that influence the expanded uncertainty the most. One way to visualize these individual contributions is by calculating the relative contributions of each uncertainty. Although the combined uncertainty was calculated through the quadratic sum of these components (eqn (6)), it was possible to obtain the relative contribution of each component to the combined uncertainty by dividing each uncertainty by the combined uncertainty, as shown in Fig. 4.

All uncertainties obtained from the studies performed (homogeneity, stability and characterization) are of equal importance for the certification of property values for the reference material. Despite the fact that higher values of uncertainty are expected for characterization process values due to different methods in the collaborative trial, other studies may demonstrate sources of high uncertainty depending on the analyte monitored. Among the sources of contribution for the associated uncertainty (Table 5 and Fig. 4), the characterization process (u_{char}) for Al, As, Ba, Pb, and Sb and long-term stability (u_{lts}) for Ag, Au, Cu, Fe, Ni, Sn, and Zn presented the major contributions. On the other hand, the homogeneity study (u_{bb}) was the main contributor for Cr while Si was significantly influenced by the short-term stability (u_{sts}).

Conclusion

A new RM for quality control of technological material analysis was developed in this study. For Ag, Au, Cr, Fe, Ni, and Sn elements, the RM was considered homogeneous, and stable for adverse conditions of transport and for storage at room temperature. The participation of laboratories in the collaborative trial was essential to obtain the mass fraction of 14 elements. The certified values and the associated uncertainty ($k = 2$) for each element were 880.04 ± 208.01 mg kg^{-1} Ag, $4.80 \pm 1.08\%$ m m^{-1} Al, 28.62 ± 10.69 mg kg^{-1} As, 236.55 ± 70.56 mg kg^{-1} Au, $0.50 \pm 0.13\%$ m m^{-1} Ba, $0.29 \pm 0.28\%$ m m^{-1} Cr, $14.08 \pm 5.67\%$ m m^{-1} Cu, $3.92 \pm 2.05\%$ m m^{-1} Fe, $0.42 \pm 0.15\%$ m m^{-1} Ni, $1.19 \pm 0.20\%$ m m^{-1} Pb, $0.45 \pm 0.15\%$ m m^{-1} Sb, $1.45 \pm 0.57\%$ m m^{-1} Si, $2.85 \pm 0.97\%$ m m^{-1} Sn, and $1.36 \pm 0.71\%$ m m^{-1} Zn. Studies of homogeneity, short- and long-term stability, and characterization, with the uncertainties of the the RM, provided an appropriate quality control material for 880.04 ± 208.01 mg kg^{-1} Ag and 236.55 ± 70.56 mg kg^{-1} Au analysis in electronic waste. Despite the complexity of the material produced and entire certification process of property values, a pioneering RM for quality assurance of precious elements in technological materials has been developed.

Abbreviations

Acronyms related to the statistical parameters of the RM.

ANOVA	Analysis of variance
b_1	Slope of the univariate model for linear regression
b_0	Intercept of the univariate model for linear regression
CRM	Certified reference material
ISO	International Organization for Standardization
K	Coverage factor
MS_{among}	Mean square deviation between bottles
MS_{within}	Mean square deviation within a bottle
RM	Reference material
$s(b_1)$	Standard error for the slope (b_1) of the univariate linear model
$s(b_0)$	Standard error for the intercept (b_0) of the univariate linear model
s_{bb}	Standard deviation of the between-bottle component for the homogeneity study
U_{RM}	Expanded uncertainty associated with a property value of the RM
u_{bb}	Standard uncertainty associated with between-bottle variability
u_{char}	Standard uncertainty associated with a value assigned in a characterization study
u_{sts}	Standard uncertainty associated with short-term stability
u_{lts}	Standard uncertainty associated with long-term stability
νMS_{within}	Degree of freedom for mean square deviation within a bottle

Acronyms related to the RM and sample preparation.

AR	Aqua regia
DB	Digester block
EEE	Electrical and electronic equipment
MWAE	Microwave-assisted extraction
PCB	Printed circuit board
SB	Sand bath
UB	Ultrasonic bath

Acronyms related to analytical techniques.

FAAS	Flame atomic absorption spectrometry
HR-CS FAAS	High-resolution continuum source flame atomic absorption spectrometry
ICP-MS	Inductively coupled plasma mass spectrometry
ICP OES	Inductively coupled plasma optical emission spectrometry
INAA	Instrumental neutron activation analysis
XRF	X-ray fluorescence

Conflicts of interest

There are no conflicts of interest to declare.

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Acknowledgements

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3.A Appendix

Additionally, in order to validate the obtained results in this study, the concentrations of Ag, Ba, Cr, Cu, Ni, Pb, Sb, Sn and Zn, reported from one laboratory in the interlaboratory comparison, were used to compare with those obtained in the characterization of the proposed RM. In this case, the sample was leached using 0.100 g and 10 mL of aqua regia (50% v/v), and a block digester kept at 100 °C for 4 hours prior to ICP OES measurements. Table 3.1 shows the mass fraction obtained in the RM characterization in comparison with the results reported by the laboratory. The trueness for most analytes were within the acceptable range of 80 to 120%, except for Pb, Sb, Sn and Zn.

TABLE 3.1 Results obtained to validation of RM mass fraction using the concentrations (mean ± standard deviation, n = 6) reported in the characterization study.

Element (% m/m)	Mass fraction ± U_{RM}	Concentrations ± standard deviation	Trueness (%)
Ag (mg kg^{-1})	880.04 ± 208.01	750 ± 105	85
Ba	0.50 ± 0.13	0.56 ± 0.01	112
Cr	0.29 ± 0.28	0.34 ± 0.04	117
Cu	14.08 ± 5.67	16.13 ± 0.71	114
Ni	0.42 ± 0.15	0.45 ± 0.02	107
Pb	1.19 ± 0.20	1.52 ± 0.10	128
Sb	0.45 ± 0.15	0.55 ± 0.01	122
Sn	2.85 ± 0.97	1.25 ± 0.23	44
Zn	1.36 ± 0.71	2.14 ± 0.05	157

Despite these out-of-range results, the laboratory showed good results with adequate precision and accuracy for most elements. In addition, given the complex composition of the proposed RM, the sample preparation of this sample is not an easy task, which can impair the quantitative elemental analysis. Figure 3.2 shows the RM sample obtained after the acid leaching procedure (a) and the filtration (b) for determination of all analytes by ICP OES.
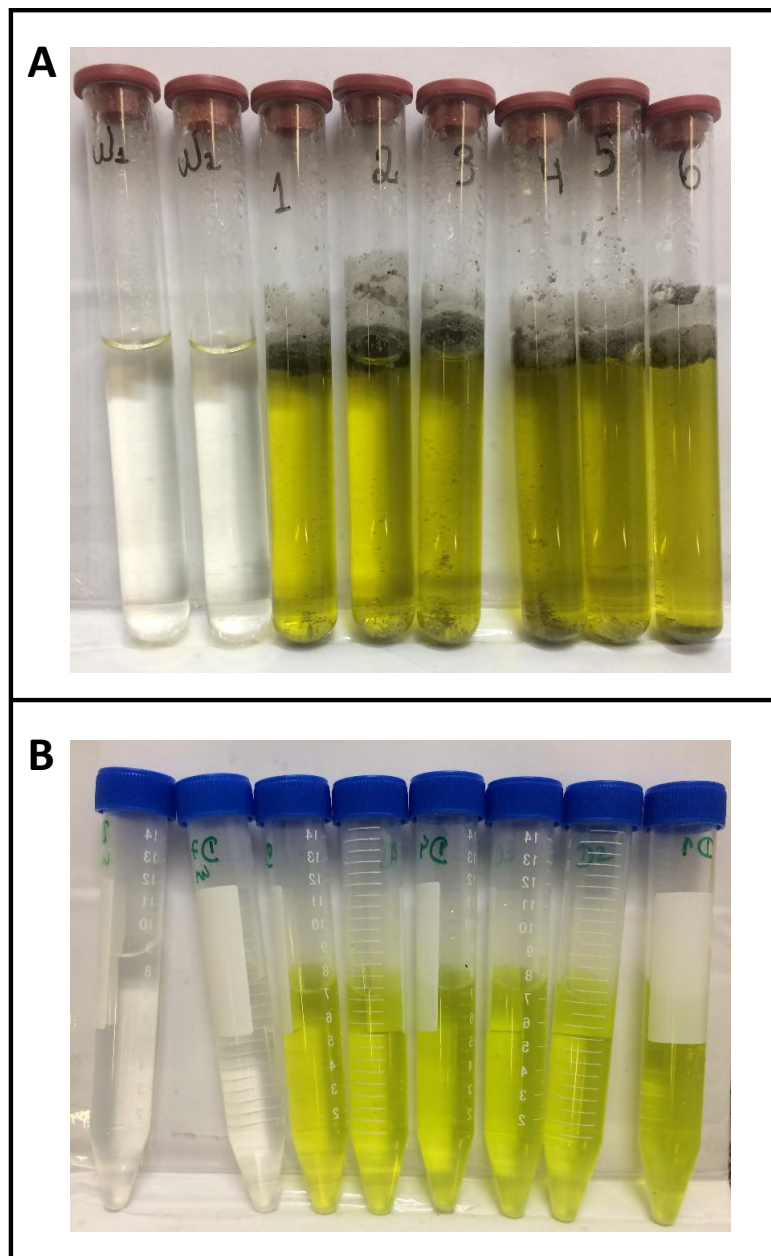
FIGURE 3.2 RM sample after the acid leaching (a), and the leached solutions obtained after filtration (b) prior to ICP OES measurements.

Chapter 4

Direct solid sample analysis of e-waste

4.1 Direct solid sample analysis

As most conventional analytical techniques are designed for liquid sampling and a large number of samples are naturally available in solid form, a sample preparation step is generally required to convert the samples into representative aqueous solutions prior to actual measurements. For this purpose, several methods have been employed using classic dry procedures, such as ash for organic materials, fusion for refractory inorganic materials and wet digestion or acid dissolution at high temperatures for organic and inorganic samples.[70] Furthermore, in order to eliminate various sample interferences, or enrich the concentration of the target components to suit the instrument's resolution skills, separation procedures and/or sample enrichment before measurements are sometimes necessary. These procedures have advantages and limitations that depend particularly on the type of sample, the analytes and their concentrations. Systematic errors due to contamination or loss by volatilization are among the most frequent issues and can directly affect the accuracy and precision of analytical results.[71,39] Considering the techniques intended for determination of trace and ultra-trace elements, a special care in sample preparation is crucial to the success of the method employed.[70]

In this context, the direct analysis of solid samples, with little or no chemical pretreatments, is a very attractive alternative. The analytical procedure is simpler and faster, thus increasing the sample throughput; less risk of contamination and/or analyte loss due to elimination (or, at least, significant reduction) of consumption of hazardous reagents; reduced waste generation; greater detectability, since the samples are not diluted; and the possibility of analyzing a small amount of sample, allowing studies of micro-homogeneity.[72,73]

In the particular field of elemental analysis, different analytical techniques are suitable for this task such as X-ray fluorescence (XRF),[74] electrothermal atomic absorption spectrometry (ETAAS),[75] graphite furnace atomic absorption spectrometry (GFAAS),[76] flame atomic absorption spectrometry (FAAS),[77] laser-

induced breakdown spectroscopy (LIBS),[78] laser ablation (LA) systems coupled to inductively coupled plasma optical emission spectrometry (ICP OES) and inductively coupled plasma mass spectrometry (ICP-MS),[79] which can be used for analysis directly.

In this chapter, a special emphasis is given to the plasma techniques (i.e. LIBS and LA-ICP) and XRF that were applied to the direct analysis of LCD and PCB samples. Therefore, in the following subsections, key aspects of fundamentals, principles and main applications of these techniques, as well as qualitative and quantitative aspects in direct solid sample analysis were briefly discussed.

4.1.1 Laser-based techniques

Due to the outstanding advantages of laser techniques, laser-based analytical methods have been in continuous expansion in all types of research fields. The analytical interest in these techniques has resulted primarily because of the multi-element analysis capability, the applicability to different sample types (i.e. gases, liquids, solids, suspensions and aerosols), the small amount of sample required (almost non-destructive), the speed of measurements, and the lack of exhaustive sample pretreatments.[78-80]

Laser-based techniques refer to the instruments in which a short-pulsed high-power laser beam is focused onto a sample surface to ablate a tiny fraction of it (hundreds of ng to a few mg) into a plasma, a particular state of matter characterized by high temperature (around 10,000K) and strong ionization.[78] Then, the ablated material is analyzed by measuring atomic/ionic emission in the induced plasma (LIBS) or by transporting the particles to another measurement system, such as the inductively coupled plasma (ICP).[78,79]

Laser-induced breakdown spectroscopy was introduced as an analytical technique at the beginning of the 1980s by Leon J. Radziemski and Tim R. Loree,[81,82] from the Los Alamos National Laboratories, New Mexico, USA. Since then, LIBS has been an appealing technique compared with many other types of elemental analysis, in which a simple instrumental setup to perform a LIBS measurement is required.[78] Figure 4.1 shows a schematic of a typical setup for LIBS illustrating the main components: (1) laser source energy; (2) mirrors and

lenses for focusing the laser beam onto the sample surface; (3) the sample holder that can be fitted into an ablation chamber; (4) optical fiber bundle to guide the plasma light to a spectrometer; (5) detection system (i.e. spectrometer and detector); and (6) computer for precise control of temporal events such as laser pulse triggering and spectrum recording.[80] In addition, there are some parameters that can be optimized to create a plasma which is in thermodynamic equilibrium and whose elemental composition is the same as that of the sample. Laser pulse energy and the diameter of the laser beam (spot size) are monitored simultaneously in the laser pulse fluence term (laser pulse energy per unit area, J cm^{-2}). And the gate delay, that is, the time between the laser incidence and the start for registering the emitted plasma light.[72,80,83]
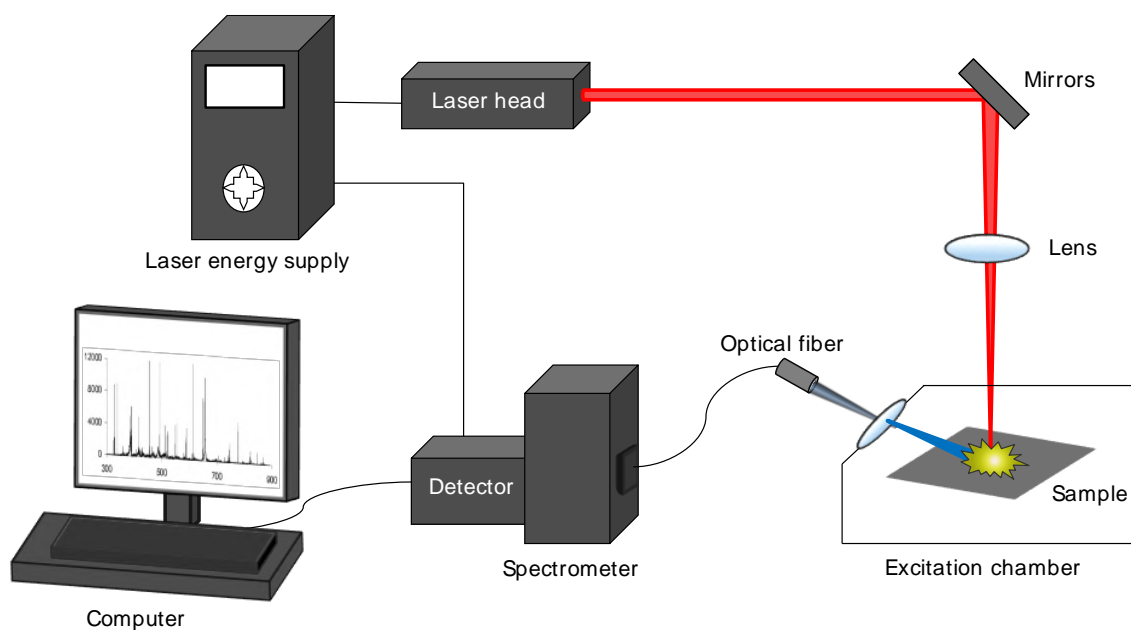

FIGURE 4.1 A typical LIBS setup.

Moreover, the possibility of coupling a laser ablation system with other analytical techniques also contributed to arouse interest in laser ablation processes. Laser ablation as a sampling technique coupled with well-established analytical techniques, such as ICP OES and ICP-MS, improved the analytical capacity for analysis of solid samples, and became an attractive alternative to acid digestion methods for chemical analysis.[84] Besides the advantages of a direct sampling technique as mentioned earlier, low limits of detection (LOD), high sensitivity and selectivity for the determination of trace elements, as well as isotope-ratio measurements (i.e. LA-ICP-MS) offers superior technology for direct

solid sampling in analytical chemistry.[79,85] Schematic of a typical laser ablation unit coupled to a ICP OES and/or ICP-MS detection is shown in Figure 4.2.
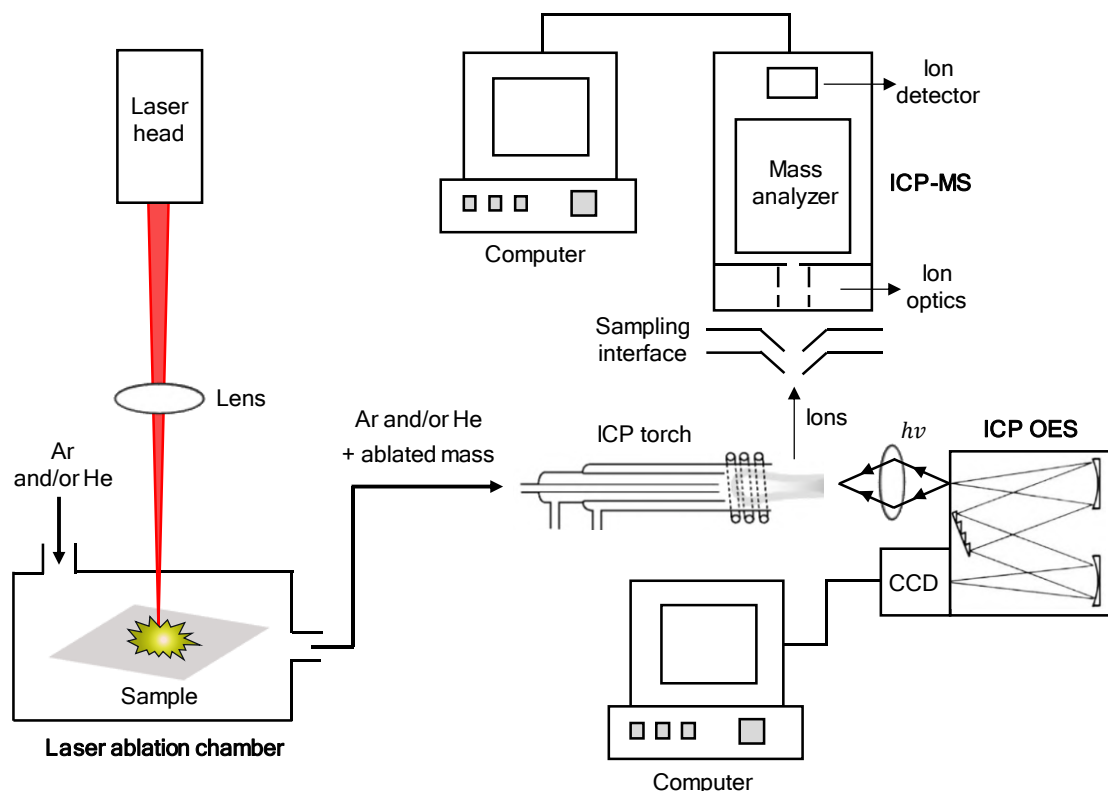

FIGURE 4.2 Experimental arrangement of LA-ICP OES and LA-ICP-MS systems.

Various types of matrices have been analyzed by LIBS and LA-ICP-MS/OES for qualitative and quantitative purposes. These techniques have attracted attention for interesting applications in different areas of study such as environment,[86,87] forensic,[88] agriculture,[89,90] food,[91,92] industrial,[93] biological[94] and e-waste.[95] The ability to make remote measurement in field environments is also one of the main advantages of LIBS. Among the out-of-the-lab applications, explosives monitoring, nuclear waste management, and space exploration are some examples.[96] And more recently, the combination of LA for ICP-MS/OES and LIBS into one integrated laser ablation system was introduced as a new laser-based technique, "tandem LA-LIBS". This system makes it possible to expand the elemental coverage (i.e. isotopic and emission signals) and increase the detection reliability, in which measurements from µg/kg (ppb) to % level matrix elements can be performed in a single ablation experiment.[97]

4.1.2 X-ray fluorescence

In general, XRF spectrometers are divided into two major branches depending on the detection system: the wavelength dispersive (WDXRF) detection mode and the energy dispersive detection (EDXRF). Both analytical techniques share the same basic principle of excitation of primary X-rays in the X-ray tube and secondary X-rays in the sample; optical components to guide, focus or shape the X-ray beam on the sample; and detection system to process and analyze the recorded XRF spectrum. The major variants for these techniques include features of the excitation source, optical components employed and the angle between them. WDXRF employs a crystal analyzer yielding higher energy resolution, precision, accuracy and sensitivity, whereas EDXRF employs detectors that are able to discriminate the energy of the X-rays that reach the detector. As a result, WDXRF spectrometer measure a single wavelength at any one time, while EDXRF register the total spectrum.[98,99] Figure 4.3 shows the basic configurations of WDXRF (Fig. 4.3a) and EDXRF (Fig. 4.3b) spectrometers.
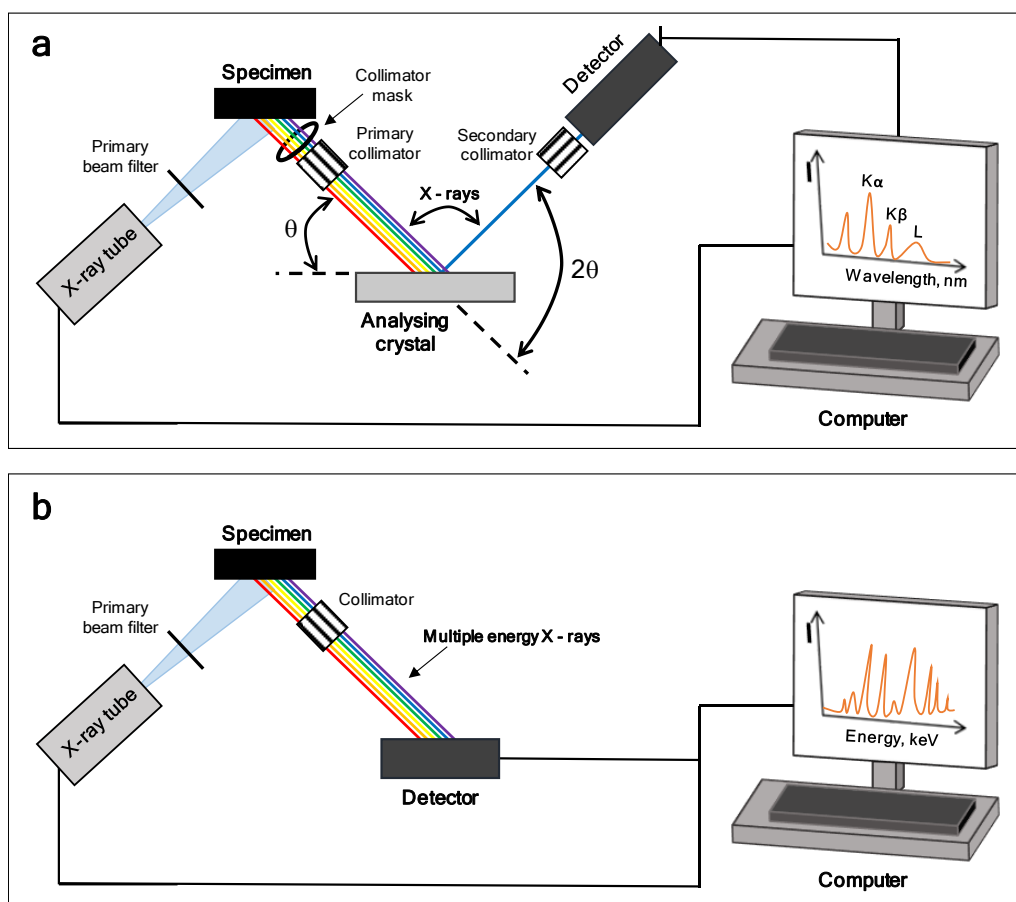

FIGURE 4.3 Basic configurations of WDXRF (a) and EDXRF (b) spectrometers.

Among X-ray-based methods, EDXRF is far more used than the WDXRF. The miniaturization of X-ray tubes and detectors allowed the manufacturing of portable XRF (P-XRF) spectrometers, which have aroused wide interests for its feasibility for *in situ* analysis. Because it can carry out non-destructive analysis at site or long-distancing monitoring, this technique has been especially practical for those objects that are hard to sample or unique, such as refractory alloys, archeological and art work.[100] Another variant of EDXRF is the micro X-ray fluorescence spectrometry (micro-XRF), where the X-ray beam is shaped/focused on the sample using collimators or slits that delimit the interrogated area. Some applications for the micro-XRF spectrometer include microanalysis or carry out scans in one or two dimensions, i.e. line or multiple scans, in order to obtain a microchemical image; the same is possible for LIBS and LA-ICP.[101,102]

4.1.3 Qualitative and quantitative analysis

LIBS, LA-ICP-MS/OES and XRF are without doubt attractive techniques for direct solid sampling of different form of samples. Both qualitative and quantitative analysis are possible; however, these techniques may suffer from severe matrix effects that can compromise the development of some analytical methods.[72]

The main matrix effects include spectral and non-spectral interferences. The spectral effects (i.e. spectral overlap or isotopic interference) can be circumvented by selecting an alternative emission line/isotope of the analyte, switching the spectrometer arrangement for a high resolution system (if possible), or using a reaction and/or collision cells to eliminate molecular interfering ions in LA-ICP-MS analysis. The non-spectral interferences are related to physical effects (e.g. particle size, irregular surface, sample moisture content, etc.) and chemical effects, where all of which occur within the sample.[72,99,103] In the case of the laser-based techniques, these effects also arise from the complex nature of laser–sample interaction and the laser characteristics (e.g., pulse duration, wavelength, fluence). For XRF methods, the thickness and surface uniformity of the sample, as well as the X-ray absorption and enhancement are relevant variables.[102]

In general, LIBS, LA-ICP-MS/OES and XRF have been considered robust and rapid techniques for obtaining qualitative information. These techniques are widely used for element identification, chemical profile distribution on sample surfaces, chemical speciation, among other applications.[72] However, calibration remains the Achilles' heel when dealing with direct solid analysis. To overcome the limitations involving quantitative methods, the development of new calibration strategies is a major current research area. Indeed, many calibration approaches have been widely used and recently proposed, including traditional, nontraditional and multivariate methods.

Regarding traditional approaches for univariate calibration, matrix-matching calibration (MMC), internal standardization (IS) and standard addition (SA) are some examples. Matrix-matching calibration is among the most used strategies, in which the standards are prepared for calibration using CRMs, a set of samples with reference concentrations or any solid standards with a similar matrix composition of the samples. However, few CRMs are suitable and commercially available for the different samples types, and with adequate minimum sample mass required for microanalysis applications (typically few μg). One limitation of IS method is related to the difficulties in the selection and addition of an appropriate internal standard in the sample. In the case of SA, the requirement of considerable amount of sample for the preparation of the standards and low analytical frequency prevents the applicability of this method.[78,104]

Many nontraditional calibration strategies have recently been developed for solid sample analysis such as multi-energy calibration (MEC), one-point gravimetric standard addition (OP GSA), one-point and multi-line calibration (OP MLC), slope ratio calibration (SRC), two-point calibration transfer (TP CT), and single-sample calibration (SSC), especially in LIBS and XRF analysis. These calibration approaches are considered nontraditional since they explore the plasma physicochemical properties, the use of analyte emission lines/transition energies with different sensitivities, accumulated signal intensities, and few standards (i.e. one or two) to obtain a linear model or calibration curve.[78,104]

In addition, different approaches are widely used within the multivariate aspects. For instance, calibration-free (CF), multi linear regression (MLR),

artificial neural networks (ANN), partial least square (PLS), principal component regression (PCR), and multivariate curve resolution alternating least squares (MCR-ALS) of particular interest to the scientific community. The analytical techniques coupled with these chemometrics methods have gained a widespread use in numerous applications, even though multivariate analysis requiring computational effort and prior chemometric knowledge. Among the possibilities for multivariate calibration, PLS is the most sought-after method, including for the data fusion strategy that combines multiple sources of data from different analytical techniques to produce a single model of calibration.[78,104]

For the qualitative purpose, CASTRO et al. (2020)[105] recently proposed the use of parallel factor analysis (PARAFAC) in the LIBS data. PARAFAC is a decomposition method for multi-way spectra data, i.e. several sets of variables. In this case, PARAFAC was able to model and remove spectral interferences to determine Al, Ag, Au and Cu in PCB samples. After removing the interferences, partial least squares discriminant analysis (PLSDA) was applied to verify the presence or absence of Au and Ag in the PCB sample.

CARVALHO et al. (2015)[106] developed a method combining LIBS and principal component analysis (PCA) to investigate the metal composition of a PCB sample. As a result, hyperspectral images were obtained to provide the elemental distribution within the sample surface. Chemical imaging of plant tissues employing micro-XRF was demonstrated by RAMOS et al. (2016).[107] The authors evaluated the benchtop micro-XRF capabilities for mapping and to differentiate elemental distribution of P, K, Ca, Cl, Cu, Zn, Fe, S, and Mn in wheat grains. LA-ICP-MS has also opened many interesting applications in forensics, archaeology, and the imaging of trace elements in animal (e.g. bone, brain, hair, kidneys, heart, etc.) and plant tissues (e.g. root, leaf, stems, seed, etc).[108,109]

For calibration of LIBS instruments, different applications have been reported such as MEC to determine Ca, Cu, Fe, Mn and Zn in mineral supplement;[110] MMC, CF, SSC, TP CT, and OP MLC for direct determination of Al and Pb in PCB;[111] external standard calibration, IS and MLR for Pb quantification in tea leaves;[112] PLS[113] and ANN[114] in the analysis of soil samples.

CASTRO et al. (2020)[115] assessed different approaches of calibration methods using WDXRF spectrometer. MEC, OP GSA, and TP CT were successfully applied to determine Nd in HD samples. The results obtained from the proposed methods were validated using reference concentrations determined by ICP OES after acid digestion, ranging from 23.52 to 26.33% m/m. For almost all samples, the trueness values were within the acceptable range from 80 to 120%.

In LA-ICP-MS application for the quantitative purpose, VANNOORENBERGHE et al. (2020)[116] recently reported the capabilities and limitations of various calibration approaches on the analysis of NIST SRM 679 (Brick Clay). To this end, four calibration strategies were compared: (1) external calibration without internal standard; (2) external calibration with Si as internal standard; (3) sum normalization approach with estimation of the Si concentration as internal standard; and (4) sum normalization approach according to HUMAYUN et al. (2010).[117]

Therefore, in this chapter was proposed calibration methods for chemical analysis of e-waste samples (i.e. LCD and PCB from mobile phones). The results were reported in the following two studies:

4.1.4 Calibration strategies for determination of the In content in discarded liquid crystal displays (LCD) from mobile phones using laser-induced breakdown spectroscopy (LIBS)

4.1.5 Chemical inspection and elemental analysis of electronic waste using data fusion - Application of complementary spectroanalytical techniques

This latter study was developed during my internship abroad at the Hampshire College, USA, under supervision of Prof. Dr. Dula Amarasiriwardena.

4.1.4 Calibration strategies for determination of the In content in discarded liquid crystal displays (LCD) from mobile phones using laser-induced breakdown spectroscopy (LIBS), Analytica Chimica Acta 1061 (2019) 42–49.

Calibration strategies for determination of the In content in discarded liquid crystal displays (LCD) from mobile phones using laser-induced breakdown spectroscopy (LIBS)

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HIGHLIGHTS

- Direct solid sample analysis using LIBS for electronic waste characterization.
- Univariate and multi-energy calibration (MEC) methods comparison for analysis of solid samples.
- Indium determination in LCD from obsolete mobile phones by ICP OES and LIBS.
- Only two calibration standards and spectral interference detection using MEC.

GRAPHICAL ABSTRACT
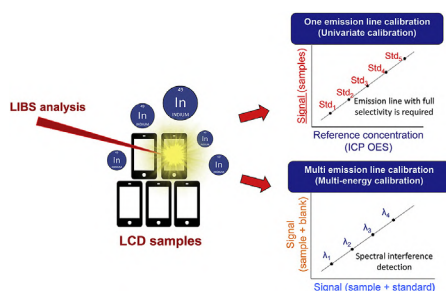
ARTICLE INFO

ABSTRACT

Mobile phones are one of the fastest growing types of electronic waste disposed of world-wide. One of the main components in these devices is the LCD (liquid crystal display) panel that contains conductive electrodes made of indium tin oxide. A large amount of In, which is categorized as a critical raw element, has been used to manufacture indium tin oxide films. This study applies laser-induced breakdown spectroscopy (LIBS) for the analysis of LCD samples from mobile phones in order to determine the In content. Both conventional univariate calibration and non-traditional calibration using different transition energies (emission lines), named multi-energy calibration (MEC), were assessed. To evaluate the accuracy of the results, Method EPA 3052 was performed for acid digestion of the samples using microwave-assistance, and the In content was determined by ICP OES. Indium concentrations ranged from 35 to 47 mg kg^{-1} for all samples evaluated. The results showed the best accuracy for LIBS methods after the spectra were normalized by the carbon line at 193.09 nm. The univariate-LIBS model showed a standard error of calibration (SEC) about 10-fold lower than the samples' concentration, LOD and LOQ of 0.3 and 1.0 mg kg^{-1}, respectively. MEC proved to be a fast and efficient alternative for direct solid analysis, and In concentrations were determined by LIBS using only two calibration pellets. The LOD and LOQ for MEC-LIBS method were 2.1 and 7 mg kg^{-1}, respectively.

1. Introduction

Since the beginning of this century, the use of electrical and electronic equipment has exponentially increased with the rapid development of modern materials and technologies. The

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accelerated obsolescence of these devices has been highlighted as a significant problem in several countries, and electronic waste (e-waste) is among the largest and fastest growing types of solid waste in the world [1]. Mobile phones are an important part of e-waste as they represent a rapidly advancing technology with a frequent and high consumption of new devices. In several countries, including Brazil, the number of mobile phones is larger than the population. The waste generated from mobile phones is particularly complex, as it is composed of hazardous and precious elements, polymers, glass and ceramics. According to the scientific literature, 80% of mobile phone components can be effectively recycled [1–3].

A typical mobile phone is composed of a battery, printed circuit boards (PCBs), front and back covers and a liquid crystal display (LCD). The LCD unit includes a glass substrate with attached polarizing films and polymers, which can also be recovered [4]. One of the main components in LCDs is the layer on the inner side of the display that contains conductive electrodes made of indium tin oxide (or tin-doped indium oxide) [5].

Indium is an important element connected with the production of electric and electronic equipment, and about 80% of the worldwide In consumption is from LCD production [6]. Of 27 materials listed, the European Commission classified In as a critical raw material based on its high supply risk and economic and strategic importance [7]. In order to solve the problem of supply risk, the most reasonable method is to increase the recycling efficiency of the secondary In resources [8]. Generally, with respect to the recycling of critical elements, the correct management of end-of-life devices is an important field that should be considered. Recently, several recycling routes have been developed throughout the world for LCD wastes, mainly via acid leaching for In extraction followed by a recovery process [9].

In this context, In plays a central role in our electronic devices, so it is also important to provide and improve the methods used to monitor the recycling input. The development of fast analytical methods with reasonable costs and sensitivity, as well as limits-of-detection (LOD) that are suitable for the analysis of LCDs, can help in the correct handling of this waste. Considering the scarcity of In and the aforementioned topics, it is important to combine strategies to achieve rapid and reliable analysis with little or no sample preparation. Laser-induced breakdown spectroscopy (LIBS) fills this need, and analytical methods can give some guidelines on how to establish and improve recycling procedures. The ability to perform fast, multi-elemental analysis makes LIBS applicable to many different types of materials and provides a reliable method for several research fields. In the last several years, LIBS has been demonstrated as a powerful technique for the direct solid analysis of e-waste materials [10] such as polymers [11,12], flame retardants [13], PCBs [14], rare-earth in magnets [15] and toxic elements [16].

One of the most challenging issues for LIBS is the development of quantitative methods, and it has often been reported that conventional linear calibration curves suffer from matrix effects [17]. In analytical chemistry, matrix effects occur due to different reasons such as spectral matrix effects (*e.g.,* strong lines of matrix interference in weak lines of an elemental analyte), different physical characteristics (*e.g.,* heat of vaporization, thermal conductivity, water content of samples), chemical composition and self-absorption. One of the main difficulties for the calibration of LIBS is the matrix dependence, and the need for matrix-matched standards is recommended [18].

Therefore, in the present paper, two different calibration methods for the quantification of In in LCD samples have been developed. The goal of this study was the application of both traditional univariate and an alternative method, named multi-energy calibration (MEC) [19,20]. MEC presents a highly

compatible strategy for LIBS calibration which is a challenge for direct solid sample analysis.

2. Experimental section

2.1. Analytical solutions, reagents and samples

High purity water (18.2 MΩ cm, Milli-Q®, Millipore Corp., Bedford, MA, USA) was used to prepare all working solutions. Microwave-assisted acid digestion experiments were conducted using trace metal grade nitric (Qhemis, Indaiatuba, SP, Brazil) and hydrofluoric acids (Nuclear, Diadema, SP, Brazil). Boric acid (Mallinckrodt, Paris, France) was used to remove the remaining fluorides in the digested materials to avoid the precipitation of CaF_2. An elemental stock solution containing $1000\,mg\,L^{-1}$ of In (Fluka, Analytical, Buchs SG, Switzerland) was used to prepare standard reference solutions and to carry out addition and recovery experiments.

A set of spent LCD panels from mobile phones were acquired in the local market of São Carlos (São Paulo State, Brazil) from technical support shops. Different discarded LCD samples were obtained by selecting the most popular models and manufacturers. Samples employed were obtained from 47 LCDs segregated into 5 manufacturer classes: S1 (10 screens from manufacturer #1), S2 (10 screens from manufacturer #2), S3 (10 screens from manufacturer #3), S4 (7 screens from manufacturer #4) and S5 (10 screens from several models and brands, named here as #5).

2.2. Manual disassembly and LCD processing

The mobile phone panels were previously dismantled to remove any components that were not used in this study. The front plate glass, LCD module, back cover and connectors were manually separated. Diffusive and reflector sheets, which are not adhered to the glass substrates of the LCD, were also removed. The polarizing filter films (polymeric sheets) that remained strongly adhered to the glass were removed in a solvent bath to improve the comminution process. Different solvents have been tested for their efficiency in the removal of the polymeric films. Among the solvents reported in the scientific literature, acetone showed the best results [21]. LCD samples were fragmented into small pieces of approximately 3 cm × 3 cm and kept in an acetone bath with agitation (130 rpm) on a stirring table for 20 h. The solvent bath was prepared at a solid/liquid ratio of 1:3 (g of LCD sample/mL of acetone). The comminution process of the samples was performed using a knife mill (IKA, model A11) after the removal of the polymeric films, and LCD powder with particle size lower than 212 μm was obtained. Fig. 1 shows a schematic representation of the initial disassembly of the mobile phone panels to obtain the glass substrates with indium tin oxide electrodes used in the comminution process.

2.3. Sample preparation for ICP OES analysis

EPA method 3052 (modified), a procedure developed for the acid digestion of high silicon and organic matter matrices, was used to mineralize the samples. Later, the resulting liquid solutions were used to obtain In reference concentrations. A total of 0.20 g of an LCD sample was accurately weighed, and 5 mL of 65% v v^{-1} HNO$_3$ and 2 mL of 40% v v^{-1} HF were added. The samples were digested in a microwave-assisted oven (Speedwave xpert, Berghof, Germany) with 60 mL volume-closure bottles (DAP 60). The heating program was composed of the following steps: (1) temperature ramp up to 200 °C in 6 min, (2) kept at 200 °C for 10 min and (3) cooled to room temperature. The digests were transferred to 50-mL falcon tubes,
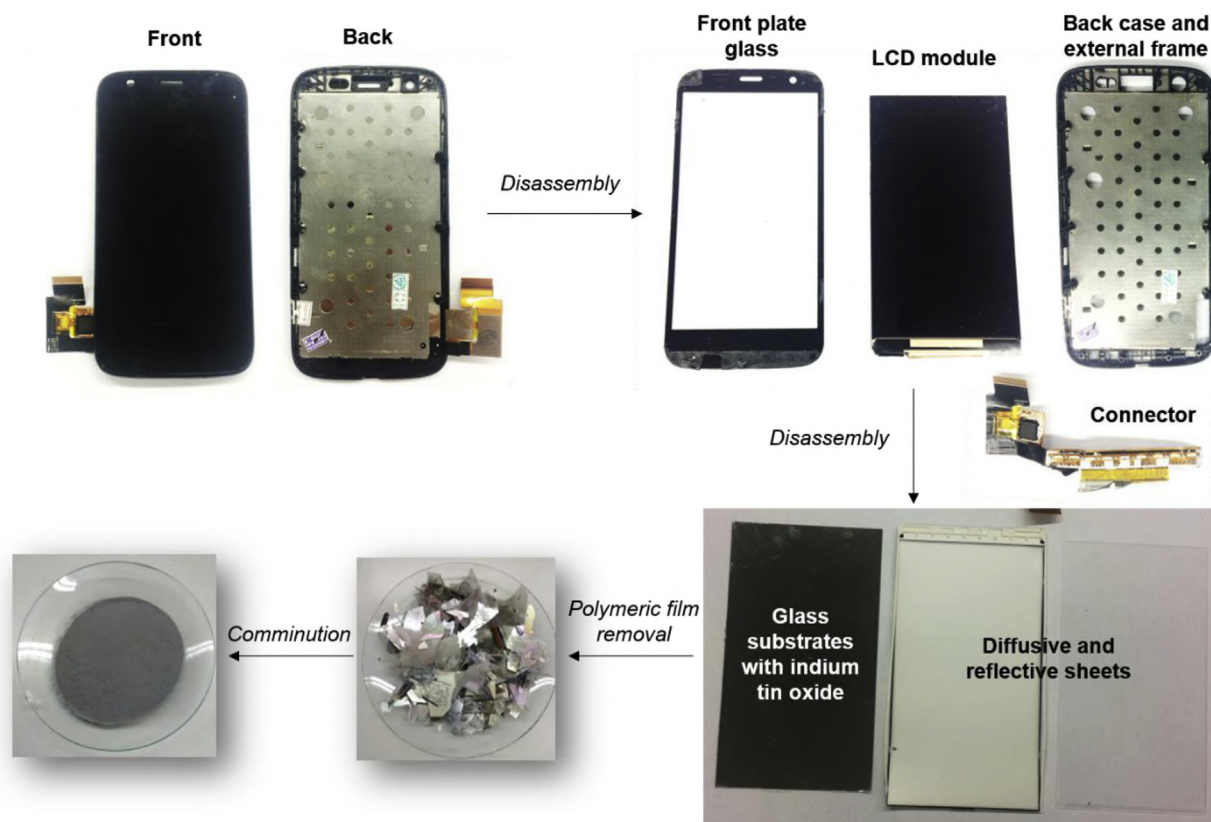
Fig. 1. Disassembly scheme used for processing the mobile phone panels and LCD samples.

and the remaining HF was complexed with 0.5 g of boric acid. The undissolved excess of boric acid was filtered prior to analysis. The digests of the LCD samples were analyzed by ICP OES model iCAP 6000 (Thermo Fisher, Madison, WI, USA), and details of the instrumental parameters are shown in Table 1. The gas used for purging and plasma generation was 99.996% Ar (White Martins-Praxair, Sertãozinho, SP, Brazil).

2.4. LIBS analysis

LCD sample analysis to determine the In content by LIBS was assessed using two calibration strategies: univariate calibration and multi-energy calibration (MEC). For both, the powder samples were pressed and directly analyzed as pellets. The spectra dataset was recorded using LIBS J200 instrument (Applied Spectra, Fremont, CA, USA) and carried out with a Q-switched Nd:YAG laser at 1064 nm, for a duration of 8 ns at a frequency of 10 Hz. The laser pulse energy

was 80 mJ, and a 100-μm spot size (1019 J cm^{-2} fluency), delay time of 0.5 μs, and data acquisition time of 1.05 ms were used. Additional laser settings used were as follows: scan length of 9.5 mm, laser repetition rate of 5.0 Hz and sample speed ablation of 1.0 mm s^{-1}. The micro-plasma emission was collected by an optical fiber beam coupled to a six-channel CCD spectrometer covering the following ranges: channel 1 from 186 to 311 nm (0.06 nm resolution), channel 2 from 311 to 466 nm (0.07 nm resolution), channel 3 from 466 to 591 nm (0.06 nm resolution), channel 4 from 591 to 694 nm (0.05 nm resolution), channel 5 from 694 to 884 (0.09 nm resolution) and channel 6 from 884 to 1042 nm (0.08 nm resolution).

2.4.1. Univariate calibration

All samples used for univariate calibration were prepared by mixing 0.40 g of sample and 0.10 g of cellulose (binder agent), homogenized using a pestle and mortar, and then pressed for 2 min under 80 kN to form pellets with a 12 mm diameter. Approximately

Table 1
Instrumental operating conditions for ICP OES analysis.

Instrumental parameter	Operational condition
Integration time (s)	15 and 5 s for low and high wavelengths, respectively
RF applied power (kW)	1.15
Coolant gas flow rate (L/min)	12.0
Auxiliary gas flow rate (L/min)	0.50
Nebulizer gas flow rate (L/min)	0.70
Sample introduction flow rate (mL/min)	2.10
Viewing positioning	Axial
Nebulizer	Concentric
Spray chamber	Cyclonic
Analyte and wavelength (nm)	In I 325.609[a]

[a] I: atomic emission line.

400 spectra were recorded for each LCD sample pellet (n = 3). Calibration curves were obtained from the regression of the analyte line intensities (peak area or peak maximum) recorded by LIBS (y-axis) against the reference concentrations (x-axis) of the samples determined by ICP OES. The concentration for fitting linear univariate calibration ranged from 35 mg kg^{-1} (S2) to 47 mg kg^{-1} (S4). Indium was determined for the ten most intense emission lines at 230.60, 293.26, 294.10, 303.93, 325.60, 410.18, 451.13, 463.81, 465.56, and 468.47 nm. With the values of area and height of a selected region of the spectra that is supposed to have the emission line of interest, the calibration models were calculated using the strategy of full cross validation. The limits of detection (LOD) and quantification (LOQ) were calculated using the background regions in the surrounding analytical signals. The standard deviation of the background noise (s) was estimated as the square root of the sum of the calculated variances.

2.4.2. Multi-energy calibration

The MEC method requires only two calibration standards for each sample (pellets 1 and 2), a fixed concentration of the analyte, and different transition energies (emission lines) to obtain a linear model. Pellet 1 was composed of sample, standard containing the analyte, and cellulose (binder), and pellet 2 was composed of sample, a blank, and cellulose. For the formation of pellet 1 (sample + standard), sample #1 was used as the standard, as no salt is commercially available with a low concentration of In or close to sample concentrations. In the case of pellet 2 (sample + blank), silica (SiO_2) was used as the blank in the preparation of the standards to resemble the samples, as the LCD matrix is mainly composed of Si in their constitution. Initially, effects of the addition of different masses of standard were studied in the formation of pellet 1 (sample + standard):

(i) addition 1: 44.5% w w^{-1} sample, 44.5% w w^{-1} standard, and 11% w w^{-1} cellulose. Using this masses, the final In concentration of sample and standard were 21 and 20 mg kg^{-1}, respectively.

(ii) addition 2: 40% w w^{-1} sample, 50% w w^{-1} standard, and 10% w w^{-1} cellulose. Using this masses, the final In concentration of sample and standard were 19 and 22 mg kg^{-1}, respectively.

(iii) addition 3: 36.4% w w^{-1} sample, 54.6% w w^{-1} standard, and 9% w w^{-1} cellulose. Using this masses, the final In concentration of sample and standard were 17 and 24 mg kg^{-1}, respectively.

In all cases the final mass was 0.5 g. For each pellet (n = 2), approximately 1500 spectra were recorded using both sides. The spectral dataset was collected in 30 scans (a straight line), and for each scan, approximately 50 pulses were obtained. Each set of 5 scans (about 250 spectra) was considered a replicate (n = 6). As many analytical emission lines (*i.e.,* points used in the proposed linear model) as possible were used, considering the number of detectable lines available for In. Atomic emission lines of In at 303.93, 325.60, 410.18 and 451.13 nm were applied for calibration by MEC-LIBS. The LOD and LOQ were calculated as 3 and 10 times the blank concentration according to IUPAC recommendations. In this case, SiO_2 was used as sample for pellet 1 (SiO_2 + standard) and pellet 2 (SiO_2 + blank), and the blank equivalent concentration was calculated using MEC (n = 10) [18,19].

2.5. Data handling

Aurora (Applied Spectra) and National Institute of Standards and Technology (NIST) web site (http://physics.nist.gov/PhysRefData/ASD/lines_form.html) were used for emission lines identification of In. All spectra obtained by LIBS were first normalized/standardized using a homemade MATLAB® 2018a (The Mathworks Inc., Natick, MA, USA) routine (libs_treat) and calculated 10 different modes of normalization: (1) average signal; (2) average signal normalized by length of vector (norm), (3) area (sum of all signals) and (4) height of the signal (higher intensity); (5) sum of the signal; (6) sum of the signal normalized by the norm, (7) area and (8) height; and (9) average and (10) sum of the signal after normalization by carbon emission atomic line at 193.09 (adapted from Castro and Pereira-Filho, 2016 [22]). After these normalizations are performed, another homemade script (libs_par) was used to calculate the peak area (sum of signals) and peak maximum (height of signal) of a selected region of the spectra for In emission lines. With these values of area and height of this selected region, Microsoft Excel was used for data matrices organization and calculating the univariate calibration and MEC models.

3. Results and discussion

3.1. Determination of In content by ICP OES

The accuracy of the acid digestion method was evaluated by analyzing the LCD samples using ICP OES, and addition/recovery tests were performed. Solid samples were spiked with In standard solutions prior to microwave-assisted acid digestion. The LCD samples were spiked in the acid digestion process to evaluate the entire analytical procedure, from the digestion method up to instrumental measurements. Adequate recoveries were obtained for the three samples assessed. Recoveries of 1.3 mg L^{-1} of In spiked into S1, S3 and S5 samples were 94, 92 and 89%, respectively. The results are the net values obtained after subtracting the concentration originally found in the LCD samples. Thereafter, the acid digestion method was applied for the rest of the samples (S2 and S4), which were analyzed by ICP OES.

3.2. Univariate calibration

A total of 20 calibration models were performed for each In emission line selected, that is, 10 calibration models for each normalization for area or height of the signal. The best univariate calibration models were evaluated according to the trueness values and lower standard error of calibration (SEC). The region of the spectra for the emission lines of In at 303.93, 325.60, 410.18, and 451.13 nm showed the best results. The parameters for the univariate-LIBS models obtained to determine the In content in LCD samples are shown in Table 2. The emission line of In at 303.93 nm showed the best figures of merit calculated. This means, from 85 to 107% of trueness and SEC of 4.2 mg kg^{-1}. In most cases, all normalizations retrieved acceptable results, and the best mode of normalization was using averaged spectra for signal area normalized by C 193.09 nm (normalization #9). As a comparison, using only the averaged spectra (normalization #1), the trueness values were from 77 to 115% and SEC of 6.6 mg kg^{-1}.

One of the advantages of the univariate method developed using a set of samples as calibration standards is its matrix-matching capability. This method can be efficient for the correction of matrix effects, but it does not correct signal fluctuations from the instrumentation used. In addition to assisting with pellet formation, cellulose also contributed as an internal standard to improve normalization using the atomic (I) emission line of carbon at 193.09 nm. In this case, the normalization of LIBS spectra before the calculation of the univariate models was an important step to obtain lower calibration error and reliable results. Furthermore, the univariate-LIBS models presented about a 10-fold lower SEC when compared to the sample concentrations (around 40 mg kg^{-1}). The

Table 2
Figures of merit for the univariate models for determination of In at 303.93, 325.60, 410.18 and 451.13 nm.

Emission line of In (nm)	R, and univariate linear model[a]	SEC (mg kg^{-1})	LOD (mg kg^{-1})	LOQ (mg kg^{-1})	Trueness range (%)
303.93	0.7462, $y = 0.05x - 0.27$	4.2	0.3	1.0	85—107
325.60	0.7028, $y = 0.01x - 0.09$	4.8	0.4	1.3	90—111
410.18	0.7043, $y = 0.08x - 0.34$	4.7	0.5	1.5	84—110
451.13	0.7339, $y = 0.02x - 0.06$	4.4	0.3	1.0	86—109

[a] Univariate models for peak area of In signal normalized by C I 193.09 and averaged.

univariate method was demonstrated as a good alternative for the determination of the In content in LCD samples in comparison to traditional external calibration method and ICP OES analysis.

3.3. Multi-energy calibration

MEC is a non-traditional strategy for calibration and explores the capabilities of many analytes in the generation of several analytical signals using multiple transition energies for calibration [19]. The potential application of this method has been recently used for aqueous solutions and three different spectrochemical techniques including ICP OES, microwave induced plasma optical emission spectrometry (MIP OES) and high-resolution continuum source flame atomic absorption spectrometry (HR-CS FAAS) [19,23]. For the analysis of solid samples, the development of MEC method in combination with LIBS was firstly proposed by Babos et al. [20] for analysis of cattle mineral supplements, as well as other applications have been reported using dietary supplements [24], and nickeliferous ores [25]. The present study is the first application for electronic waste and technological elements determination. In contrast to the other solution sampling techniques, the MEC-LIBS methods represent compatible strategies for the direct analysis of solid samples, avoiding complex and time-consuming preparation procedures.

3.3.1. Study of standard added in pellet 1

For calculation of sample concentration, MEC method only considers the slope of the linear model and standard concentration added to pellet 1. The added standard concentration is known, and the sample concentration can be determined by correlating this information (slope and standard) [19,20]. One of the drawbacks related to development of a calibration method by MEC is that initially requires *a priori* knowledge of the chemical composition of the samples (analyte concentrations). This limitation is observed only in the initial stages of the proposed calibration models. After calibration protocol establishment, few samples should be tested using the reference methods.

In LIBS analysis of powder samples, proper homogenization of the samples is a crucial parameter to obtain satisfactory results. For MEC method, standard concentration added in pellet 1 (standard + sample) can be monitored to assess the homogeneity of the calibration standards. In this way, the LCD samples were analyzed in three different sample/standard ratios (addition 1, 2, and 3), and precision and accuracy of measurements were evaluated using ten different normalization modes.

The results shown in Fig. 2 demonstrate that the addition 2 was the best condition for all normalization modes assessed. Trueness of 86% (normalization #2 and #6) to 108% (normalization #10) using peak area (Fig. 2a), and 87% (normalization #2 and #6) to 109% (normalization #9 and #10) for the peak maximum (Fig. 2c) were obtained. With different added masses of the standard, the adequate trueness (between 80 and 120%, the dotted lines in Fig. 2a and c) was obtained after the normalization of the spectra using the carbon atomic emission line (normalization #9 and #10). Adequate precisions (reported as relative standard deviation) calculated for

MEC-LIBS in addition 2 were also obtained after normalization (Fig. 2b and d). In this context, addition 2 (40% w w^{-1} of sample, 50% w w^{-1} of standard, and 10% w w^{-1} cellulose) was selected and applied in further experiments using MEC.

3.3.2. Analytical performance

One of the main advantages of MEC with respect to the traditional external calibration is the matrix-matching compatibility, as both pellet 1 (sample + standard) and pellet 2 (sample + blank) contain a constant amount of sample. In addition, by using MEC, it is possible to identify spectral interference in the specific analytical lines of In that may affect the analytical signal at a given emission line for pellets 1 or 2. Fig. 3 shows an example of spectral interference that could jeopardize the calibration results. The calibration linear model was initially calculated with five emission lines selected for In: 325.60 (λ_1), 303.93 (λ_2), 410.18 (λ_3), 451.13 (λ_4), and 230.60 (λ_5) nm. The specific calibration point for the fifth emission line of In at 230.60 (λ_5) nm appeared outside the linear range of the first linear model (see red line in Fig. 3a). Indium signal at 230.60 nm presents spectral interference around 230.5 nm (Fig. 3b), and this problem was evident in the calculated linear model. This emission line can be ignored, and the model can be recalculated (see blue line in Fig. 3a). The emission lines selected to obtain the linear model are depicted in Fig. 3c for pellet 1 (sample + standard, solid line) and pellet 2 (sample + blank, dotted line). The correlation of the linear model improved from 0.9778 (with 5 emission lines) to 0.9994 (with 4 emission lines). For comparison, the univariate model proposed using LIBS cannot identify spectral interference because it is obtained using the traditional one-wavelength calibration method.

Besides the improvements in the linear model correlation by MEC-LIBS using different transition energies for In that are free of interferences, the most significant variation is related to the angular coefficient (slope). In the MEC calibration procedure applied here, the mathematical treatment and predicted analyte concentration for the sample is strongly dependent on variations in the slope. The slope values of the respective plot's linear regressions can be anticipated using the following Eq. (1) [19]:

$$Slope = \frac{[In]_{sample}}{[In]_{sample} + [In]_{standard}} \quad (1)$$

where the $[In]_{standard}$ is known *a priori*, and the In concentration in the sample can also be determined. Equation (2) represents an example using Eq. (1) to calculate the slope value by MEC for S3.

$$Slope = \frac{18.8 \ (mg \ kg^{-1})}{18.8 \ (mg \ kg^{-1}) + 22 \ (mg \ kg^{-1})} = 0.461 \quad (2)$$

As shown in the slope calculation of Eq. (2), the angular coefficient for the linear model was 0.461 for S3. If one considers an error of 20%, linear plots with a slope between 0.369 and 0.553 can predict accurate results for this sample. The theoretical slope values for the evaluated samples varied from 0.389 (S2) to 0.461 (S3 and S4), and good concordance among these values and the obtained
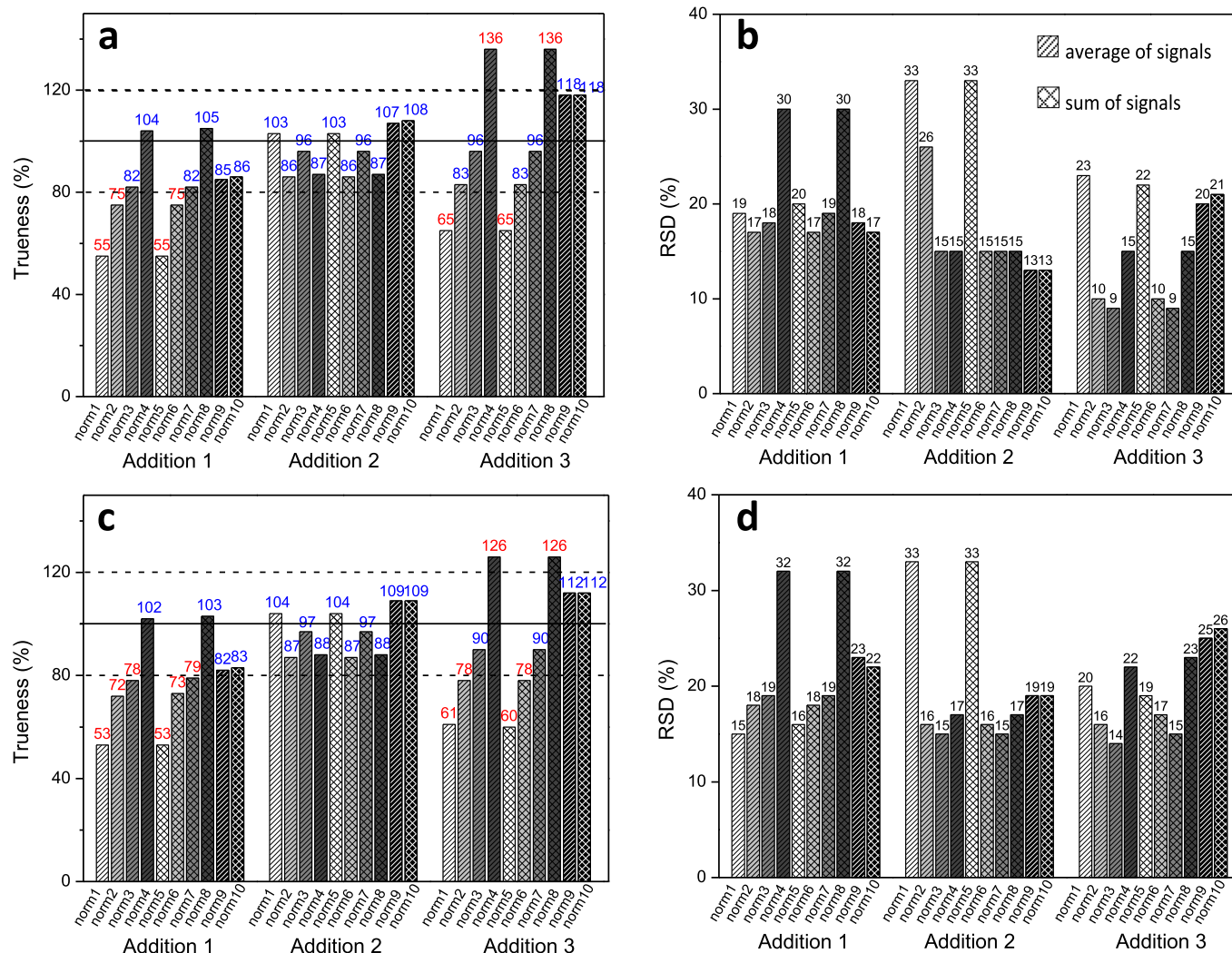
Fig. 2. Study of the addition of different proportions of sample and standard. Figures of merit (trueness and RSD) for the peak area (a and b) and the peak maximum (c and d) for ten different normalizations.

using MEC-LIBS was noted. Table 3 shows the slope values obtained and other multi-energy linear models parameters for determination of In in LCD samples. The best results presented were using the area of In signals normalized by C I 193.09. The precision calculated for samples S2, S3, S4, and S5 were 21, 12, 15 and 20%, respectively. Samples S2 and S5 show the worse precision of the measurements, which can be related to different issues. Problems with measurement precision are currently a drawback of using the LIBS technique [25], and RSD values above 10% can be observed [26—28] depending on the sample characteristics (e.g., homogeneity, matrix), particle size, and laser setup. For direct analysis of solid samples using MEC-LIBS, RSD values of 30% can be expected and generate results with adequate trueness [20,24]. Furthermore, problems with the laser pulse energy, laser repetition rate, number of laser sparks, and gate delay were found to affect the RSD in LIBS analysis of iron ores [29].

Table 4 shows the concentrations of In determined by MEC-LIBS in comparison to univariate-LIBS and reference method (ICP OES). The concentration of In content in LCD samples determined by the univariate method ranged from 35 (S2) to 50 mg kg^{-1} (S3). For MEC, In concentrations ranged from 34 (S2) to 42 mg kg^{-1} (S3). Indium

was not determined in S1 because it was used as the calibration standard for MEC. No statistically significant difference was observed between MEC-LIBS, univariate-LIBS and ICP OES determined values at the 95% confidence level (Student's t-test). Based on the results obtained, LIBS in combination with univariate and MEC methods proved to be efficient alternatives for the traditional calibration and determination of In by ICP OES.

4. Conclusion

Both univariate (single wavelength) and MEC (multi-wavelength) calibration methods were developed with adequate precision and accuracy for determination of In content in LCD samples. Simplicity and efficiency in matrix-matching are the main advantages of the developed methods in comparison to traditional external calibration for direct analysis of solid samples in LIBS. If the microwave-oven-assisted sample preparation is not considered, a superior sample throughput was obtained for the proposed LIBS methods. Only two calibration pellets must be prepared per sample in MEC-LIBS, and the easy identification of emission lines with spectral interference can help in obtaining accurate calibration
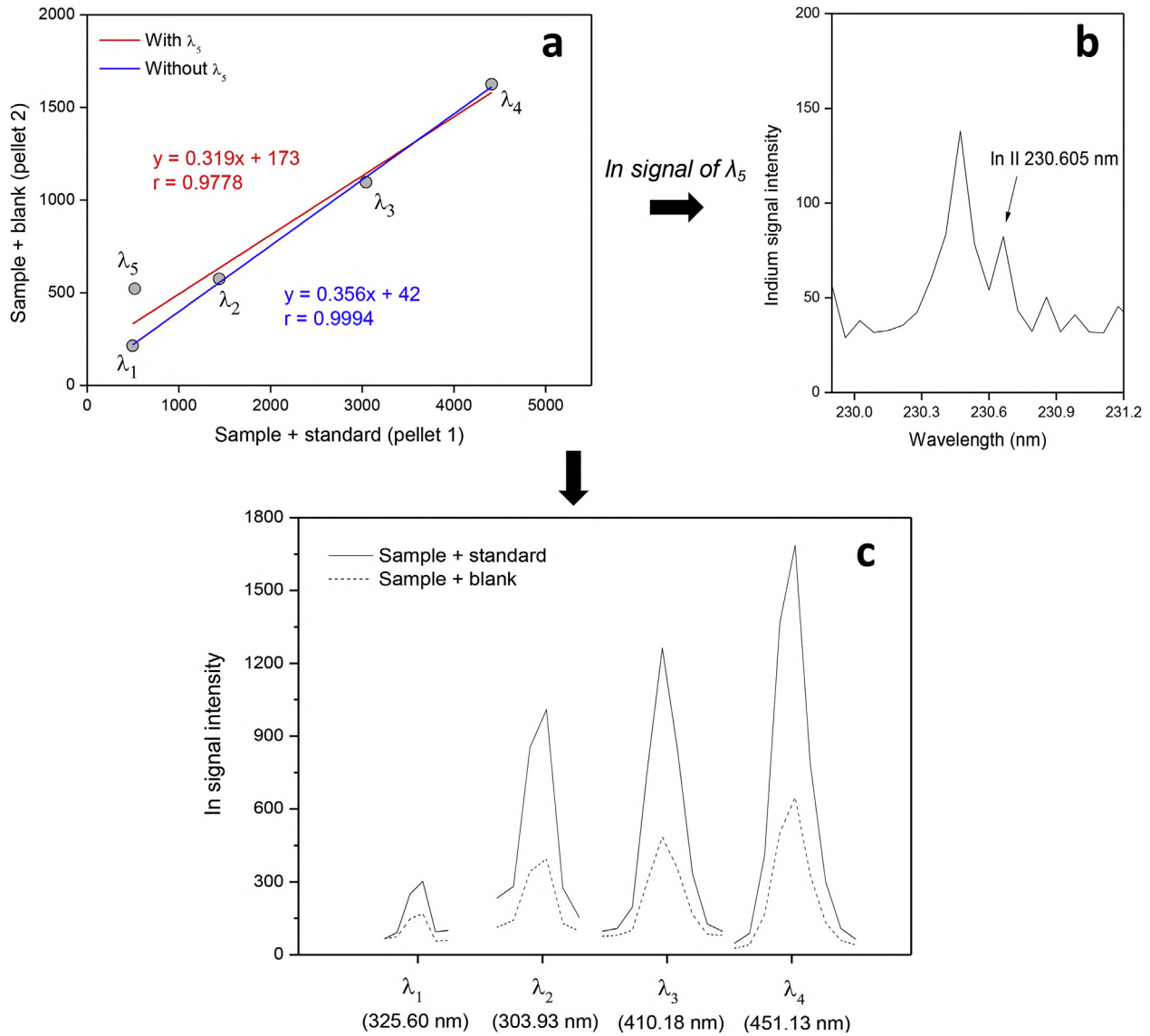
Fig. 3. Spectral interference of multi-energy calibration plots (a and b) and emission lines selected (c) to determine In in LCD samples by LIBS.

Table 3
Analytical parameters of linear models for determination of In by MEC.

Parameter	S2	S3	S4	S5
Signal type	area	area	area	area
Normalization mode	Normalized by C I 193.09 and averaged	Normalized by C I 193.09 and averaged	Normalized by C I 193.09 and averaged	Normalized by C I 193.09 and averaged
RSD (%)	21	12	15	20
R	0.9977	0.9968	0.9977	0.9989
Obtained slope using MEC	0.379	0.433	0.423	0.417
Theoretical slope (equation (1))	0.389	0.461	0.461	0.415

LOD: 2.1 mg kg^{-1}; LOQ: 7 mg kg^{-1}

models. If applied for the routine analysis of In in LCD samples, both strategies can present remarkable results and help in e-waste management. LCD panels from discarded mobile phones have interesting concentrations of In, and the recycling of these residues can be an important source of raw material for the future production of these devices.

Declaration of interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Table 4

Indium concentrations determined in LCD samples by ICP OES (n = 3), MEC (n = 6), and univariate calibration (n = 3) methods. The results are presented as the mean ± standard deviation and trueness (in parenthesis).

Sample	In (mg kg^{-1})		
	ICP OES	Univariate-LIBS[a]	MEC-LIBS[b]
S1	44 ± 2	37 ± 4 (85)	–
S2	35 ± 2	35 ± 2 (99)	34 ± 7 (97)
S3	47 ± 3	50 ± 4 (107)	42 ± 5 (90)
S4	47 ± 2	48 ± 2 (101)	41 ± 6 (87)
S5	39 ± 2	42 ± 2 (107)	40 ± 8 (103)

"-" not determined.

[a] Peak area of In I 303.93 normalized by C I 193.09 and averaged.

[b] Peak area of In signal normalized by C I 193.09 and averaged.

Acknowledgments

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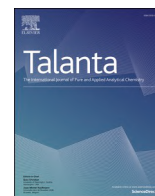
Chemical inspection and elemental analysis of electronic waste using data fusion - Application of complementary spectroanalytical techniques

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ARTICLE INFO

ABSTRACT

This study is focused on the development of analytical methods for characterization of printed circuit boards (PCBs) from mobile phones by direct analysis using three complementary spectroanalytical techniques: laser ablation-inductively coupled plasma-mass spectrometry (LA-ICP-MS), laser-induced breakdown spectroscopy (LIBS), and micro X-ray fluorescence spectroscopy (micro-XRF). These techniques were combined with principal component analysis (PCA) to investigate the chemical composition on the surface and depth profiling of PCB samples. The spatial distribution of important base metals (*e.g.* Al, Au, Ba, Cu, Fe, Mg, Ni, Zn), toxic elements (*e.g.* Cd, Cr, Pb) as well as the non-metallic fraction (*e.g.* P, S and Si) from conductive tracks, solder mask and integrated components were detected within the PCB samples. Univariate and multivariate approaches were also performed to obtain calibration models for Cu determination. The results were compared to reference concentrations obtained by inductively coupled plasma-optical emission spectrometry (ICP-OES) after microwave-assisted acid leaching using *aqua regia*. To this end, two PCB samples (50 × 34 mm^2) were cut into small parts of 40 subsamples (10 × 8.5 mm^2) and analyzed by ICP-OES and the Cu concentrations ranged from 13 to 45% m m^{-1}. Partial least squares (PLS) regression was used to data fusion of analytical information from LIBS and micro-XRF analysis. The proposed calibration methods for LIBS and micro-XRF were tested for the 40 PCB subsamples, in which the best results were obtained combining both data sources though a low-level data fusion. Root mean square error of cross validation (RMSEC) and recoveries were 3.23% m m^{-1} and 81–119% using leave-one-out cross validation.

1. Introduction

The use of electrical and electronic equipment (EEE) has exponentially increased over the last decades with fast development of advanced materials and modern technologies. The global rise in technology, tied in with frequent replacement of these devices by items with better functionalities, has been related to a growing amount of electronics with short lifespans [1]. As a result, electronic waste (e-waste) is one of the largest- and fastest-growing waste streams. The last report in Global E-waste Monitor calculates that 53.6 million metric tonnes (Mt) of e-waste was generated in 2019, which the recycling rates was estimated around 17% [2,3]. Printed circuit boards (PCBs) are frequently found in end-of-life electronics and play a vital role in the ever-increasing production of e-waste. A typical PCB unit has a complex composition and may contain up to 60 elements that comprises 40% metals, 30% plastics and 30% ceramics by weight [4,5]. Although it offers valuable recyclable materials but the treatment of waste generated during the material recovery process is hazardous and could pose a chemical exposure hazard [6]. As such, recycling of e-waste presents both challenges and opportunities.

In this context, it is important to provide a better overview of the e-waste stream and improve the pre-processing technologies available in the recycling chain. A chemical inspection of e-waste by analytical techniques is an important step towards addressing the e-waste challenge [7]. Valuable materials from an unsorted large waste stream could be retrieved by manual sorting, which is often performed by informal

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Table 1
Instrumental operating parameters for ICP-OES analysis of PCB samples.

Instrumental parameter	Operational condition
Integration time (s)	15 and 5 s for low and high wavelengths, respectively
RF applied power (kW)	1.15
Coolant Ar [99.996% pure] gas flow rate (L/min)	12.0
Auxiliary Ar gas flow rate (L/min)	0.50
Nebulizer Ar gas flow rate (L/min)	0.70
Sample introduction flow rate (mL/min)	2.10
Nebulizer	Concentric
Spray chamber	Cyclonic
Analyte and wavelength (nm)	Al I 308.215[b], Au I 242.795[a], Ba II 455.403[b], Ca II 393.366[b], Cr II 284.325[a], Cu I 327.396[b], Fe II 259.940[b], K I 769.896[b], Mg II 279.553[b], Mn II 257.610[b], Mo I 202.030[b], Ni II 231.604[a], Pb I 216.999[a], S I 182.034[a], Si I 212.412[a], Sn I 283.999[b], Sr II 421.552[b], and Zn I 213.856[b]

[a] Axial viewing mode.
[b] Radial viewing mode.

sectors through "backyard recycling" or using substandard recycling procedures [1,2]. As a consequence, it leads to contamination of the environment and pose a threat to human health.

Spectroscopic techniques that are based on direct solid sampling analysis are commonly used to obtain a qualitative and quantitative information of several e-waste materials [8,9]. To this end, different analytical techniques have been applied such as wavelength dispersive X-ray fluorescence spectrometry (WD-XRF) to analysis of hard drive disks magnets [10]; near-infrared spectroscopy (NIR) and Raman spectroscopy for polymer characterization [11,12]; laser-induced breakdown spectroscopy (LIBS) to evaluate PCB [13], liquid crystal displays (LCD) [14], and polymer composition [15]; and laser ablation-inductively coupled plasma-mass spectrometry (LA-ICP-MS) for the direct elemental analysis of advanced materials [16]. The ability to perform direct and reliable multi-elemental analysis with a little or no sample preparation as well as their capability to provide elemental/molecular spatial distribution information make these spectroscopic techniques appropriate for characterization of various types of e-waste materials.

However, using several analytical techniques that offers different analytical information, as emission, fluorescence and mass/charge spectra in data matrices, poses new challenges and opportunities into development of novel data mining/analysis methods. Chemometric has been a common approach for extracting relevant hidden chemical information from large datasets. Using significant findings from chemometric methods one can facilitate novel sustainable e-waste management practices [17]. In this quest to gather more and better information, the combination (*i.e.* fusion) of outputs from multiple analytical information sources have demonstrated to be a powerful alternative to obtain an improved detection, confidence and consistency of data [18–20]. Indeed, the fusion of the different data into a single model can enhance the knowledge about features among samples and also allows assessing the extent of correlation and the information about similar/dissimilar content derived from diverse analytical techniques [21].

Generally, the combination of data can be accomplished at different levels: low-, mid-, and high-level data fusion, including supervised and unsupervised methods of data analysis [18,22]. In low-level data fusion the raw data from complementary analysis are directly concatenated into a single matrix that is used for multivariate classification and regression. Preprocessing, standardization or variable selection methods may be required in each of the data source. These processes are partially similar in the mid-level fusion, in which first extracts relevant features

from each data source independently, and then these features are fused into a single matrix. Finally, the high-level data fusion combines the results that were gathered from each individual models to provide a final prediction [18,23].

Considering that the future recycling infrastructure needs to be further developed or improved, an appropriate detection and sorting schemes using advanced analytical techniques to facilitate proper and efficient e-waste management need to be formed. Therefore, this study was focused on two different and complementary strategies: (1) development of analytical methods for qualitative chemical inspection of printed circuit boards (PCBs) using micro X-ray fluorescence spectroscopy (micro-XRF), LIBS, and LA-ICP-MS and (2) quantitative characterization using micro-XRF and LIBS. Chemometric approaches including fusion of the spectral features with multivariate data analysis was invoked to gather complementary information for quantification purposes.

2. Material and methods

2.1. Reagents, analytical solutions, and samples

High purity water (18.2 ΩM cm) produced by a Milli-Q® Plus Total Water System (Millipore Corp., Bedford, MA, USA) was used to prepare all working solutions. Microwave-assisted acid leaching experiments were carried out using HCl (Qhemis, Indaiatuba, SP, Brazil) and HNO$_3$ (Neon, Suzano, SP, Brazil) previously purified using a sub-boiling distillation system (BSB-939-IR model, Distillacid, Berghof, Germany). Element stock solutions containing 1000 mg L^{-1} (Merck, Darmstadt, Germany) were serially diluted with high purity water to obtain standard solutions at an appropriate calibration range for inductively coupled plasma-optical emission spectroscopy (ICP-OES) determination of Al, Au, Ba, Ca, Cr, Cu, Fe, K, Mg, Mn, Mo, Ni, Pb, S, Si, Sn, Sr and Zn. An in-house reference material (RM) for electronic waste (RM – PCB) was developed and used to verify the accuracy of the acid leaching and ICP-OES measurements [24,25]. This RM was developed by the Group of Applied Instrumental Analysis (GAIA) and employed around 5 kg of raw PCB waste material for production of this in-house RM. All characterizations studies (*e.g.*, homogeneity, short- and long-term stability tests) and statistical parameters were performed. More details about the preparation, certification and availability of the material can be found in references 24 and 25.

A set of four PCB samples from mobile phones were used to assess the proposed method. The mobile phones were acquired in the local market of São Carlos (São Paulo State, Brazil) from technical support workshops, where these devices were discarded by its owners as waste without the intent of reuse. The set of mobile phones were from the same model and same manufacturer to ensure an identical material composition in each of the four PCB samples assessed. These devices were manually disassembled to obtain the PCB units. Before the analysis, the PCB external surface was cleaned using ethanol 50% (v/v).

2.2. Initial qualitative inspection of PCB samples

The goal of this section is to present the capability of each instrumental analytical technique in order to obtain qualitative information from PCB samples. In this case, the four samples were analyzed by micro-XRF using a 25 × 32-point matrix (800 points) for both sides of each board (also called as PCB front and back side). A total of 1600 points were analyzed for each of the two PCB samples. The horizontal and vertical distances between each point were 1.6 mm (rows) and 1.4 mm (columns), and an area of 1700 mm^2 (50 × 34 mm) was probed.

The laser-based techniques (LIBS and LA-ICP-MS) were then used to analyze the samples in the same position of micro-XRF measurements. In addition, 10 consecutive laser pulses *per* point were used to obtain information of the analyte within the sample (*i.e.,* for elemental mapping and depth profile analysis). In both laser-based instruments a tiny
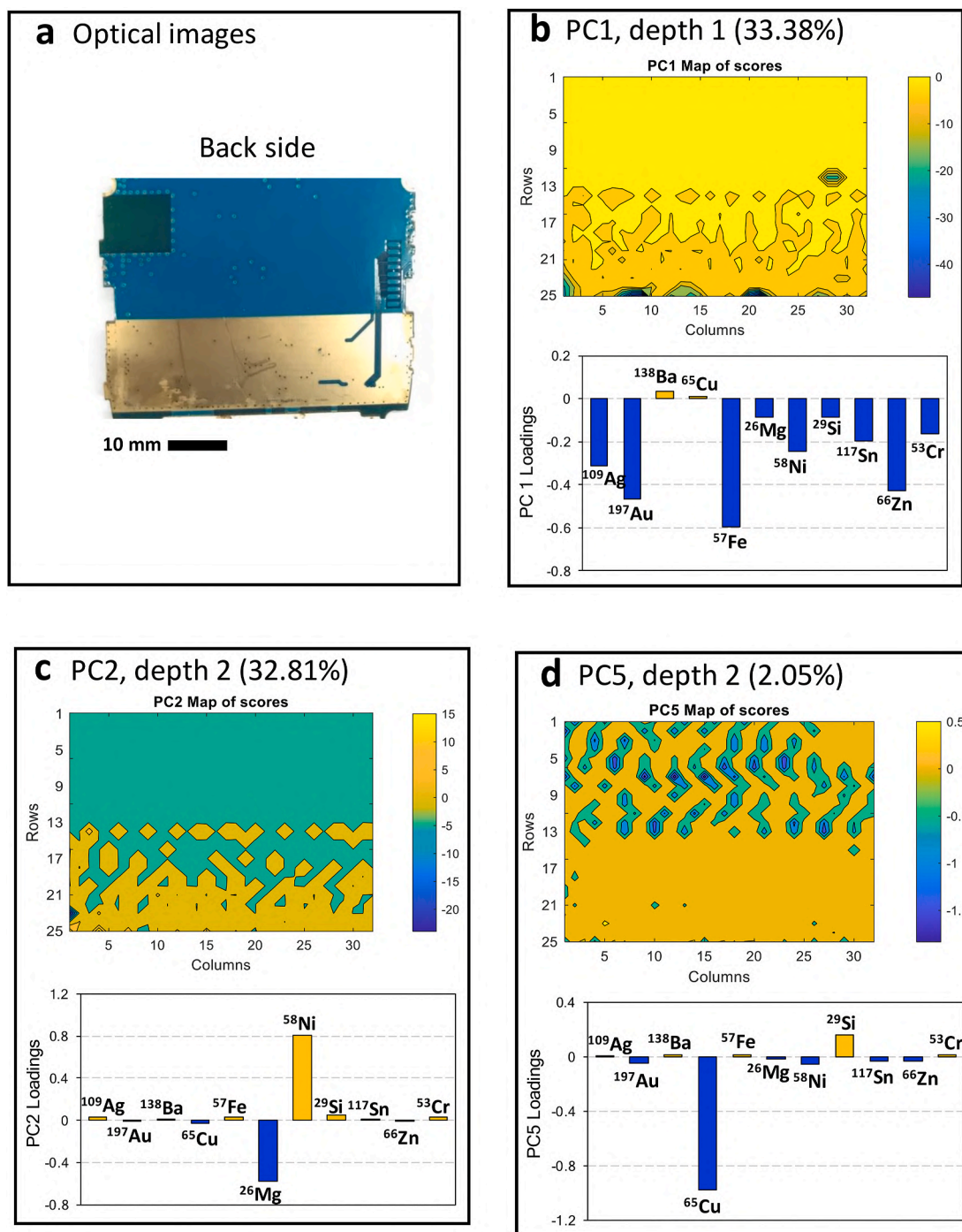
Fig. 1. Elemental mapping of (a) PCB sample using LA-ICP-MS. Score maps and loadings (b–f) to the back side of the PCB sample. The black solid line at the bottom of the image denotes its scale factor.

sample is ablated (hundreds of ng to a few mg) *per* point. Then, the LIBS spectra were recorded in two of the PCB samples and LA-ICP-MS system was used to obtain isotopic information in the remaining two boards.

2.3. Direct solid sampling techniques

The micro-XRF measurements were performed using Orbis PC Analyser, EDAX, New Jersey, USA. X-rays were focused by a collimator of 1-mm-wide. This instrument is a benchtop system dedicated to micro-analysis with a *x, y,* and *z* sampling stage and silicon drift detector (SDD). The signals for all elements were recorded under vacuum using a

Rh anode X-ray tube set to 40 kV and 200 µA, and the dwell time of 2 s.

The LIBS spectra were recorded using a LIBS J200 instrument (Applied Spectra, Fremont, CA, USA) equipped with a Q-switched Nd: YAG laser operating at 1064 nm wavelength with a pulse duration of 8 ns. Laser instrumental configurations used were: laser pulse fluence of 1019 J cm^{-2} (80 mJ of laser pulse energy and a 100-µm spot size), delay time of 1 µs, and data acquisition time of 1.05 ms. Additional laser parameters were 5 Hz of frequency and 10 mm/s ablation rate. The spectrometer of this instrument consists on a 6-channel charge-coupled device (CCD) which ranges from 186 to 1042 nm with 12,288 pixels. All operational parameters were controlled by Axiom software with an
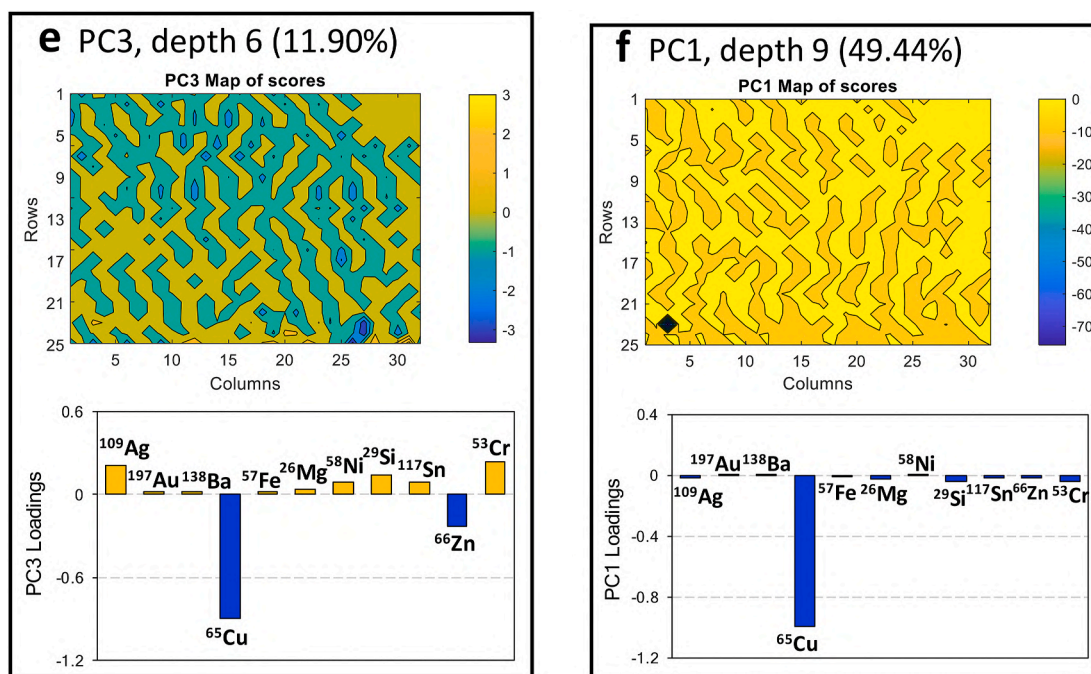
Fig. 1. (*continued*).

automated x, y, and z sampling stage and a 1280 × 1024 complementary metal-oxide semiconductor (CMOS) color camera imaging system.

The LA-ICP-MS analyses were carried out using a 213 nm UV laser ablation system (ESI instruments, Freemont, CA, USA) coupled to a NexION-2000B inductively coupled plasma-mass spectrometer (ICP-MS, PerkinElmer Instruments, Shelton, CT, USA). For all measurements the ablation chamber was sealed and evacuated several times before helium gas was set to flow through it at a rate of 500 mL min^{-1}. The laser pulse frequency was 10 Hz, and 105-μm spot size. Laser fluences generally varied from point to point depending on the composition of the sample, ranging from 16 to 240 J cm^{-2}; different PCB components (*i.e.*, battery, transistors, integrated circuit, polymers, metallic surfaces) have different laser-sample interaction. The analyte masses (*m/z*) of ^{109}Ag, ^{197}Au, ^{138}Ba, ^{65}Cu, ^{53}Cr, ^{57}Fe, ^{26}Mg, ^{62}Ni, ^{29}Si, ^{117}Sn, and ^{66}Zn were selected for elemental inspection. The raw intensity (cps) *vs.* time (s) data were downloaded as .csv file and later converted to Excel (Microsoft Corp., Redmond, WA) spreadsheet format for further analysis.

2.4. Microwave-assisted acid leaching and ICP-OES determination

To establish reference concentrations, two PCB samples (previously analyzed by micro-XRF and LIBS) were subjected to microwave-assisted (Speedwave Xpert, Berghof, Germany) acid leaching prior to ICP-OES determinations (iCAP 7000, Thermo Fisher, Madison, WI, USA). Each PCB sample (n = 2) was cut into small parts of 20 subsamples (10 × 8.5 mm). These subsamples were then leached separately with 7 mL of *aqua regia* (a 1:3 mixture of nitric and hydrochloric acids) using 100 mL volume-closure flasks (DAK 100). The microwave-assisted heating program presents the following steps: (1) 5 min ramp up to 120 °C, holding at 120 °C for 5 min; (2) 5 min ramp up to 180 °C, holding at 180 °C for 2 min; and (3) 5 min ramp up to 220 °C, holding at 220 °C for 15 min. To evaluate the accuracy of the proposed method 100 mg of the PCB reference material was also digested using 7 mL of *aqua regia* and the three-step heating program. The samples were then cooled to room temperature, the supernatant was separated, and diluted for elemental determination. Table 1 shows the instrumental operating parameters for ICP-OES measurements.

2.5. Chemometric tools for data processing

2.5.1. Chemical inspection using PCA analysis

The micro-XRF, LIBS, and LA-ICP-MS data were first processed by principal component analysis (PCA) to obtain maps of scores and investigate the elemental composition of major elements within the surface of PCB samples. The emission signals were selected from the spectral dataset and calculated the signal area for each analyte. The resulting matrix for LIBS and LA-ICP-MS were rearranged as 10 images related to the order of the laser pulses, with one image obtained per pulse, from the first through the tenth pulse. The data matrix from each technique was submitted to PCA calculation using the auto scaled data, the score values were arranged to build the maps of scores and associated with its corresponding loading vector (*i.e.* spectral information). All PCA calculations and data processing were performed using Matlab R2018b (MathWorks Inc., Natick, MA, USA) software platform. For more details about this approach, readers are encouraged to consult the study published by Carvalho et al. [13], in which the metal composition of a printed circuit board (PCB) was investigated.

2.5.2. Calibration methods for micro-XRF and LIBS analysis

Two chemometric approaches were used for calibration purposes: univariate and multivariate. Univariate strategies were tested after selection of emission signals for each element monitored. In this method, the correlation between the ICP-OES results (*x* axis, reference values) and analytical signals (*y* axis) are selected to build a linear model. To multivariate calibration, partial least squares (PLS) regression was used to concatenate the auto scaled analytical signals from both spectroanalytical techniques and reference concentrations determined using ICP-OES. All spectra obtained by LIBS were previously preprocessed [26], and then used to calculate the peak area and height of a selected region of the spectra for emission lines examined. The XRF intensities were background subtracted to represent the net counts. The data were then fused to build a new single calibration model at low-level employing the leave-one-out cross validation approach.

For data processing and evaluation, the following computer programs were used:
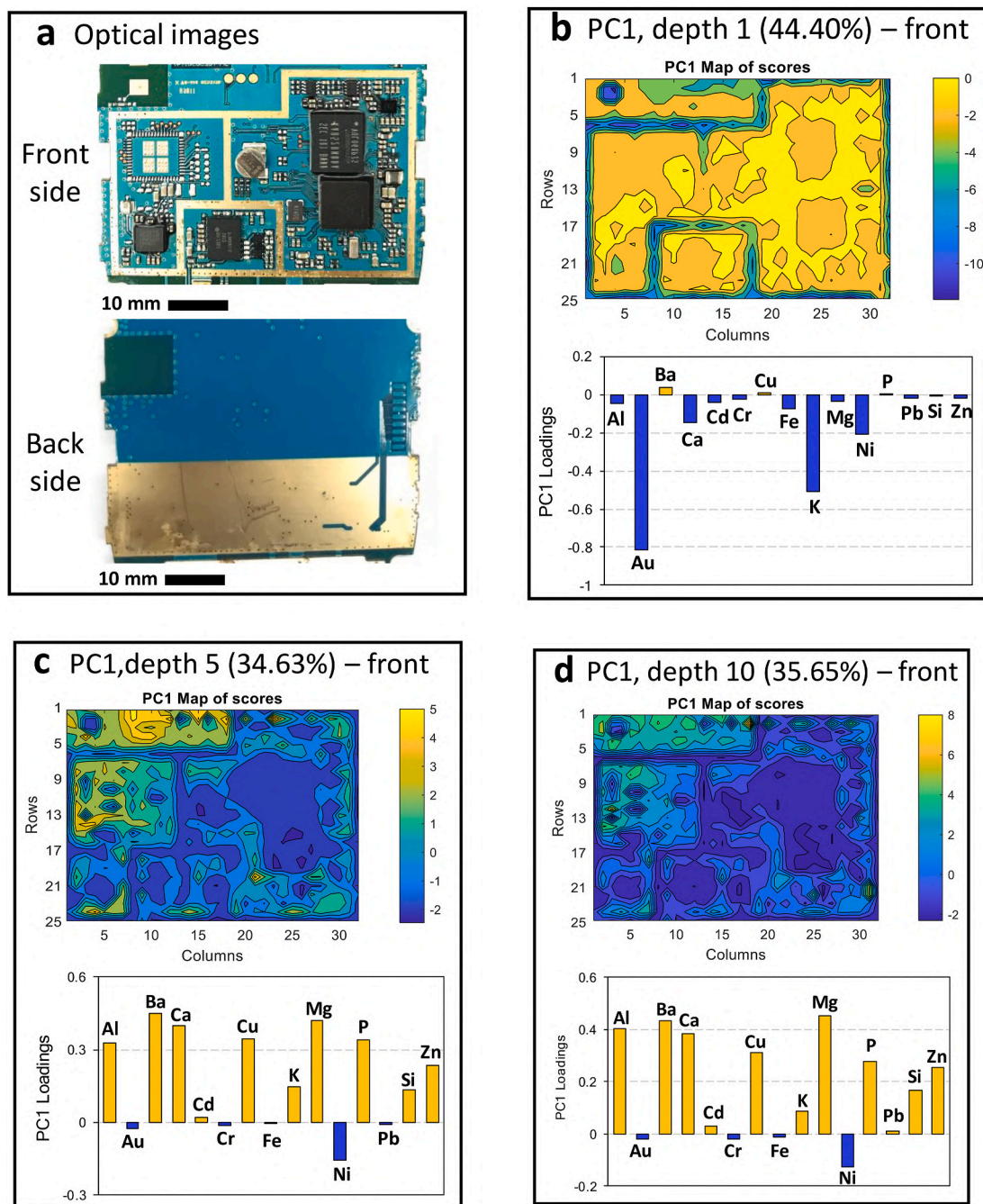
Fig. 2. Elemental mapping of (a) PCB sample using LIBS. Score maps and loadings to (b, c, and d) the front side and (e and f) the back side of the PCB sample. The black solid line at the bottom of the image denotes its scale factor.

- Microsoft Excel (Microsoft Corp., Redmond, WA, USA): data preparation and calculating univariate models;
- Matlab® R2018b: data matrices organization, normalization, and spectral data selection. All spectra obtained by LIBS were first normalized using a homemade script. In this process, spectral area (sum of all signals), maximum (highest signal intensity), Euclidean norm, and carbon emission atomic lines at 193.09 and 247.85 nm were used (adapted from Castro and Pereira-Filho, 2016 [26]). Other homemade scripts were then used to calculate the peak area and height of a selected region of the spectra for emission lines assessed;
- Pirouette version 4.5 (Infometrix, Bothell, WA, USA) was used to calculate the PLS models.

3. Results and discussion

3.1. Elemental mapping using PCA analysis

LA-ICP-MS, LIBS, and micro-XRF applications benefiting from their fast response technologies and high spatial resolution capabilities are rapidly becoming routine and thus making elemental/isotope mapping a reality. Moreover, multivariate analysis was found viable to handle large datasets of raw spectral information and brought new insight into high-dimensional mapping [13,27]. Due to complexity of PCBs elemental composition and the emission spectra for thousands of elemental responses (mainly for LIBS spectra), a robust data analysis strategy to process the large number of information was required. The use of PCA in
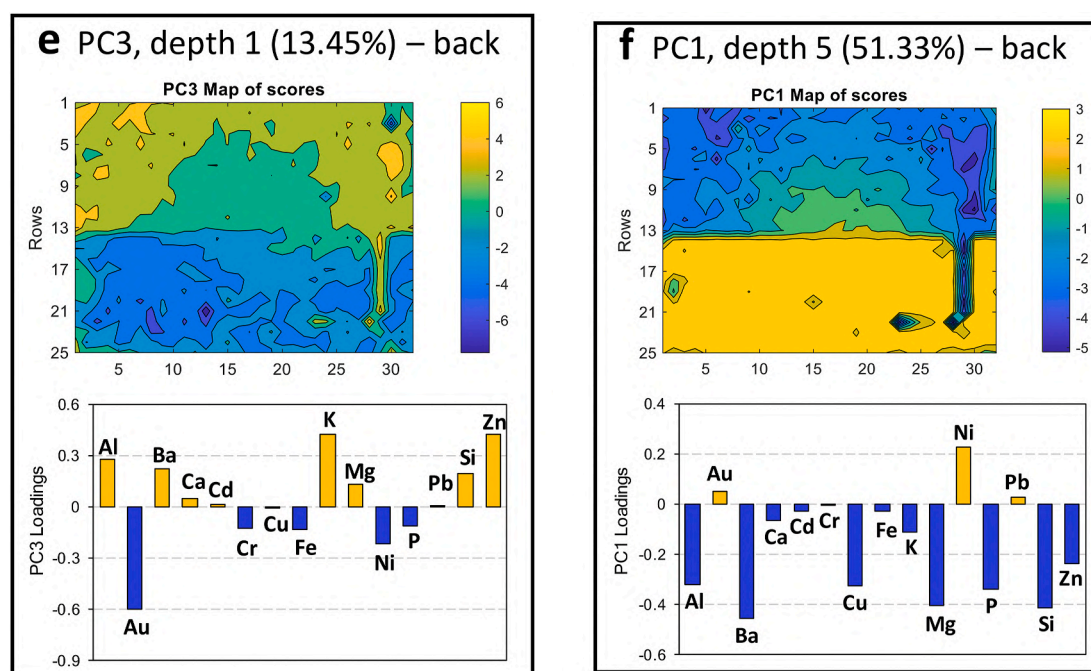
Fig. 2. (*continued*).

the elemental mapping of LA-ICP-MS, LIBS, and micro-XRF allowed the visualization of main elements composition and helped to reveal their complex distribution on the PCB matrices. Each principal component (PC) provided the elemental information within the surface of the sample. The score images display the contribution for each PC and the loading vector shows correlations among the analytical signals (*i.e.*, isotopic signals, fluorescence, and emission) of the elements present in the PCB surface. Large loadings (positive or negative) indicate that a particular analytical signal has a strong relationship to a particular PC. The sign of a loading indicates whether a variable and a PC are positively or negatively correlated.

In this study, the multi-elemental imaging of Ag, Al, Au, Ba, Ca, Cd, Cr, Cu, Fe, K, Mg, Mn, Mo, Ni, P, Pb, S, Si, Sn, Sr and Zn was conducted using the three complementary techniques combined with PCA analysis. Figs. 1–3 show the scores images associated with its corresponding loading vector obtained for LA-ICP-MS, LIBS, and micro-XRF analysis, respectively. Elemental maps were recorded using micro-XRF and LIBS on both sides of the PCB, and only the back side of the board was analyzed using LA-ICP-MS. Given the complex spectral structures, especially for LIBS spectra with thousands of emission lines, the appropriate spectral lines for the elements of interest were selected before generating elemental images. To this end, the emission signals free of interferences were selected and calculated the signal area using a homemade routine in the Matlab software.

With respect to LA-ICP-MS and LIBS analysis, the elemental mapping was obtained from the surface and depth profiling, with score maps and loading vectors of laser pulse 1 (depth 1) to 10 (depth 10). Fig. 1 shows (a) the real physical PCB image and (b-f) the LA-ICP-MS analysis in the back side of the PCB sample for depth 1 (PC1, 33.38% of the total explained variance), depth 2 (PC2 and PC5, 34.86% of the total explained variance), depth 6 (PC3, 11.90% of the total explained variance), and depth 9 (PC1, 49.44% of the total explained variance) of laser pulse. The score maps depicted in the Fig. 1 were selected from the depth profile and PC that show a significant isotope spatial distribution for the elements monitored. In this case, due to the highly sensitive elemental analysis capability of LA-ICP-MS, a heterogeneous distribution was observed. That is, mainly [109]Ag, [197]Au, [57]Fe, [58]Ni, and [66]Zn were detected in the depth 1 (higher negative loading, Fig. 1b), [58]Ni signals on the metallic area of the board (positive loading, Fig. 1c) as well as [65]Cu

and [26]Mg signals on the solder mask in the depth 2 (negative loadings, Fig. 1c and d). In addition, the depth profiling of laser pulses 6 and 9 show predominantly the distribution of [65]Cu signals (negative loading, see Fig. 1e and f).

Fig. 2 shows the score images and loading vectors obtained by LIBS in the front side of the board (Fig. 2b, c and d) for the first PC in the depth 1, depth 5, and depth 10 with 44.40%, 34.63%, and 35.65% of the total explained variance, respectively. In this case, the electrical components in the front side of the board were identified in the score map for depth 1 (Fig. 2b), with Au, K and Ni predominant in the conductive tracks (negative loadings). Moreover, in the score maps for the fifth and tenth laser pulses (Fig. 2c and d), the positive contributions correspond to other elements assessed such as Al, Ba, Ca, Cu, K, Mg, P, Si and Zn. The back side of the PCB sample for the third PC in the depth 1 (13.45% of the total explained variance) and first PC in the depth 5 (51.33% of the total explained variance) are also shown in Fig. 2e and f. Examining the score maps and its corresponding loading vector, it can be clearly seen that the metallic area is mainly composed of Au and Ni, whereas the solder mask part seems to be associated with Al, Ba, Cu, K, Mg, P, Si and Zn emission lines. In general, besides the normal metallic fraction (*i.e.* Al, Au, Ba, Cu, Fe, Mg, Ni, Zn), non-metals like P, S and Si can also be detected within the PCB samples. Metals make up most of the conductor materials, while those non-metals that don't allow electricity to flow through them act as insulators (*i.e.* plastics in PCB). However, these materials can be far more complex than this. Many researches have been paying special attention to precious metals as well as critical elements mainly due for their economic and strategic value.

Fig. 3 shows the micro-XRF images for the first, second and third PCs (46.44% of the total explained variance) for the front side of the PCB sample, the first and second PCs (81.05% of the total explained variance) for the back side of the board, and their corresponding loadings vectors. Examining the loading vector in the first PC for the PCB front side, is it possible to see in the score images that the negative contributions correspond with Ba, Cu, and S in most area of the sample surface (blue part, Fig. 3b). Moreover, the positive contributions pointed mainly to Cr and Fe originating from the battery in the sample. The positive loadings in PC2 (Fig. 3c) displays the spatial distribution of Au, Cu, Ni, P, S and Si in conductive tracks, whereas the negative contributions correspond mainly with Al, Ba, Cr, Fe, Mn, Pb and Zn for the other areas
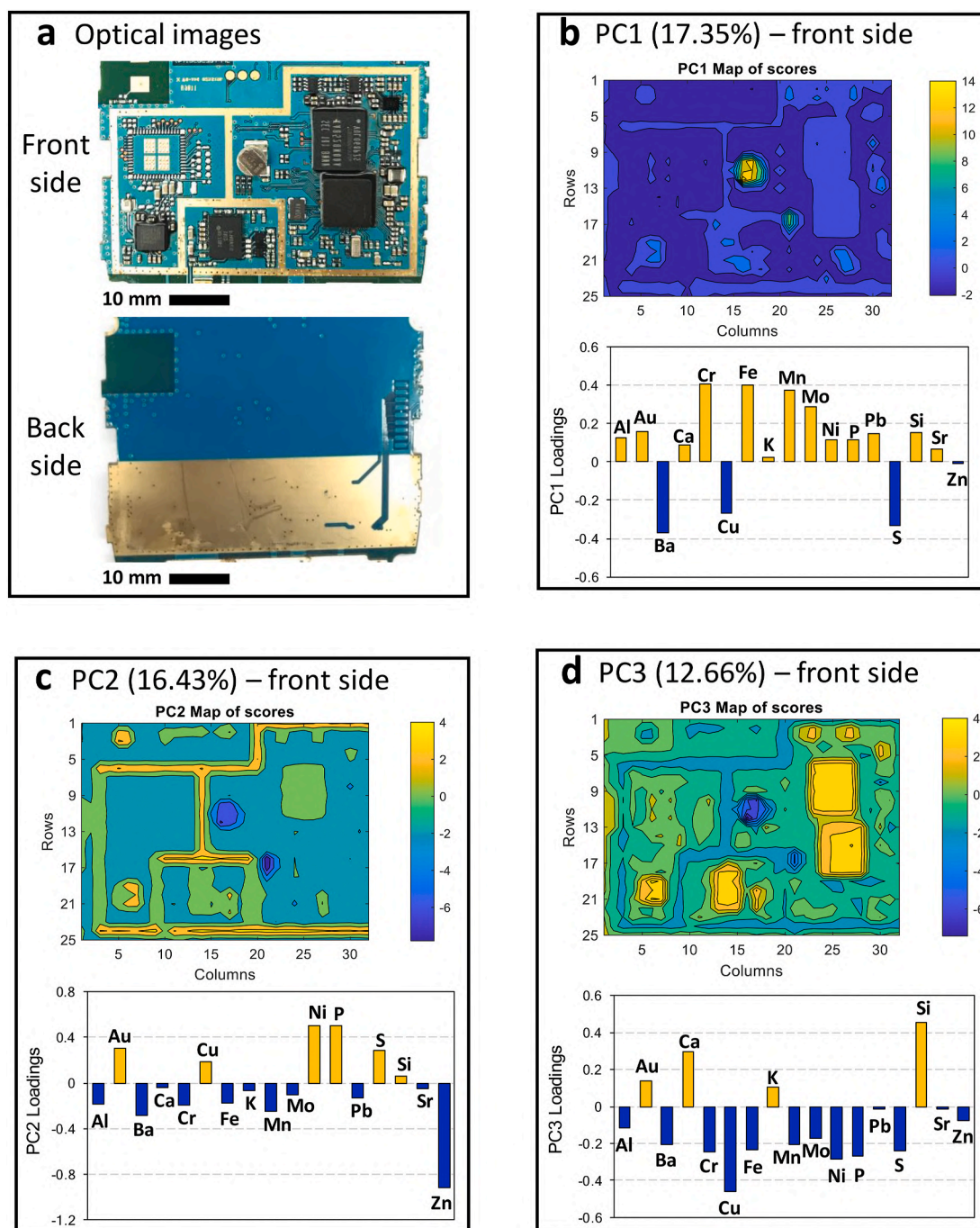
Fig. 3. Elemental mapping of (a) PCB sample using micro-XRF. Score maps and loadings to (b, c, and d) the front side and (e and f) the back side of the PCB sample. The black solid line at the bottom of the image denotes its scale factor.

of the sample. In addition, the score image for the PC3 displays Au, Ca, K and Si in the integrated circuits (yellow part, Fig. 3d). The back side of the PCB sample is clearly associated with Au, Ni, P and a small contribution of Cu and Fe in the metallic area, as shown in negative loadings for PC1 (see Fig. 3e). This score image also shows in positive the presence of Ba as well as Ca, S, Si, Sr and Zn in the solder mask (*i.e.* green surface of optical image) onto the outer layer of the board. In the score map for the PC2 in the Fig. 3f, Cu was the predominant constituent as observed in the blue region, probably related to Cu foil laminate used for circuitry in PCBs.

Undoubtedly, these techniques perform as powerful technologies for direct analysis of PCBs. The spatial distribution and composition of important elements can foster new recycling routes, and help in the process of disassembly, reuse, sorting, and so on. However, the use of these techniques must be carefully evaluated. For example, micro-XRF and LIBS can easily identify/classify base metals (*e.g.*, Al, Cu, Fe, Zn) present at high concentrations, and may not identify strategic elements (*e.g.*, In, Pd, Ga) occurring at lower concentrations in waste electrical and electronic equipment (WEEE). In latter case, LA-ICP-MS is more suitable for development of methods that offer most sensitive spatial elemental distribution information.
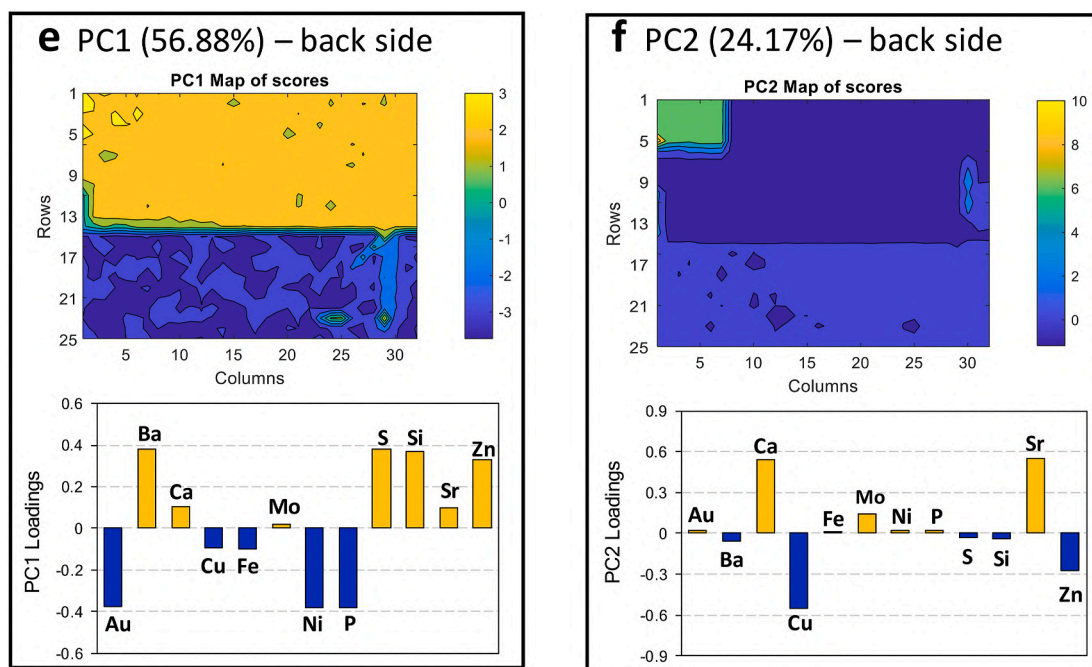
Fig. 3. (*continued*).

Table 2

Concentrations (mean ± standard deviation, n = 3) and recoveries values for the PCB reference material analysis.

Element	Certified values (% m m^{-1})	Found values (% m m^{-1})	Recovery (%)
Al	4.80 ± 1.08	4.30 ± 0.23	90
Au	236.55 ± 70.56 (mg kg^{-1})	241.21 ± 31.98 (mg kg^{-1})	102
Ba	0.50 ± 0.13	0.89 ± 0.01	180
Cr	0.29 ± 0.28	0.34 ± 0.01	119
Cu	14.08 ± 5.67	12.96 ± 3.29	92
Fe	3.92 ± 2.05	3.96 ± 0.62	101
Ni	0.42 ± 0.15	0.48 ± 0.02	115
Pb	1.19 ± 0.20	1.40 ± 0.02	118
Si	1.45 ± 0.57	1.00 ± 0.05	69
Sn	2.85 ± 0.97	3.26 ± 0.25	115
Zn	1.36 ± 0.71	2.43 ± 0.27	178

3.2. Reference concentrations: acid leaching and ICP-OES determination

After the micro-XRF and LIBS analysis, the PCB samples were submitted to a microwave-assisted acid leaching using *aqua regia* to obtain reference concentrations by ICP-OES determination. Each PCB sample (n = 2) was cut into 20 small parts (10 × 8.5 mm), totaling 40 subsamples. Then, each subsample was leached separately with *aqua regia* for 37 min. Due to the incomplete digestion, the supernatant was separated for elemental determination of Al, Au, Ba, Ca, Cr, Cu, Fe, K, Mg, Mn, Mo, Ni, Pb, S, Si, Sn, Sr, and Zn using ICP-OES. To evaluate the sample preparation and ICP-OES procedures, a reference material of electronic waste (RM – PCB, an in-house production) was also analyzed. Table 2 shows the obtained concentrations in accordance with the certified values (Student *t*-test at 95% of confidence level). Except for Ba, Si and Zn the recovery of other analyte elements were within 90–119% range. However, significant over recoveries (*i.e.*, Ba and Zn) were observed probably related to inhomogeneity of the sample material while the incomplete digestion was revealed due to low recovery value of Si with *aqua regia*.

The concentration range determined for each element in the 40 PCB subsamples were 0.65–4.02% m m^{-1} Al, 4–4917 mg kg^{-1} Au, 0.22–6.55% m m^{-1} Ba, 1.07–7.86% m m^{-1} Ca, 5–7425 mg kg^{-1} Cr, 13–45% m m^{-1} Cu, 0.01–2.02% m m^{-1} Fe, 60–286 mg kg^{-1} K, 0.03–0.23% m m^{-1} Mg, 1.41–450 mg kg^{-1} Mn, Mo < 0.18 mg kg^{-1} (limit of detection, LOD), 0.06–3.64% m m^{-1} Ni, 0.72–0.84% m m^{-1} Pb, 0.03–0.44% m m^{-1} S, 0.05–0.80% m m^{-1} Si, 0.38–5.30% m m^{-1} Sn, 0.02–0.61% m m^{-1} Sr, and 0.01–1.16% m m^{-1} Zn. It is important to point out that the concentrations determined for both PCB samples were similar for most elements monitored. For example, Fig. 4 shows the correlation plots for Ba, Cu, Ni and Sn determined in the subsamples. That is, the comparisons between the concentrations determined for the 20 subsamples of PCB1 *vs.* 20 subsamples of PCB2 demonstrate strong positive correlationships for those tested elements. However, other monitored elements such as Au, Cr, Mn, and Mo showed significant differences among the samples, that may be related to their minor presence in the PCBs.

3.3. Univariate calibration using micro-XRF and LIBS data

To obtain univariate calibration models for LIBS, 16000 spectra were obtained *per* board (800 points × 10 laser pulses per point × both-sided analysis) and then pretreated using 12 normalization modes [26]. The signal area and height of each analyte was calculated, considering the availability of emission lines free of interferences. The monitored elements and its respective emission line (*i.e.* atom or line in nm) with high relative intensity were: Al I 392.40, Au II 208.20, Ba II 455.40, Ca II 393.36, Cd I 508.58, Cr II 283.56, Cu I 324.75, Fe II 274.64, K I 766.49, Mg II 280.27, Ni I 361.93, P I 213.61, Pb I 405.78, Si I 288.15 and Zn I 481.05 nm. The signals corresponding to each subsample (n = 40) from the PCB samples were selected, and then the average signal for each analyte was calculated. Finally, the univariate calibration models were obtained and the best results were observed considering the lower standard error of calibration (SEC), trueness values, and the best correlation between the predicted concentration and reference values (ICP-OES).

For micro-XRF technique, 1600 spectra were recorded (800 points × analysis of both sides) from the PCB samples and revealed the following characteristic X-ray peaks: Al Kα 1.49, Au Lα 9.71, Ba Lα 4.47, Ca Kα 3.69, Cr Kα 5.41, Cu Kα 8.05, Fe Kα 6.40, K Kα 3.31, Mn Kα 5.90, Mo Kα 17.48, Ni Kα 7.48, P Kα 2.02, Pb Lα 10.55, S Kα 2.31, Si Kα 1.74, Sr Kα
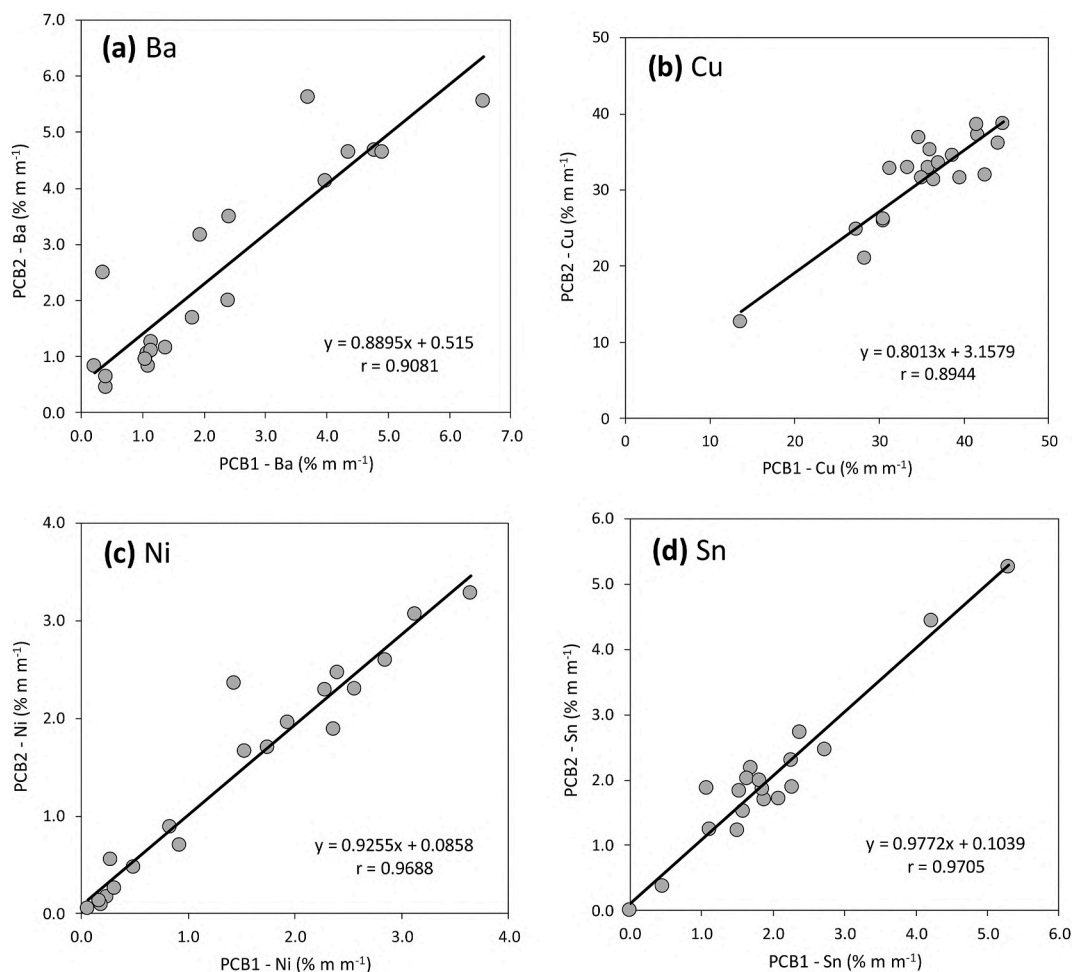
Fig. 4. Correlations for the determined concentrations to (a) Ba, (b) Cu, (c) Ni and (d) Sn in the PCB samples (PCB1 vs. PCB2) using the reference method (ICP-OES determination).

Table 3
Univariate model parameters to determine Cu using LIBS.

Copper emission line (nm)	Relative intensity	Normalization mode	Signal type	Laser pulse (depth)	r, and univariate model	SEC[a] (% m m^{-1})	Trueness range (%)
324.75	16,256	Euclidean norm	area	9	0.5749, y = 2.5 × 10^{-9} x – 1.4 × 10^{-4}	9.95	23–165
327.39	15,301	Euclidean norm	height	8	0.5859, y = 7.0 × 10^{-10} x + 4.5 × 10^{-6}	9.67	33–166
521.82	12,349	C 247.85	height	8	0.5832, y = 1.4 × 10^{-6} x – 0.08	9.74	72–196
515.32	8297	C 247.85	area	8	0.5609, y = 2.3 × 10^{-6} x – 0.18	10.32	69–333
224.70	8046	C 247.85	height	6	0.6142, y = 1.4 × 10^{-6} x + 0.17	9.00	52–241
224.26	7634	area	area	10	0.5888, y = 4.1 × 10^{-6} x – 1.2 × 10^{-4}	9.60	38–203
213.59	6104	C 247.85	area	7	0.5753, y = 3.6 × 10^{-6} x – 0.34	9.94	47–184
510.55	4707	C 247.85	area	9	0.5640, y = 3.03 × 10^{-6} x – 0.27	10.24	13–177
205.49	2413	C 193.09	area	7	0.5224, y = 2.20 × 10^{-6} x + 0.04	11.41	28–201
210.47	2231	Euclidean norm	area	10	0.4921, y = 9.23 × 10^{-10} x – 6.5 × 10^{-5}	12.37	22–187
204.38	1757	Euclidean norm	area	10	0.5510, y = 1.09 × 10^{-9} x – 4.8 × 10^{-5}	10.59	27–176

[a] SEC = Standard Error of Calibration.

14.14 and Zn Kα 8.64 keV. The XRF intensities were background subtracted to represent the net counts. Then, the univariate models and its analytical parameters were obtained (*i.e.*, SEC, trueness and correlation coefficient). To this end, the step for normalizing X-ray emission signals were not necessary due to selection of the signals free of interferences, thereby providing fast and reliable data extraction.

In general, the univariate models using LIBS and micro-XRF data failed to predict the concentrations for most elements monitored in the PCB samples. This is evident for the high SEC calculated and trueness values out of the acceptable range of 80 to 120%. For instance, in LIBS analysis, the SEC values were 0.65% m m^{-1} for Al, 0.71% m m^{-1} for Au, 2.48% m m^{-1} for Ca, 782 mg kg^{-1} for Mg, and 0.89% m m^{-1} for Ni, and
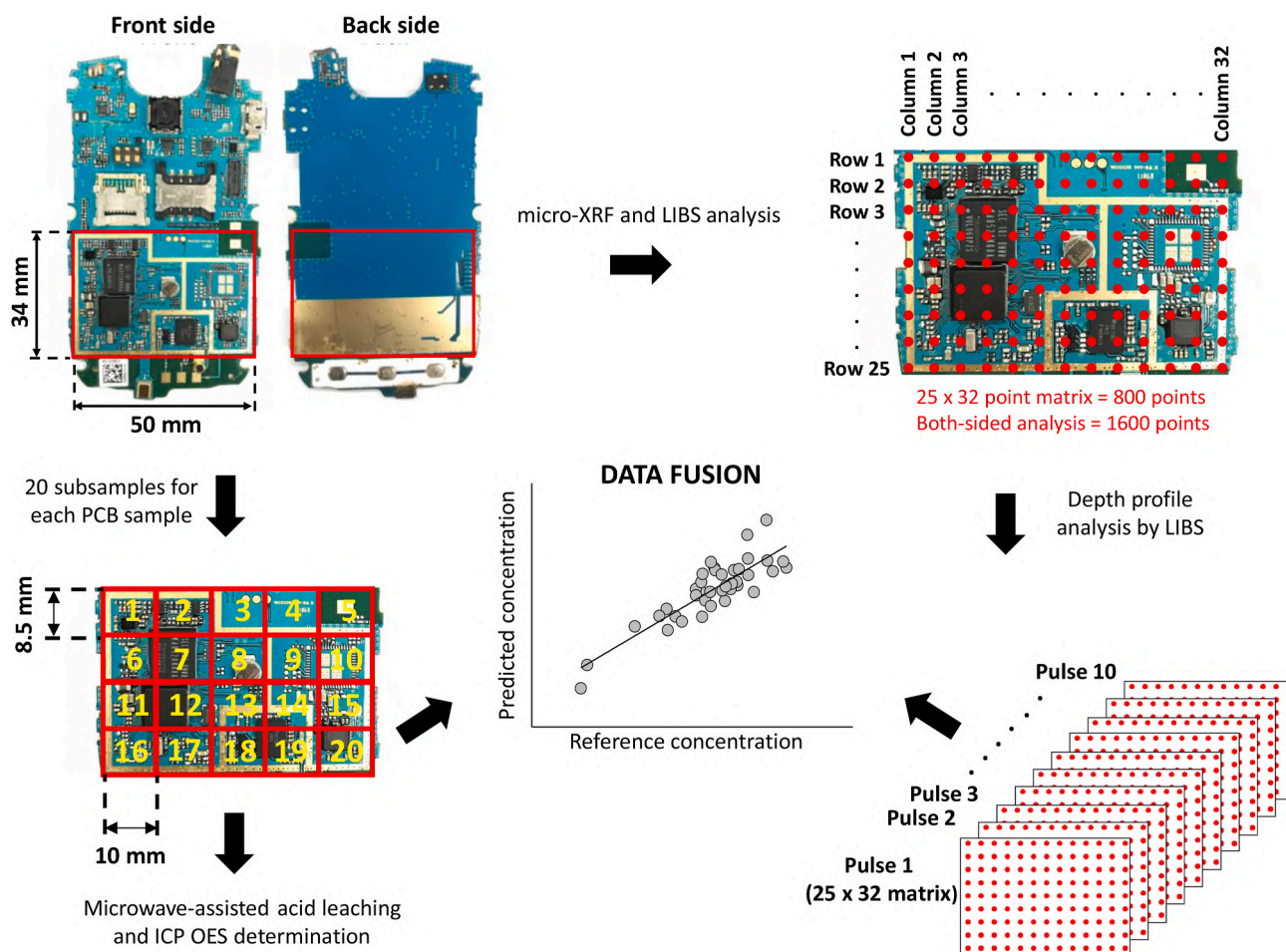
Fig. 5. Pictorial description showing the PCB analysis and data fusion approach.

Table 4
Results of calibration models (cross validation dataset, n = 40) of micro-XRF and LIBS data fusion for Cu determination.

Normalization mode[a]	Signal type	Laser pulse (depth)[a]	Latent variables	RMSEC (% m m^{-1})	RMSECV (% m m^{-1})	bias (% m m^{-1})	r, and multivariate model	Trueness range (%)
no normalization	area	2	4	3.25	3.57	−0.0208	0.8108, y = 0.7x + 10.4	76–140
Area	height	3	4	3.04	3.66	0.1586	0.8512, y = 0.7x + 8.0	73–121
C 193.09	height	2	3	3.09	3.39	0.0081	0.8721, y = 0.8x + 7.1	80–129
C 247.85	area	2	3	3.10	3.36	−0.0022	0.8739, y = 0.8x + 7.2	80–136
maximum	height	2	3	3.18	3.55	−0.0695	0.8586, y = 0.7x + 8.4	82–134
Euclidean norm	area	2	4	2.93	3.23	−0.0708	0.8846, y = 0.8 x + 6.5	81–119

[a] LIBS data.

the correlation coefficients were 0.6430, 0.1747, 0.4942, 0.4293, and 0.7802, respectively. Regarding to micro-XRF data, the SEC values were 0.24% m m^{-1} for Au (r = 0.4996), 11.06% m m^{-1} for Fe (r = 0.046), 1.00% m m^{-1} for Ni (r = 0.7410), 0.10% m m^{-1} for S (r = 0.6637), 0.22% m m^{-1} for Sr (r = 0.5797), and 0.87% m m^{-1} for Zn (r = 0.3190). Given the complexity of PCB samples, namely due to the heterogeneous nature of the PCB composition due to different integrated components within the sample surface, as well as spectral interferences, and matrix effects may all compromised the direct elemental determination using above calibration models.

On the other hand, promising results were obtained for the determination of Cu using LIBS and micro-XRF. The results related to Cu determination using LIBS employing different emission lines are shown in Table 3. The normalization mode, signal type and laser pulse (depth) are also highlighted. The best normalization was chosen considering the

trueness and SEC values which were the signal normalization by Euclidean norm, area and carbon lines (at 193.09 and 247.85 nm). In this case, the best results were obtained for Cu I 224.70 nm with the lowest SEC value of 9.00% m m^{-1}, and the trueness ranged between 52 and 241%. Using the univariate model proposed for micro-XRF (r = 0.8495, y = 0.01x + 1339) the SEC decreased around 2-fold (4.34% m m^{-1}), and the trueness ranged from 39 to 145%. Despite these upper/lower trueness range limits look very high or very low, 50% and 80% of the results for LIBS and micro-XRF, respectively, were between the acceptable range of 80 to 120%. The micro-XRF technique presented even better results than those obtained by LIBS. However, such improvements were not sufficient to accurately predict Cu concentrations in all PCB subsamples. Thus, the strategy using micro-XRF and LIBS data fusion was evaluated to improve the predictive capacity of the calibration models.
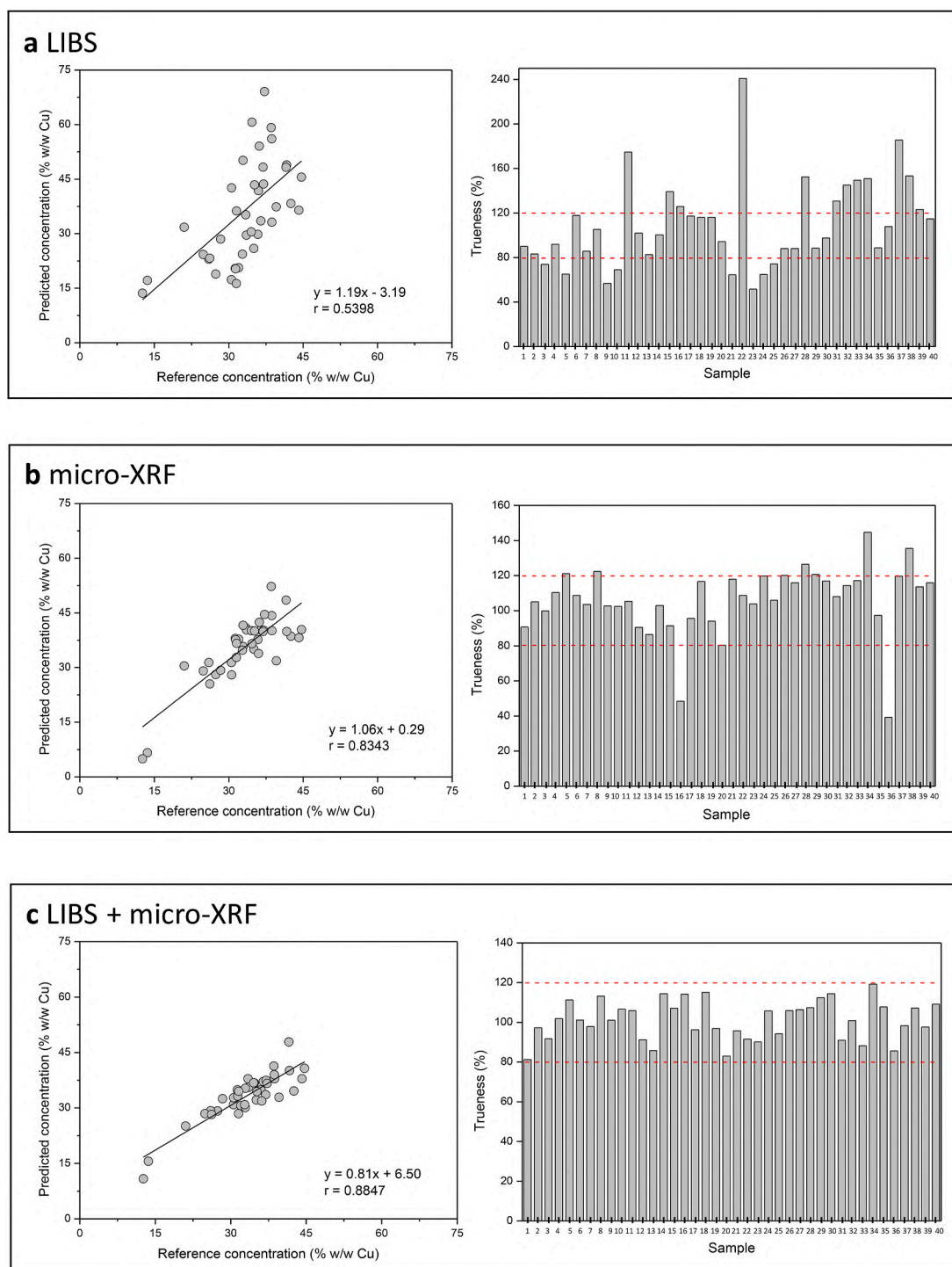
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Fig. 6. Correlation graphs (measured vs. predicted concentrations) and trueness using (a) LIBS data, (b) micro-XRF data, and (c) micro-XRF + LIBS data fusion.

3.4. Multivariate calibration using micro-XRF and LIBS data fusion for copper determination

In the case of multivariate calibration, PLS was applied combining the resulting information from micro-XRF and LIBS, and reference concentrations (ICP-OES). Fig. 5 shows a pictorial description for the PCB sample analysis, the area analyzed (red squares), sample dimensions, and data organization for data fusion using Cu signals from micro-XRF and LIBS. Data fusion models were built at low-level employing PLS with leave-one-out cross validation approach using the 40 PCB subsamples. The evaluation of the efficiency of calibration

strategy employed was performed with the assistance of root mean square error of calibration (RMSEC) and of cross validation (RMSECV), normalization modes, as well as the trueness of Cu prediction compared to Cu concentrations measured using ICP-OES. Table 4 summarizes the parameters for the multivariate models and the best results obtained using micro-XRF and LIBS data fusion.

The results for data fusion clearly indicate improvements in the predictive capacity of the calibration models. In this case, the normalization modes slightly improved the results and the errors. Using the signal area normalized by norm, the trueness values obtained were in the range of 81 to 119%, RMSEC of 2.93% m m^{-1}, RMSECV of 3.23% m

m^{-1}, and bias of -0.0708 m m^{-1}. The calibration error decreased around 3-fold compared to LIBS (9.00% m m^{-1}) and more than 1.0% m m^{-1} when compared to micro-XRF (4.34% m m^{-1}) univariate model.

Moreover, using the data normalized by norm, a second multivariate calibration approach was assessed. A set of 80% of the total samples (n = 32) was used as the calibration dataset, and then the 20% of the remaining total samples (n = 8) as the validation dataset to fit to the PLS model and predict the Cu concentration. In this case, selecting 3 latent variables, the resulting RMSEC was 2.94% m m^{-1}, bias was 0.0773% m m^{-1}, and a correlation coefficient of 0.9240. With respect to the prediction dataset, a RMSEP of 3.15% m m^{-1}, bias of -0.0330% m m^{-1}, and a correlation coefficient of 0.8529 were obtained. In addition, the trueness varied between 86 and 119%. To assess the systematic errors of all models in the Table 4 and in the calibration and validation dataset approach, a test for bias significance was performed, and for all cases, no systematic errors were found using a *t*-test calculated with a significance level of α = 0.05 [28,29].

Finally, Fig. 6 shows the best linear model (*i.e.*, correlation between reference and predicted concentrations) and the trueness for each proposed method. Examining the trueness for the 40 PCB subsamples, it is possible to infer that the techniques individually predicted promising results for Cu analysis. However, these results clearly indicate that the effect of the matrix during measurements, especially in the case of LIBS, given the poor prediction of concentrations for some samples and the correlation coefficient obtained (r = 0.5398, Fig. 6a). In addition, only through the fusion of analytical information gathered from both analytical techniques (*i.e.* micro-XRF and LIBS data) resulted the trueness values within the range of 80 to 120% (between red dotted lines). Indeed, the data fusion strategy demonstrated as the best calibration approach for direct solid sample analysis, in which the errors were around 4-fold lower than the measured lower Cu concentration (12.4% m m^{-1}).

4. Conclusions

LA-ICP-MS, LIBS, and micro-XRF showed as powerful analytical technologies suitable for direct analysis of electronic waste. The combination of these techniques and PCA analysis for elemental mapping was a useful approach for obtaining information about valuable metals (Au, Ag), base metals (Al, Cu, Fe, Ni), toxic elements (Cd, Cr, Pb), and others in the PCB samples. Moreover, the locating of the spatial distribution of these elements in e-wastes can nurture development of efficient and well directed recycling methods. Ultimately, this will facilitate the process of disassembly, reuse, and identification and sorting of valuable materials from WEEE.

Within the calibration strategies evaluated, it is clear that combining multiple data sources derived from complementary analytical techniques through data fusion is the best approach for analyzing PCB samples. In fact, data fusion approach was a powerful alternative to gain an improved detection of metals in PCBs and has enabled us to build regression models with better statistical parameters such as lower percent errors, better accuracy, and reliability. This approach was tested with two PCBs represented in 40 subsamples as a proof of concept, and given the complexity of the e-waste stream and the inherent calibration problems for direct analysis of solid samples, it was only possible to obtain quantitative results for Cu analysis. However, this study opens the possibility for improved measurement of valuable elements in e-waste recycling streams and the chemical investigation of millimeter sized solid samples like these without resorting to labor intensive and time consuming sample preparation methods.

Credit author contribution statement

Daniel F. Andrade: design the research, formal analysis, conceptualization, visualization, writing, review, and editing; **Eduardo de Almeida**: formal analysis, conceptualization, visualization, review, and editing; **Hudson W. P. Carvalho** for editing, review, supervision, funding acquisition, and resources; **Edenir R. Pereira-Filho:** design the research, conceptualization, visualization, writing, review, editing, supervision, and funding acquisition; **Dulasiri Amarasiriwardena:** design the research, conceptualization, visualization, writing, review, editing, supervision, and funding acquisition.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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5 Conclusion

The ever-increasing e-waste generation and lack of proper management of e-waste is undoubtedly a current problem that surrounds the modern society. We have seen that in addition to causing problems to the environment and human health, a large amount of valuable materials is still wasted (see Chapters 1 and 2).

Given these issues, it was initially proposed an electronic waste RM for monitoring the chemical composition of this waste stream. The in-house produced material is a pioneer in this field, which opens other possibilities for developing more studies on RMs for samples that are physically and chemically complex as e-waste. Successfully as presented in this thesis, an RM for monitoring precious elements (i.e. Ag and Au) was developed with suitable homogeneity and stability (see Chapter 3).

Direct solid sample analysis using laser-based techniques and XRF appear as promising technologies for both qualitative and quantitative aspects (see Chapter 4). First, the chemical inspection by fast direct analysis techniques discussed previously, allows a continuous feedback to facilitate the effective sorting process for subsequent actions such as reusing, repairing, refurbishing, recycling or an appropriate final disposal. To this end, LIBS, LA-ICP-MS and XRF were successfully applied for the chemical investigation of PCB samples measuring a few millimeters in dimension without sample preparation (chemical mapping).

Despite the various problems related to direct analysis of solids, new quantitative approaches were proposed for the determination of In content in LCD samples combining MEC and LIBS, as well as data fusion of LIBS and XRF data using PLS for determination of Cu in PCB samples. For MEC, only two calibration standards for each sample were required, matrix effects were minimized, and a spectral interference was identified. However, this method requires effective sample homogenization with blank or standard, and an appropriate blank (diluent). For multivariate calibration, PLS allowed the fusion of complementary information and results with higher analytical performance than univariate calibration strategies.

Finally, different chemometric approaches (i.e. design of experiments, PCA and PLS) were of paramount importance in the development of those methods for the analysis of e-waste, such as in the optimization of the acid extraction process for RM characterization (Chapter 3); exploratory analysis using PCA to provide as much relevant information as possible by analyzing the chemical data obtained in the acid leaching of RM (Chapter 3); PCA to obtain the score maps in the chemical inspection of PCB sample surface (Chapter 4); and to fusion the data obtained by LIBS and XRF to obtain a multivariate calibration model (Chapter 4).

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