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EVALUATION OF ELEMENTS DISTRIBUTION IN PRINTED CIRCUIT BOARDS FROM MOBILE PHONES BY MICRO X-RAY FLUORESCENCE

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ABSTRACT

A micro X-ray fluorescence-based approach for the chemical characterization of spent printed circuit boards (PCBSPCBSS) from mobile phones was applied. More in detail, twelve spent mobile phones were grouped into three clusters according to brands, models and year of release, and a study to evaluate the technological evolution of PCBSs over time was carried out. Precious metals and hazardous elements were investigated, revealing a few differences between samples from the different groups. For instance, the distribution of gold on PCBS layers was more widespread for the older analyzed samples, and smaller quantities of bromine and lead were detected in the more recent models in accordance with the *Restriction of Hazardous Substances Directive 2002/95/EC*. Analysis of PCBS composition should contribute towards correctly managing such a complex waste, maximizing the recovery of base, critical and precious metals and considering the possible presence of harmful elements requiring careful management. The experimental results showed how, using the proposed approach, distribution maps for chemical elements present in PCBSs could be obtained, thus allowing the definition of optimal strategies for further handling (i.e. classification) and processing (i.e. critical/precious metal recovery).

1. INTRODUCTION

Mobile phones are one of the main items present in WEEE (Waste from Electrical and Electronic Equipment). In recent decades, a dramatic increase has been witnessed in the use of this kind of product in line with the progress of technology (Kasper et al., 2011a; Hira et al., 2018; Singh et al., 2019). Although the technical lifespan of mobile phones is approx. 10 years, consumers frequently upgrade their devices, limiting use to 1-2 years (Tan et al., 2017). Moreover, the increasingly low cost of electronic equipment, together with the adoption of ever more aggressive marketing strategies for items such as mobile phones, has resulted in a continuous renewal of these devices by consumers (Paianoa et al., 2013). Therefore, the amount of spent mobile phones is constantly rising, thus implying a need to develop efficient strategies for the recycling of such a complex waste.

PCBSs from mobile phones are viewed as "rich boards" comprising a large quantity of components (i.e. processors and capacitors made up of precious and critical metals, such as rare earth elements) "concentrated" over a small surface with a characteristically reduced thickness. This aspect affects the future recovery of valuable elements. It is therefore evident that the recycling of materials from spent mobile phones represents a compelling challenge both from an economical and an environmental point of view.

Mobile phones represent a rich reserve of precious metals, i.e. gold (Au), silver (Ag), palladium, (Pd), etc. and critical raw materials, including tantalum (Ta), indium (In), rare earth elements such as yttrium (Y), lanthanum (La), neodymium (Nd) and praseodymium (Pr); indeed, specific recycling treatments should be implemented to recover the highest possible quantities of these metals.

On the other hand, the disposal of discarded mobile phones is fast becoming a serious problem, particularly due to the presence of hazardous elements such as arsenic (As), bromine (Br), cadmium (Cd), lead (Pb), mercury (Hg), dioxins and furans which, when released, are harmful to both the environment and human health (Kasper et al., 2011b). In this perspective, the preliminary detection of these substances using non-destructive methods could provide useful information for subsequent recycling treatments.

In Italy, the estimated rates of WMP (Waste Mobile Phones) alone are not effectively recorded, being included in an extensive heterogeneous group of electronic wastes known as "R4", which includes a large range of devices

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such as: mobile phones, personal computers, printers, tablets and notebooks and other small electronic units (Legislative Decrees 151/2005, 152/2006 implementing the EU Directives 2002/96/EC, 2003/108/EC and "ROHS" Directive 2002/95/EC). These wastes represent approx. 21 % of total household WEEE (Annual Report of WEEE - www.cdcraee.it). In addition, the structural and compositional complexity of WMPs largely depends on the period of manufacture.

Although WEEE composition strongly influences the performance of recycling operations, the implementation of a "recycling oriented characterization" of wastes fed to the process (Chancerel and Rotter, 2009) will enhance effectiveness. Accordingly, the aim of this study was to define a systematic method of characterization to be applied as a preliminary phase in the recycling of End Of Life (EOL) PCBSs, starting from information obtained in previous studies (Palmieri et al., 2014; Bonifazi et al. 2018). Namely, the possibility of using a micro X-ray fluorescence (micro-XRF) based approach to perform chemical element detection and mapping of discarded electronic boards from mobile phones of different brands and different years of release, was investigated.

2. MATERIALS AND METHODS

2.1 Investigated samples

Twelve spent mobile phones of different brands, models and/or year of release (Table 1) were collected and divided into 3 groups based on the technological evolution linked to year of release. A short description of the main "technological" characteristics of these groups is provided below:

- Group A: "*mobile phones*" (release period: 1999-2009), enabling phone calls, text messaging and little else. The majority of these devices were GSM phones, using digital rather than analog networks and the first ARM processors. They adopted a similar but smaller brick-style form factor. Parts and components on the PCBS structure were "easy" to access. Antenna and antenna switch were normally located at the top of mobile phone PCBS and the power frequency oscillator (PFO) was present beside the antenna switch, Network IC was located below or beside the antenna switch and PFO, the power IC was at the bottom of the PCBS and identified by several brown-colored capacitors. The Central Processing Unit is easily recognizable, being the largest integrated circuit (IC). Finally, to complete the mobile phone PCBS: RAM, charging, audio, flash and logic IC were present.
- Group B: "*Feature phones*" (release period: 2011-2012), with a wide range of features (i.e. built-in cameras), more advanced than mobile phones but not as advanced as smartphones. Feature phones represent a midway point between smartphones and basic phones. Indeed, compared to smartphones, these phones are typically easier to use and cheaper to boot. Feature phones usually have a limited proprietary operating system and do not all support third-party software. Should they do so, they usually run on Java or BREW environment and are often standalone items that do not integrate with other phone features. The majority of these phones were equipped with 3G technology. Accordingly, feature phone PCBSs were similar to mobile phones, with numerous miniaturized elements and a higher performance CPU capable of managing the presence of a series of multimedia apps and the first camera-phone.
- Group C: "*Smartphones*" (release period: 2013-2015), i.e. forefront phones. Smartphone devices combine computing functions of feature phones and mobile computing functions in a single device. They are distinguished from feature phones by their higher hardware capacities and extensive mobile operating systems, which facilitate extended software, internet and advanced multimedia functionality, alongside core phone functions such as voice calls and text messaging. PCBSIn addition to components of feature phones, Smartphone PCBSs contain a number of metal–oxide–semiconductor (MOS) integrated circuit (IC) chips, including various sensors that can be leveraged by their software (such as a magnetometer, proximity sensors, barometer, gyroscope, or accelerometer), and support wireless communications protocols (such as Bluetooth, Wi-Fi, or satellite navigation).

Mobile phones were manually dismantled in order to select PCBSs for analysis. PCBSs were investigated by means of micro-XRF to detect the presence and distribution of the different chemical elements on the sample surface.

2.2 Micro-XRF equipment

Micro-XRF tests were carried out at the Raw Materials Laboratory (RawMaLab) of the Department of Chemical Engineering, Materials & Environment (Sapienza - University of Rome, Italy). Micro-XRF was utilized to map the chemical composition of entire PCBSs.

A μ-XRF benchtop spectrometer (M4 Tornado, Bruker®), equipped with an Rh X-ray tube with polycapillary optics and XFlash® detector, providing an energy resolution of more than 145 eV, was used for analysis. Polycapillary optics enable tube radiation to focus on a very small spot size (approx. 30 μm) by multiple reflections, thus providing a spot intensity increase of up to 104x compared to use of a collimator, promoting the obtaining of faster results and more detailed (i.e. spatial resolution) analysis. Spectrum energy calibration was performed on a daily basis prior to analysis of each batch using zirconium (Zr) metal (Bruker® calibration standard). The sample chamber can be evacuated to 25 mbar and, therefore, light elements such as sodium measured. At constant excitation energies of 50 kV and 500 μA, measurement conditions were adapted for the different investigated samples. The estimated thickness of the material that fluoresces was complex to determinate in multilayer matrix as SPCB. As element maps show, PBCs are composed by different layers of materials and electronic components, as a results is X-ray absorption is strongly affected by the investigated area (i.e. lead solder cover the presence of other elements and silica wafer, mainly composed by plastic material, allows the detection of copper

TABLE 1: Mobile phone samples utilized to perform micro-XRF analyses on PCBSs.

Sample image	Brand	Model	Release year
	Nokia	3210	1999
	Sony Ericsson	T300	2002
	LG	KU 385	2007
	Nokia	5230	2009
	Samsung	GT S 5250	2010
	Samsung	GT N 7000	2011
	LG	E 610	2012
	Samsung	GT i8160	2012
	Samsung	GT S 6310	2013
	Samsung	GT i9505	2013
	Samsung	GT i9195	2013
	Wiko	Ridge 4S	2015

TABLE 2: Analytical set up adopted to perform micro-XRF analyses.

Tube parameter		Acquisition parameter		
High voltage	Anode current	Vacuum	Pixel time	Frame count
50 kV	499 µA	20 mbar	6 ms/pixel	3

layer under its surface). The thickness of the sample was found to be critical and had to be carefully determined for each group of elements (Al-Merey et al., 2005). In metal alloys, for example, the coating thickness determination, using X-ray, can be calculated through point analysis (Giurliani et al., 2019). In complex matrices, such as SPCBs it is possible to determine as thickness of the material that fluoresces changes from 0 to a few microns according to the detected elements (Ming-qing, 2016). Measurement conditions used for the operated mapping are reported in Table 2.

3. RESULTS AND DISCUSSION

An example of the results obtained by micro-XRF chemical analysis, in terms of false color maps, for one of the analyzed PCBSs (i.e. NOKIA 3210, released in 1999) is illustrated in Figure 1. Following identification of the chemical elements detected for each PCBS, a correlation with the different electrical and electronic components was defined (Figure 2). A comparison of the differences and similarities between PCBSs belonging to the three investigated mobile phone sets, revealed how topological assessment of the elements detected on PCBSs reflected, in all cases, the component characteristics. Copper (Cu) and silicon (Si) were the most extensively detected elements in all three Groups studied (A, B and C), comprising respectively PCBS layers (Cu) and electronic component housings (Si).

Copper concentration and distribution were mainly related to the multiple thin layers constituting the PBC structure. A non-conducting layer, largely made up of insulating support (i.e. resin) providing mechanical resistance to the PCBS was located between the copper layers.

The main components of the insulating layers included fiberglass, identifiable by silicon, and resins. This structure is well evidenced by XRF mapping allowing identification of the majority of CU present under PCBS surface.

Si was present over the entire surface, although at varying concentrations, identified on the board in the fiberglass in the PCBS structure; moreover, a higher concentration of silicon was detected in chip protection covers.

The elements found most extensively in the antenna were Cr and Fe.

Ca was detected in numerous small components, and was particularly abundant in the buzzer.

Pb and Sn were distributed throughout the same area, confirming the presence of an alloy for solder based on these elements.

Au was present in two different forms. A relevant concentration of Au was identified in the CPU, while a lower concentration was present as an alloy with Ni. In general, Ni-Au alloy is used in mobile phones as a conductor to connect analog devices such as the keyboard, the vibration motor, the jack connection or the connection for battery charging. The Ni-Au alloy is also present on the surface of the PCBS while the Au of the CPU is enclosed in the silicon cover of the CPU rendering extraction more complex.

Another interesting technological aspect concerns bromine (Br). The XRF map highlights how Br distribution is not uniform, but is located only in the areas characterized by a greater danger of overheating (i.e. CPU and power supply). This information is crucial, as Br concentration might differ based on the particle size selected in the comminution process.

Figure 3 illustrates examples of chemical map distribution obtained for three PCBSs deriving from the three groups analyzed. The variations detected in terms of distribution and concentration of elements were caused mainly by technological needs and reduction in the use of several elements deemed potentially harmful to humans and the environment.

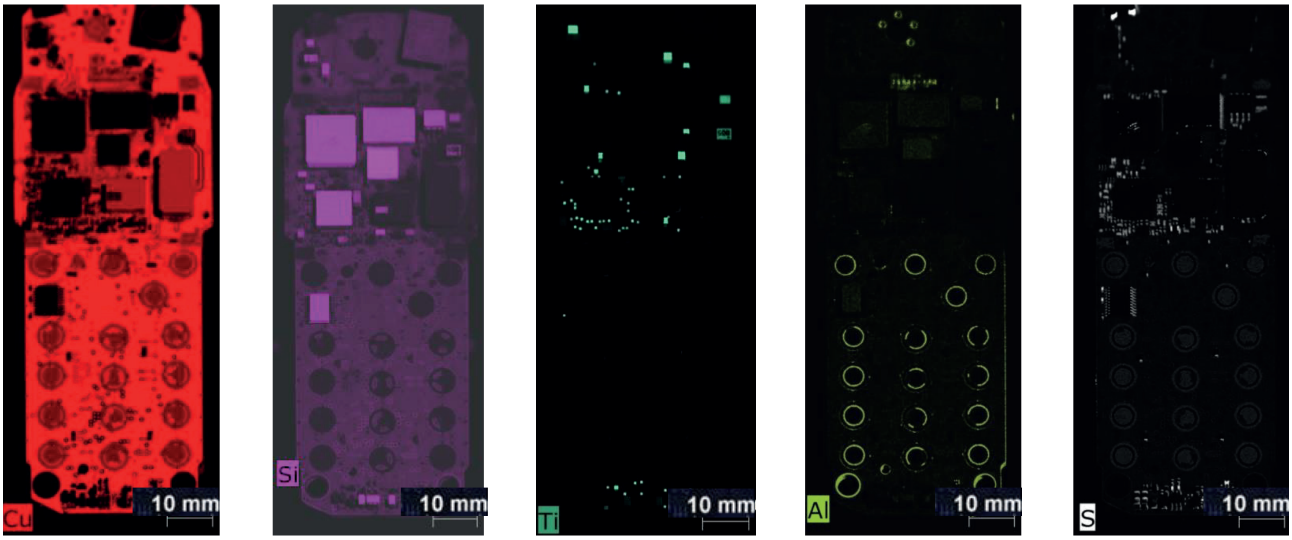
It was however consistently observed that: titanium (Ti) is present both in capacitors due to its heat resistance properties and in PCBS pins, chrome (Cr) is used as protective coating for iron (Fe) components and nickel (Ni) is present as an alloy with Au in printed circuits, but also as an alloy with zinc (Zn) for circuit protection. Several hazardous elements, such as Br, used as flame retardant, and Pb, used in connection solders, displayed a decrease in values over time (Figure 4). This could be a consequence of the Restriction of Hazardous Substances Directive 2002/95/EC emanation limiting the use of some substances in the production chain.

On the contrary, with regard to precious metals, Au was detected in all groups investigated, with a fairly constant percentage over time (Figure 5). It is however interesting to note how the older models of mobile phones analyzed (i.e. 1999) featured a widespread distribution of Au on the PCBS layer: on contacts, under the buttons and in the microprocessors. Au is concentrated in some specific areas as Ni alloy for all other samples. Feature phones and, particularly, smartphones were characterized by a low presence of Au on the surface, being concentrated in CPU chips. As previously mentioned, Au present in these technological components is more complex to extract compared to the Ni-Au alloy present on the surface of mobile phones.

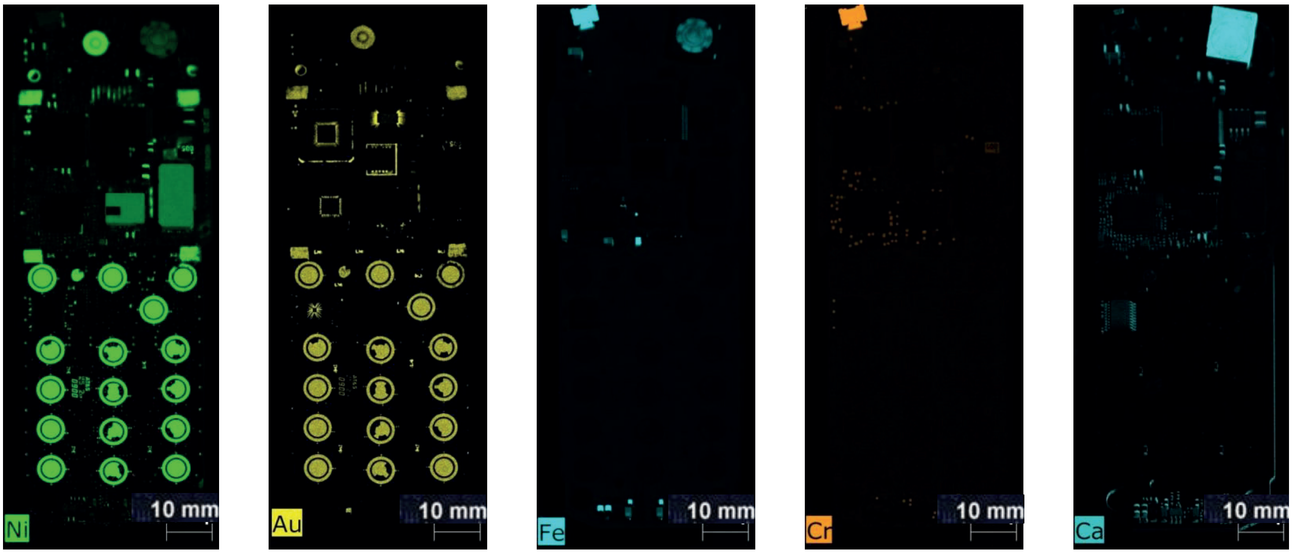
4. CONCLUSIONS

Micro-XRF was applied to perform a preliminary characterization of PCBSs from spent mobile phones. More in detail, 12 mobile phones grouped into 3 sets according to their year of release and characteristics were analyzed. The results highlighted how analysis of the single element map facilitated both identification of the main elements of each PCBS component and evaluation of the issues to be addressed in maximizing the recovery of precious metals.

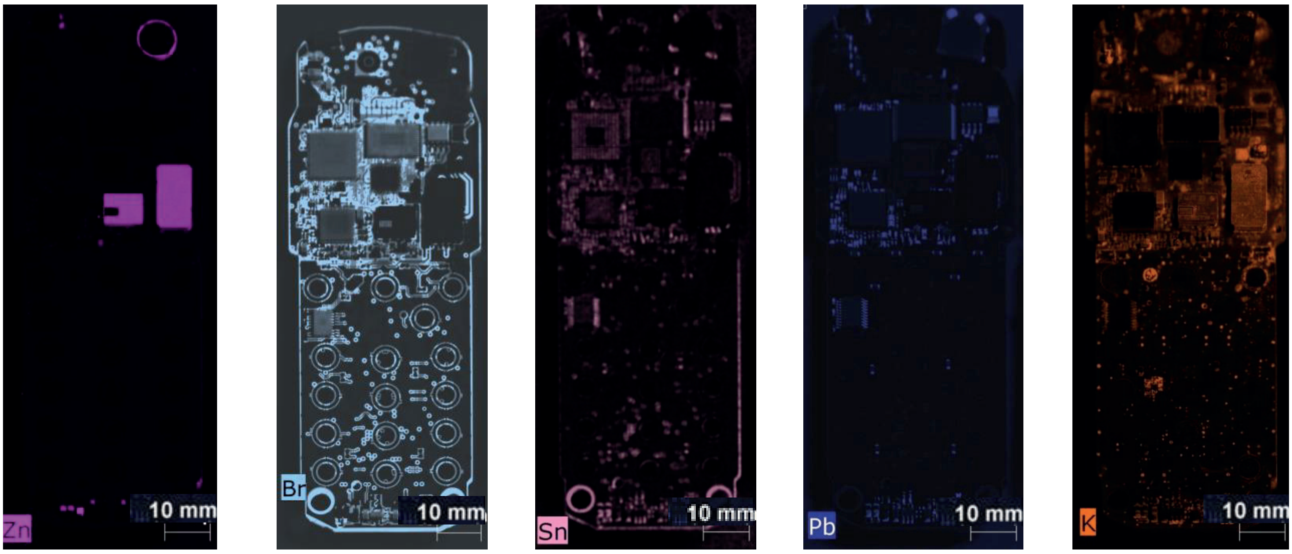
The procedure adopted enabled mapping of chemical element distribution throughout the entire PCBS surface,



Copper **Silicon** **Titanium** **Aluminum** **Sulfur**



Nickel **Gold** **Iron** **Chrome** **Calcium**



Zinc **Bromine** **Tin** **Lead** **Potassium**

FIGURE 1: Distribution of chemical elements (i.e. maps) detected by micro-XRF on the PCBS front of NOKIA 3210 mobile phone.

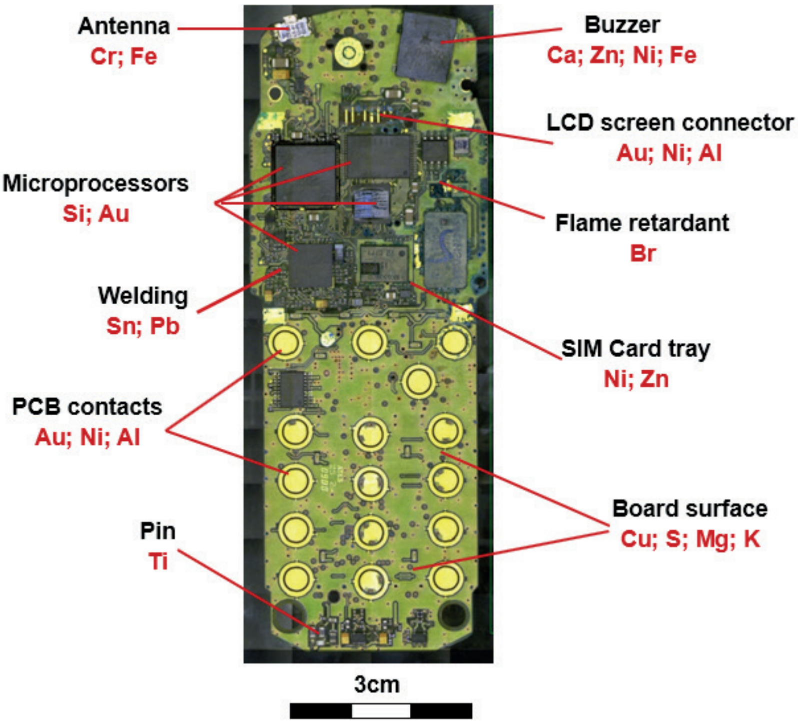


FIGURE 2: Summary of the outcomes, in terms of chemical elements, resulting from micro-XRF analysis carried out on NOKIA 3210 entire PCBS.

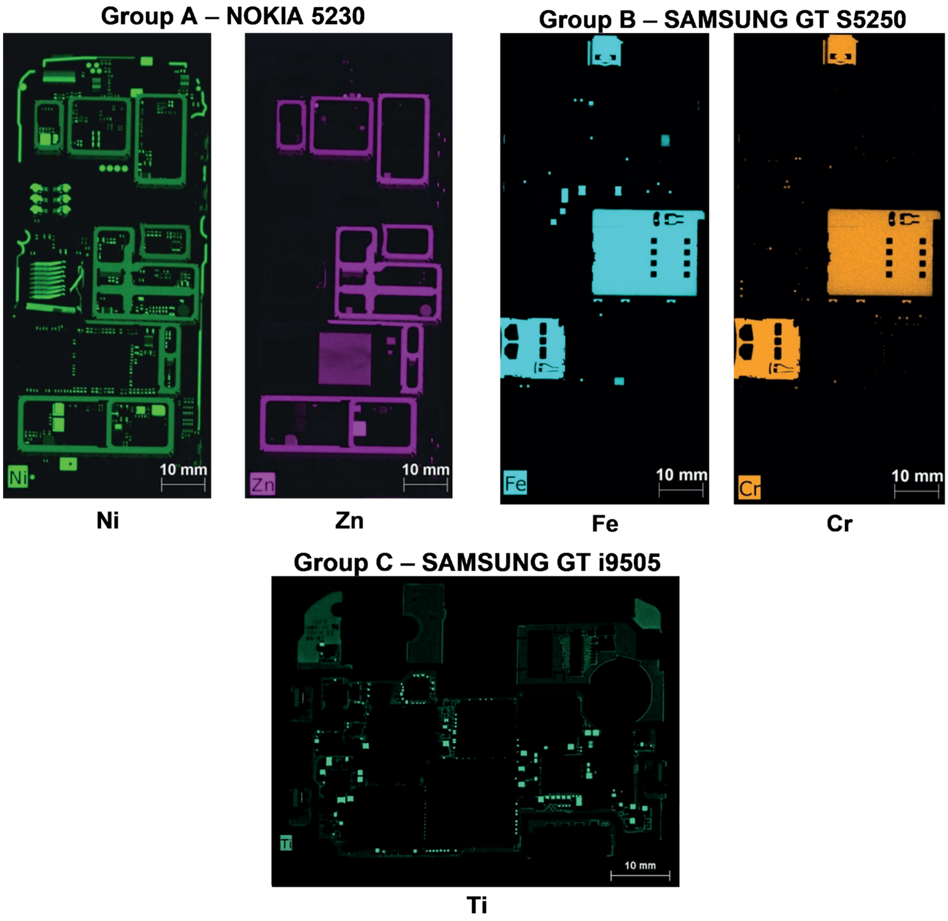


FIGURE 3: Examples of chemical element distribution (i.e. maps) on three PCBSs, belonging to the three different analyzed groups, detected by micro-XRF: Ni-Zn alloy for Nokia 5230 (a), Fe-Cr alloy for Samsung GT S5250 (b) and Ti pins for GTi9505 (c).

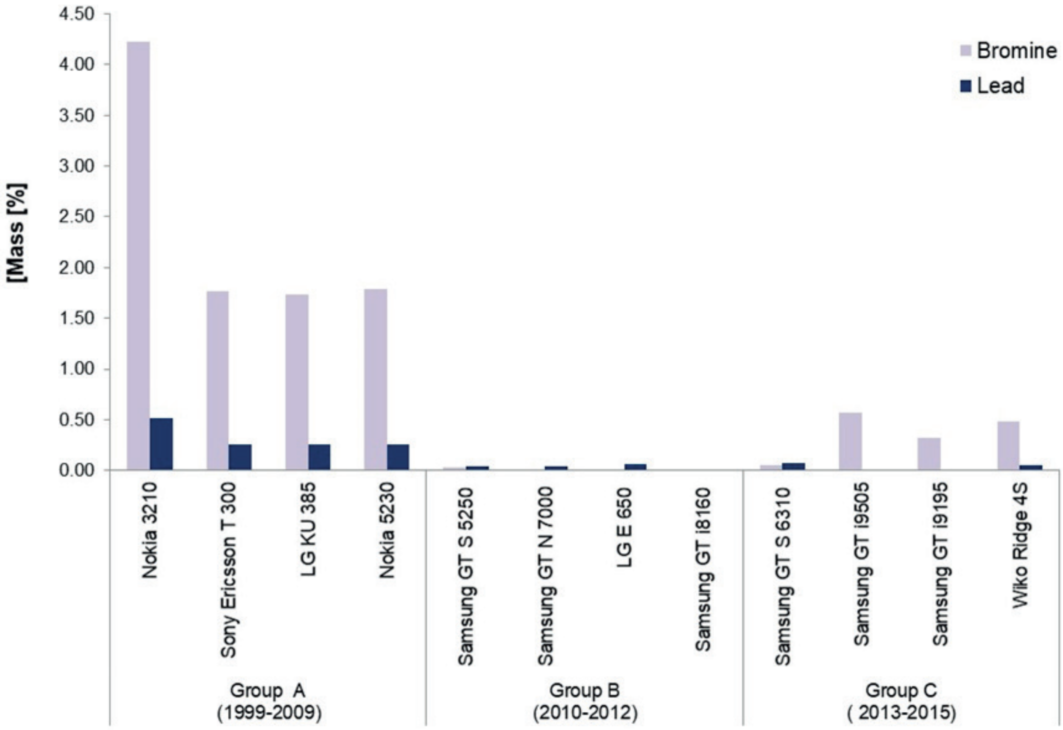


FIGURE 4: Evolution over time of hazardous Br and Pb elements inside PCBSs of mobile phones.

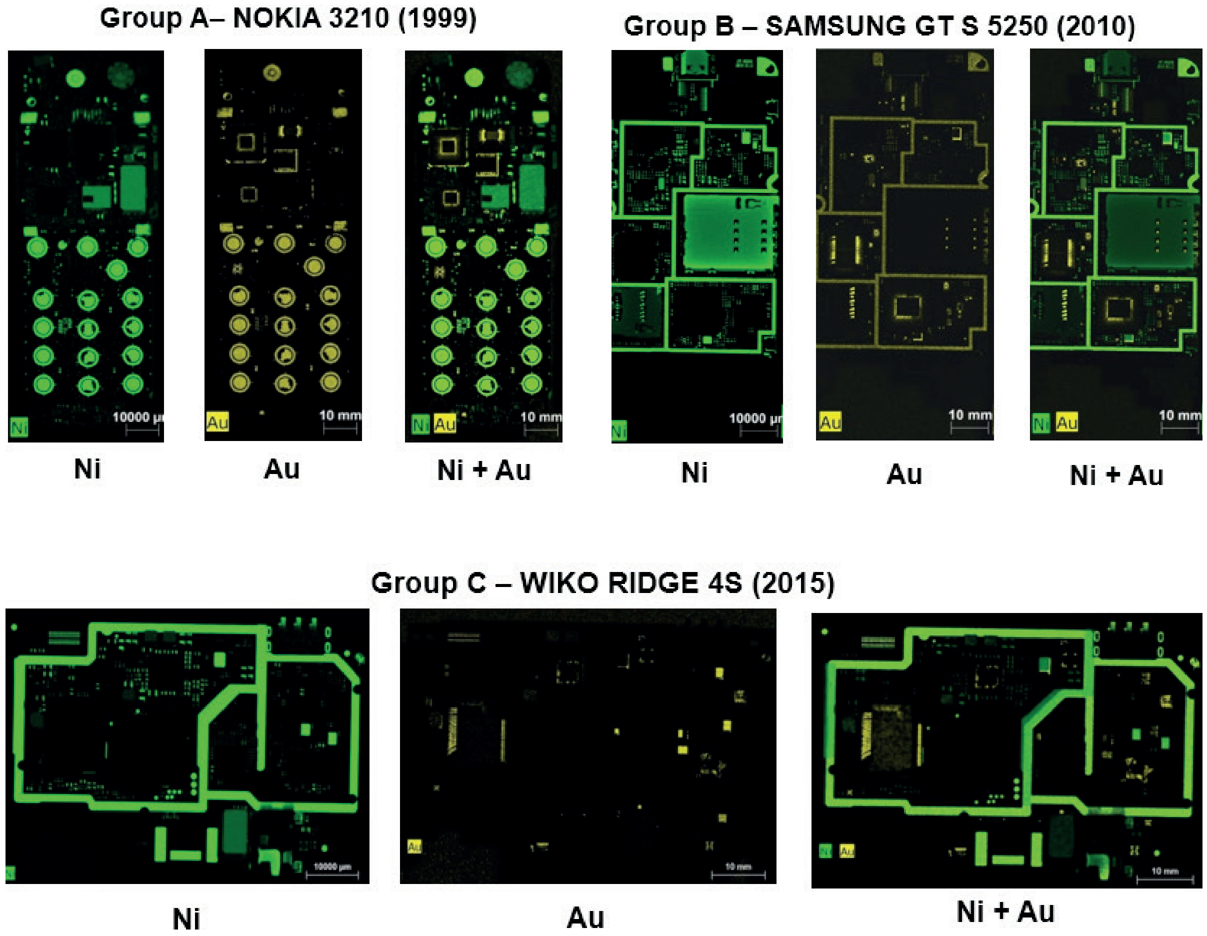


FIGURE 5: Examples of Au and Ni distribution (i.e. maps) on three PCBSs belonging to the three different analyzed groups, detected by micro-XRF: Nokia 3210 belonging to Group A (a), Samsung GT S 5250 belonging to group B (b) and WIKO RIDGE 4S belonging to group C (c).

thus promoting study of their evolution over time. The study confirmed that technological evolution influences the concentration and distribution of precious elements. This information suggests the advisability of adopting a different approach based on the utilized production technologies or the age of PCBS with an aim to optimizing the extraction process.

Further studies should be carried out to extend systematic application of the proposed approach to a larger quantity of PCBSs. Moreover, milled samples will be analyzed to explore the possibility of pre-concentrating useful chemical elements into defined particle size classes. A similar strategy could contribute towards developing "good practices" addressed at improving efficiency of the recycling chain, reducing and optimizing the number of processing stages by characterizing handling of the entire WMP, leading to a consequent reduction in costs and environmental impact.

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