

EVOLUTION OF SMARTPHONES METAL CONTENT WITH ITS FAST- IMPROVING FUNCTIONALITIES

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To my family and Fiancée Nour

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LIST OF ABBREVIATIONS

WEEE	Waste electrical and electronic equipment
PCBA	Printed circuit board assembly
ICP-OES	Inductively Coupled Plasma- Optical Emission Spectroscopy
HCl	Hydrochloric acid
HF	Hydrofluoric acid
HNO ₃	Nitric acid
DI water	Type 1 water
MWAD	Microwave assisted acid digestion
NFC/WC	NFC antenna/wireless charging chip
REEs	Rare earth elements
ISD	Spectator internal standard
Criticality EI	Criticality environmental implications
USGS	US Geological Survey
PGMs	Platinum group elements

ABSTRACT

Smartphones, one of the most common consumer electronic devices, are an essential part of daily activities in modern society. Smartphones provide faster communication, easier access to information and many other important services. However, with a compressed product life cycle and growing consumer demand, a significant number of smartphones reach End-of-Life (EoL) annually. At the same time, due to many special physical properties, rare earth, critical and other important metals are essential for the manufacturing of smartphones. Hence, from various economic, resources availability and environmental perspectives, it is crucial to understand how metal content of different smartphones generations change over time. To this end, a high production smartphone series, produced between 2010 and 2015 were considered in the scope of this study. The devices were disassembled, sorted into different components and size reduced. Printed circuit boards assembly, back cameras and NFC antenna/wireless charging chips were then digested using a novel microwave assisted acid digestion method. Inductively Coupled Plasma-Optical Emission Spectroscopy was used to detect and quantify 60 elements. Obtained results indicate that up to 70% of different smartphones components by weight are important recyclable metals. The highest concentration elements, Cu, Ni, Sn, Zn and Fe, accounted for 93.3% while REEs and PGMs collectively accounted for 0.53% of the total recoverable elements by weight. In 2019, the total addressable market value of metals reclamation from only three smartphone components at their end of life is estimated at 298.69 million USD in USA. Gold and Platinum were determined to be the most environmentally critical elements and efforts should made to reduce their use. Finally, and most importantly, smartphones manufacturers should design their products with an extended lifetime due to the high concentration of critical elements used to make them.

1. INTRODUCTION

Digital consumer and personal electronic devices play an integral role in our modern society^{1,2}. The growing demand on consumer electronics, such as televisions, smartphones and laptops, is expected to experience a significant growth over the coming few years while many devices are being discarded as electronic waste^{3,4}. Electronic waste, or e-waste, is defined as waste electrical and electronic equipment (WEEE) discarded by its owner without the intent of reuse⁵. According to the 2019 World Economic Forum PACE report, the total electronic waste, or e-waste, circulating around the world was 48.5 million metric tons in 2018, and is projected to double reaching 120 million metric tons by 2050⁶. This number is only expected to increase given the insufficient and ineffective recycling and metals recovery strategies currently being employed⁶. It is also estimated that only 20% of WEEE generated in 2018 was recycled worldwide. However, recycling and metals recovery, is a necessity and a matter of national security for many nations⁷. For instance, due to the vulnerable supply chains and the vital role of high-technology minerals in the economy, global powers such as the European Union⁸ and United States^{9,10} are currently looking for new ways to close the loop and identify new sources.

New state-of-the-art technologies rely heavily on critical material and rare earth metals to achieve the desired performances¹¹. Recent research studies validate and document the importance and use of every critical and rare earth element in our modern communication technologies such as mobile phones and smartphones^{11–15}. The main difference between mobile phones and smartphones is that the latter is equipped with higher computational capacity expanding its use beyond communication such as web browsing. In the last ten years, smartphones consistently dominate the consumer electronics market: accounting for over 45% of its worldwide sales revenue, and reaching 1.5 billion devices in sales to end users by 2019¹⁶. Due to a smartphone's considerably superior computing capacity, convenient internet connection, improved camera resolution and mobility, smartphones accounted for over 75% of all worldwide computing devices shipments from 2013 to 2020¹⁷. Despite smartphones being small in size, several research studies have proved the presence of a considerable amount of precious, critical and rare earth elements in smartphones, especially in their computing center, the printed circuit board assembly (PCBA)^{11,18–20}. And, these elements are being discarded. For instance, Hagelüken²¹ estimated that the

concentration of precious and rare earth elements in e-waste is at least a hundred times more compared to natural ores with several other studies investigating landfills as potential urban mines for these metals; ^{12,22,23} and more recent papers claiming that recovering valuable metals from WEEE is more cost-effective than mining and extracting from ores ²⁴.

2. LITERATURE REVIEW

The growing interest in WEEE as a source for metals reclamation is reflected by the increasing number of publications attempting to develop novel WEEE characterization and recycling methods^{25–28}. Among these studies, recovery of metals from obsolete smartphones was at the focus of many studies due to higher concentrations of precious, critical and rare earth metals²⁹. In addition, the economic value of these metals' recovery was evaluated in many papers. For instance, Buechler et al¹⁹ estimated that the economic worth of 1 kg of waste mobile phones to be 443.52 \$ with Pt and Pd accounting for \$ 209.72 and \$ 197.63 of the total value. Even though smartphones PCBAs accounted for less than 30% of total smartphones weight, PCBAs gained significantly higher attention over the other four main smartphone components³⁰ (i.e. display unit, PCBs, battery and case) due to its notably high tech minerals concentration such as gold and silver^{31,32} and copper³³.

Despite many studies focusing on total metals recovery, to the best of our knowledge, only three studies investigated the change in consumer electronics metal composition over time. Such studies are critical to empower the scientific community and policy makers to develop a better understanding of how technological innovation impacts the environment and sustainable resources management practices. In 2014, Christian et al³⁰ conducted a study aiming to understand the change in metals composition of different phones brands and generations. Eighty-five used phones, manufactured between 1998 and 2013, were disassembled, digested using open vessel digestion and metals were quantified using inductively coupled plasma-optical emission spectroscopy (ICP-OES). Thirty-eight elements were detected and/or quantified in all the tested devices including rare earth and precious metals, such as platinum (Pt), dysprosium (Dy) and gold (Au). Iron (Fe) and copper (Cu) constituted on average over 10 grams per device followed by nickel (Ni), aluminum (Al), tin (Sn) and magnesium (Mg). Au and silver (Ag) concentrations were found to be decreasing over the years from 0.04 to 0.03 grams and 0.13 to 0.06 grams, respectively. Lead (Pb) concentrations exhibited a constant decrease over the years from over 1-gram 1998 to less than 0.5 gram in 2013. Tungsten (W) concentrations were found to be present as much as three times the amount of tantalum (Ta), Au, Ag and niobium (Nb) combined. Antimony (Sb) concentrations significantly increased in recent years due to the development of a memory devices

known as “GSt” with enhanced speed. As for the rare earth elements (REEs), Neodymium (Nd) and erbium (Er) were found in large quantities of 4.75 g and 1.57 g in devices produced in 1998. The two elements concentration then took a declining trend as many other rare earth elements did too.

In 2016, Adie et al ³⁴ conducted a study of the impact of television technological evolution overtime. In their study, PCBAs of televisions produced between 1980 and 2005 were studied for the quantification of Pb, As, Cu, Sn and Ag. The obtained results showed that there was no significant change in Pb and Sn concentrations while Cu concentration peaked in the mid-1990s. Ag, Au and arsenic (As) concentrations appeared to be steadily decreasing over time attributed to the development of more compact and thinner devices. EPA 3051A microwave-assisted digestion method for total recoverable metals was adopted and ICP-OES was used for metals quantification.

Most recently, in 2018, Chen et al ³⁵ studied the impact of mobile phones technological innovation and the effect of regulations on WEEE toxicity. Thirty-six different used devices manufactured between 2002 and 2013 were disassembled, digested using HF-HClO₄-HNO₃ system and analyzed using ICP-OES. USEtox life cycle impact assessment tool was used to assess different devices generations impact on human toxicity and ecotoxicology. As concluded in several previous studies, Chen et al reported that Fe, Cu and Al accounted for around 36% of total metallic content. In addition, on average, Cr and Ni accounted for 12.83% and 10% by weight. Most precious and REEs were determined at levels lower than 1% while beryllium (Be) and cadmium (Cd) were not detected. Among the 36 tested devices, 5 devices were classified as hazardous waste where Cu, Al and Ni posed the most significant ecotoxicity risk. Phones potential ecotoxicity over all life cycle stages increased from 2002 and peaked in 2007 followed by a declining trend. The observed trend was attributed to the release of the first iPhone in 2007, driving the market innovative technologies development to more sustainable and lighter weight designs. As oppose to decreasing Ni, zinc (Zn), molybdenum (Mo), Fe and Cr content in phones, cobalt (Co), Mg and vanadium (V) concentrations increased after the launch of iPhones in 2007. Au and palladium (Pd) content in phones were determined to be relatively constant regardless of brands and year of manufacture contradicting other findings by Christian et al’s ³⁰ study.

3. STUDY SCOPE AND OBJECTIVES

In spite of the various attempts by different research groups to understand the impact of smartphones metal evolution over time, several gaps could be identified. To the best of our knowledge, in trying to understand smartphones metal content evolution over time, all studies reported in the literature considered a large pool of devices produced by different manufacturers offering different functionalities and technological advancements. Hence, their obtained results might not necessarily reflect changes in the devices technology adding another important variable to the study. In addition, all studies used discarded devices which could potentially have had aftermarket upgrades or even missing certain parts. Furthermore, all studies include a sub-sampling step creating potential biases in the data due to the highly heterogenous nature of electronic components. Finally, no comprehensive recovery studies were conducted demonstrating the full recovery of all target elements but rather a handful of elements were used as to represent all. Therefore, the below described work will address the abovementioned gaps and attempt to (1) optimize the analytical method for metals quantification in electronics, (2) identifying elemental composition of different key parts in smartphones, (3) understand how smartphones metal content changed with improving functionalities, and (4) estimate the environmental impact, namely on water and climate change, of metals mining activities to be used for smartphones manufacturing.

4. MATERIALS AND METHODS

The selected smartphones (see section 4.2) were disassembled, size-reduced and digested to solubilize the metals for detection and quantification with ICP-OES. All work was conducted in the Delon and Elizabeth Hampton Hall of the Lyles School of Civil Engineering. The overall procedure was based on previously published processes for consumer electronics metals analysis developed by Bookhagen et al ²⁰, Buechler et al ¹⁹ and Korf et al ¹¹.

4.1 Materials and Equipment

Eight new factory sealed and two used Samsung smartphones were purchased from different suppliers on Amazon and eBay (Table 1). The full inventory of smart phones specifications is available in Appendix A. Trace metal grade 70% Nitric acid (HNO₃), 47-51% hydrofluoric acid (HF) and hydrochloric acid (HCl) were purchased from Fisher Chemical, Canada. Reagent grade Ethanol was stored in polypropylene squeeze bottle for rinsing and micropipette tips were purchased from Thermo Fisher, USA. Type 1 water (DI water) was locally produced using GenPure Pro UV/UF manufactured by Thermo Scientific, Germany. Metal free 15- and 50-mL polypropylene centrifuge flasks used for samples preparation, storage and analysis were purchased from VWR, China. All samples were digested using ETHOS UP (Milestone Srl, Italy) microwave assisted acid digester equipped with a maximum of 15 Polytetrafluoroethylene - TFM (PTFE-TFM) digestion vessels rotor (SK-15 easyTEMP) and an easyTEMP temperature sensor. The easyTEMP temperature sensor, which is essentially an IR sensor, is capable of providing real-time temperature measurement of the solution in the PTFE-TFM digestion vessels. iCAP™ 7400 ICP-OES Duo was used for metals quantification and analysis (Thermo Scientific, Germany). Argon and liquid nitrogen gases for ICP-OES and cryogenic milling were purchased from Indiana Oxygen, USA. All ICP-OES standard solutions were purchased from Inorganic Ventures, USA. Smartphones were disassembled (ORIA Precision Screwdriver Kit (Repair-kit, USA)) and cryogenically milled (A11 Basic Analytical Mill (IKA, USA)). Mettler-Toledo GmbH analytical balance manufactured in Switzerland was used for weighing and preparing samples. Ampad 11" x 17" white graph paper were used as a background to help estimating parts sizes after phone disassembly. HERATHERM oven manufactured by Thermo Scientific in USA was used as part

of microwave digestion vessels cleaning process. Parafilm used for sample preparation was purchased from Penchiney, USA. 0.1-1 ml Eppendorf Research, Germany and 0.5-5 ml Fisherbrand, Finland were used for all dilutions and for transferring acids. Polystyrene spatulas (Bel-Art- Scienceware, USA) and single use polystyrene weighting boats (Fisherbrand, USA) were used for all electronic parts weighing and transferring.

Table 1 Smartphones inventory.

Smartphone ID	Smartphone	Model #	Total Mass (g)	Total # Components	Unique Components	Release date
S1	Samsung Galaxy S	GT-19000	112.4	14	-	June 4, 2010
S2	Samsung Galaxy S2	GT-19100	109.0	13	-	May 2, 2011
S3	Samsung Galaxy S3	SGH-1747	133.1	17	-	May 29, 2012
S4	Samsung Galaxy S4	SGH-i337	130.3	21	-	April 27, 2013
S5	Samsung Galaxy S5	SM-G900A	139.9	17	-	April 11, 2014
S6	Samsung Galaxy S6	SM-G920W8	137.8	21	Wireless charging coil	April 10, 2015
S7	Samsung Galaxy S6 Edge	SM-G925A	131.1	22	Wireless charging coil	April 10, 2015
S8	Samsung Galaxy S6 Edge Plus	SM-G928VUD	153.2	22	Wireless charging coil	August 21, 2015

4.2 Samples and Samples Preparation

Before analyzing the phones in the study series, two post-consumed smartphones from the same manufacturer (Samsung Galaxy S3, 2012 and S4, 2013) were used to optimize sample preparation (disassembly and cryogenic milling) and the microwave assisted digestion (MWAD) process. The optimized method was finally applied to eight factory sealed smartphones of the same series (Samsung S series) manufactured between 2010 and 2015, chosen because of the relatively higher number of units sold and their top end technological features³⁶. The entire smartphone was weighed, including batteries, and disassembled to the smallest parts possible, while preserving parts integrity, using the ORIA Precision Screwdriver Kit. Parts were then weighed using an analytical balance and placed on an Ampad 11" x 17" white graph paper, labeled and photographed

as presented in Appendix B. Under a fume hood, PCBAs, NFC antenna/wireless charging chip (NFC/WC), and back cameras were milled using an A11 basic Analytical mill equipped with A11.1 stainless steel spare beater blade after treatment using liquid nitrogen. Milled parts, consisting of a powder, were weighed and stored in 50 mL metal free polypropylene centrifuge tubes. These powders are the “samples” that are digested, as described in section 4.3. A minimum of 96.9 % of studied smartphone parts was recovered after milling. All used tools were extensively washed between uses with lab produced DI water and reagent grade ethanol to limit cross contamination between parts.

iFixit smartphones Samsung Galaxy S series teardown manuals were used to guide the smartphones disassembly and parts identification process³⁷. The identification was also confirmed with an expert (Divinitha Sreenivas³⁸, Personal Communication) and further validated using official SamsungParts website³⁹. The main smartphone parts identified were printed circuit boards, screens, frames, screws, charging ports, batteries, front and back cameras, vibration motors, antennas, speakers and smart card inside the (SIM) tray. For safety reasons, batteries were excluded from further processing. This method of disassembly into components was conducted to ultimately determine elemental composition and materials allowing for third party materials inventory for comprehensive LCA studies as well as construction “Bill of Materials”^{40,41}.

4.3 Microwave Assisted Acid Digestion Method

Due to the large mass of some components, the microwave digestion method was optimized for complete digestion and maximum mass of sample per digestion tube per run. Digestion time, acid mixtures and element specific percent recovery were considered for the development and optimization of the microwave assisted acid digestion method. The digestion methods were developed based on an existing method reported by Bookhagen et al²⁰ and technical input from the manufacturer (Milestone Srl, USA).

4.3.1 Optimized Digestion Protocol

In each PTFE-TFM digestion vessel, 70% HNO₃ (15 mL) and 36% HCl (5 mL) were added to 1 gram of sample and sealed with parafilm for 12 hours of pre-digestion, to oxidize organic materials. Using the tip of a needle, a small pressure release opening was made in the parafilm sealing. After pre-digestion, 70% HNO₃ (2 mL), 47-51% HF (2 mL) and 36% HCl (1 mL) were added to the solution after the addition of 0.25 mL of 1000 µg/g of Yttrium standard solution. Yttrium was added as a spectator internal standard (ISD) only to PCBAs samples to validate and track all dilutions done²⁰. The sample preparation procedure is summarized in Fig. 1.

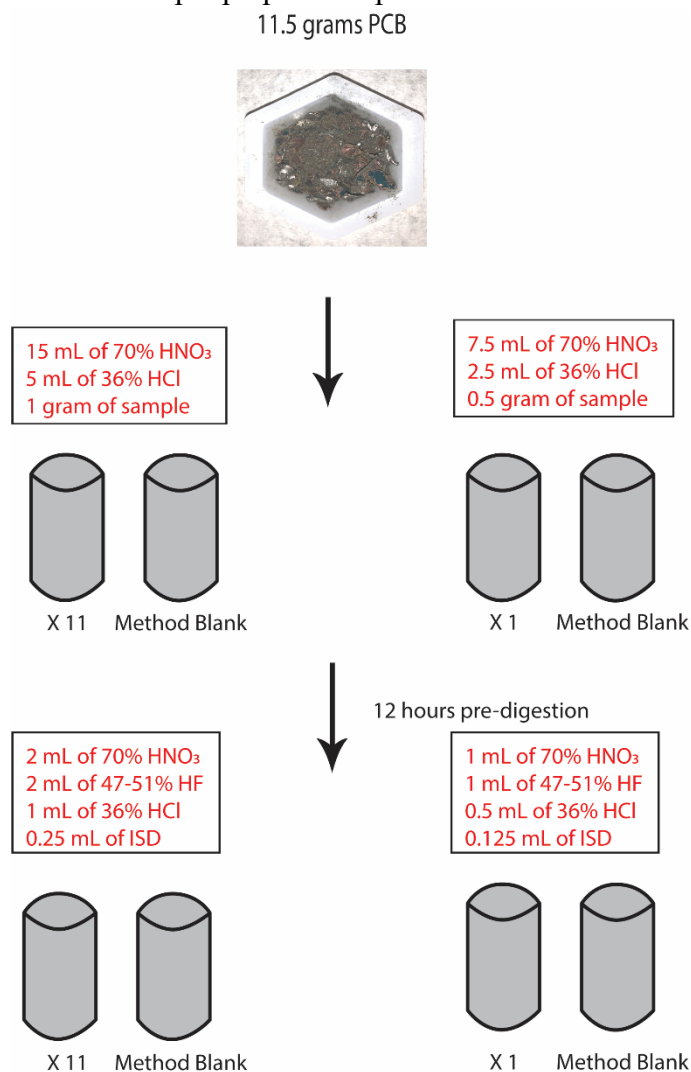


Figure 1 Example of sample preparation for digestion procedure. Gray tubes are PTFE-TFM digestion vessels.

A single smart phone component was digested in multiple PTFE-TFM tubes with the same volume ratio of acids, and the same solid:acid ratio. To digest a smartphone component having total mass of, for example, 11.5 grams would require 14 out of the 15 possible, digestion tubes. One gram of sample would be added per digestion tube resulting in 11 digestion tubes having total added acids volume of 25 mL labeled from s1 to s11. To maintain a consistent mass to volume ratio, the last 0.5 gram would be added to the 12th digestion tube with a total acids volume of $\frac{1}{0.5} \times 25 \text{ mL} = 12.5 \text{ mL}$. Two blanks, 25- and 12.5-mL total acids volume labeled b1 and b2 respectively, would be processed along with the tubes containing sample. The samples would then be split over two digestion batches. For the first digestion batch, all 11 samples, s1 to s11, and b1 would be digested; while for the second digestion batch, s12 with b2 would be digested. The purpose of this method is to avoid extra sample dilution which would negatively impact the quality of the data. However, in low volume samples, higher volume to power ratio would be attained further catalyzing the digestion process (Fig. 1).

Three digestion cycles with a maximum temperature of 230 °C and 1800 W microwave power were conducted to achieve full digestion. Each digestion cycle consisted of 90 min split over four phases. The solution was first heated up to 230 °C over 25 min, maintained at 230 °C for another 25 min, followed by 25 min to cool the solution down to 60°C and maintained at 60°C for 15 min (Table 2). After three digestion cycles, 5 mL of DI water were added to the vessels. Complete digestion after three cycles was observed in 96 % of the tubes, while incomplete digestion was observed in the remaining 4 %.

Table 2 Table describing one digestion cycle.

Phases	Time (minutes)	Microwave Power (W)	Temperature (°C)
1	25	1800	230
2	25	1800	230
3	25	0	60
4	15	0	60

In the case of incomplete digestion (i.e. metal parts or particulates could be observed by visual inspection), the digest was allowed to settle for 30 minutes followed by decantation of the liquid solution from the undigested solid. The liquid solution was stored in a 50 mL metal free polypropylene VWR centrifuge tubes. Then, 3 mL, 1 mL and 1 mL of 70% HNO₃, 36% HCl and

47-51% HF respectively were added to the undigested mass, transferred into the digestion vessel used for the same sample and subject to another MWAD cycle. This was repeated until complete digestion. In all cases, a fourth MWAD cycle was enough to fully digest the solid. The digest was then added to the original solution and mixed well. All digests were stored overnight allowing for suspended undissolved silicon particles to precipitate out of solution⁴² (Fig. 2).

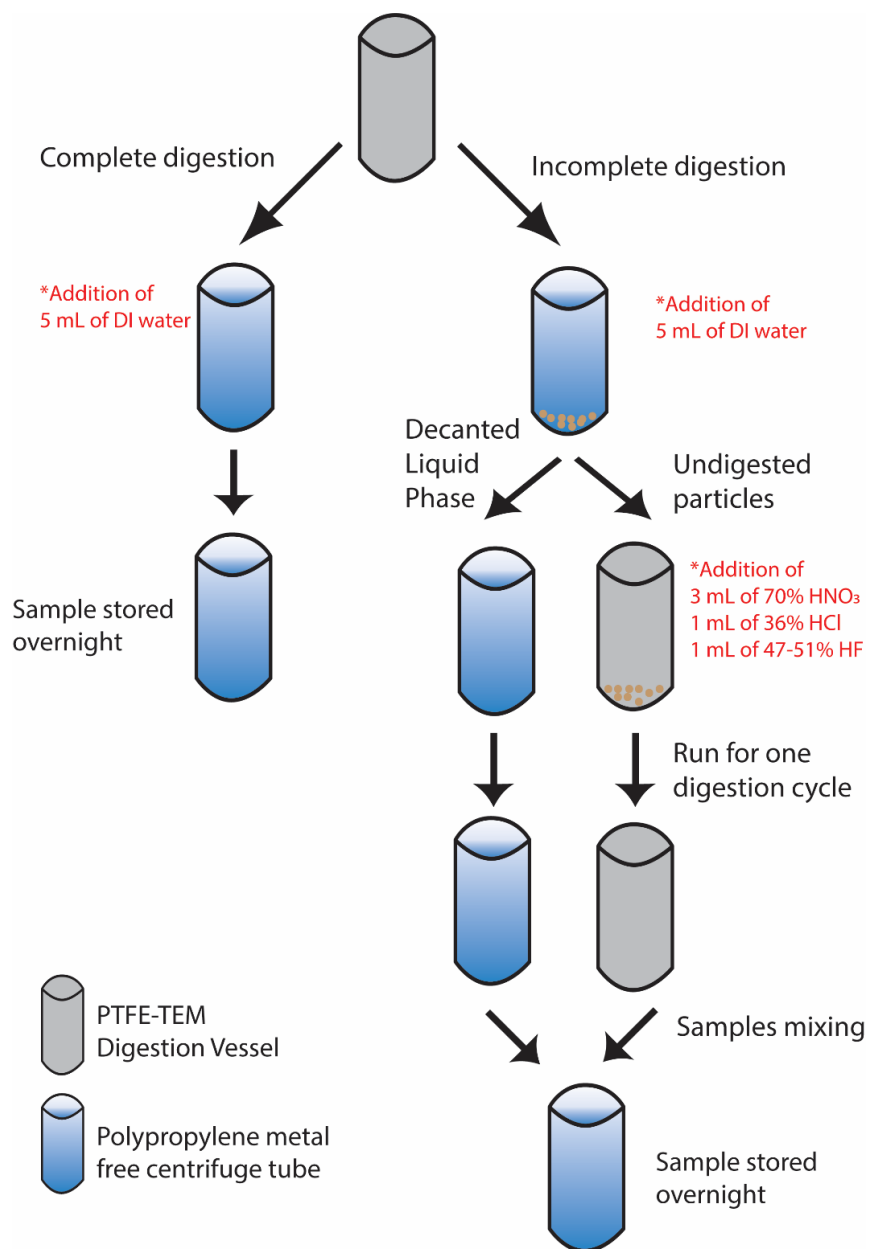


Figure 2 Sample preparation procedure for ICP-OES analysis.

Then, the homogenous liquid solution was transferred by decantation into a fresh 50 mL metal free polypropylene VWR centrifuge tube. To achieve full dissolution, 1 mL of 70% HNO_3 was first added followed by gradual addition in 0.25 mL increments of 47-51% HF until a clear solution was reached. The obtained solution was then mixed with the original digest and more DI water was added to adjust the total volume to 40 mL (Fig. 3). The final obtained digest was stored and used for ICP-OES analysis. A method blank consisting of only added acids and ISD (17 mL 70% HNO_3 , 6 mL 36% HCl , 2 mL 47-51% HF and 0.25 mL ISD) was prepared for every digestion batch to evaluate contamination from the complete sample preparation and analysis

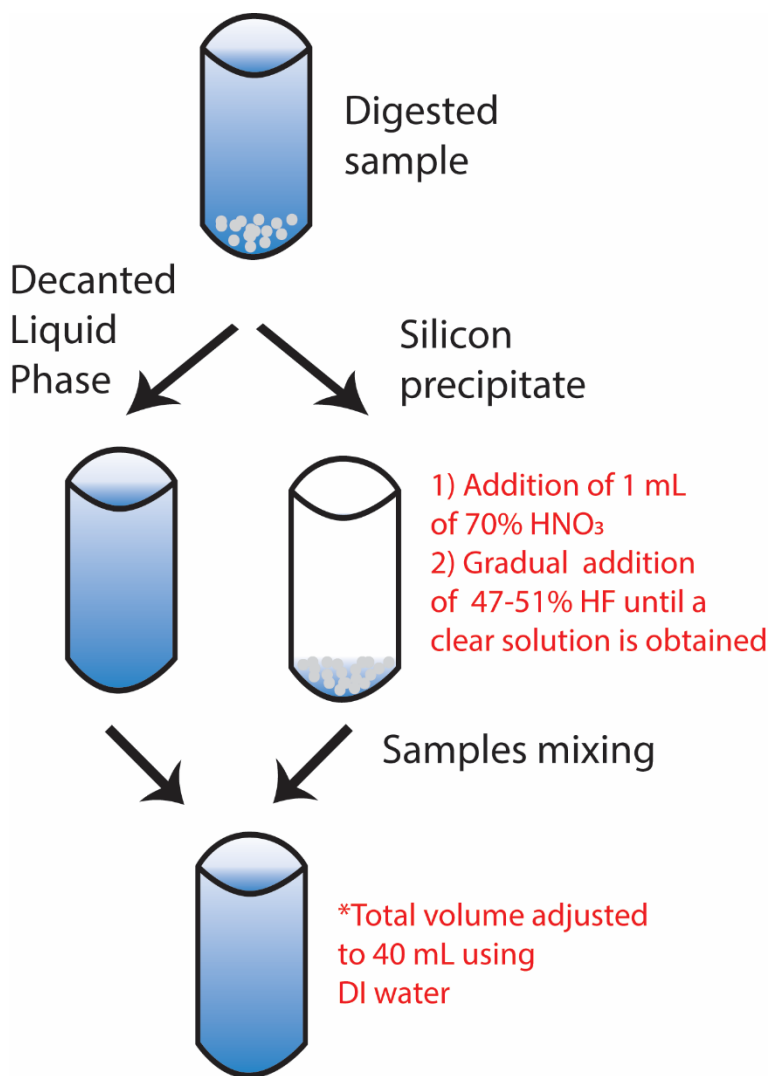


Figure 3 Post digestion sample treatment.

procedure.

4.3.2 Method Recovery

A recovery study was conducted to quantify percent recovery for all elements of interest. A 5 mL aliquot of 20 µg/mL mix of 68 elements standard solution was prepared and added to three digestion vessels. Two blank solutions were also prepared by the addition of 5 mL of DI water. Then, the same optimized microwave digestion protocol developed previously was applied. To assess the impact of overnight pre-digestion on the recovery study, the same experiment was repeated by adding fresh acids and 68 elements standard solutions directly before placing the vessels into the microwave digester.

4.3.3 Spiking Experiment

To study matrix effect on the recovery of all elements of interest, a spiking experiment was conducted. Three smartphone PCBAs digest samples were randomly selected, and two blanks were each spiked with 10 µg/mL standard solution containing all 60 elements of interest. Samples were then diluted 50 times with DI water and analyzed before and after spiking.

4.3.4 PTFE-TFM digestion vessels cleaning protocol

After each digestion run, two cleaning cycles of the PTFE-TEM vessels were done. During each cleaning cycle, microwave digestion tubes were first rinsed with 2% HNO₃ followed by DI water. Tubes were then baked at 140 °C in HERATHERM oven for 4 hours. After cooling to room temperature, 15 mL, 5 mL and 5 mL of 70% HNO₃, 36% HCl and DI water respectively were added to each tube and run for one digestion cycle. After two cleaning cycles, the microwave digestion tubes were baked again at 140 °C for 2 hours. The PTFE-TFM digestion vessels cleaning protocol is summarized in Fig. 4. For every digestion batch, a different PTFE-TFM digestion vessel was used for the preparation of a method blank.

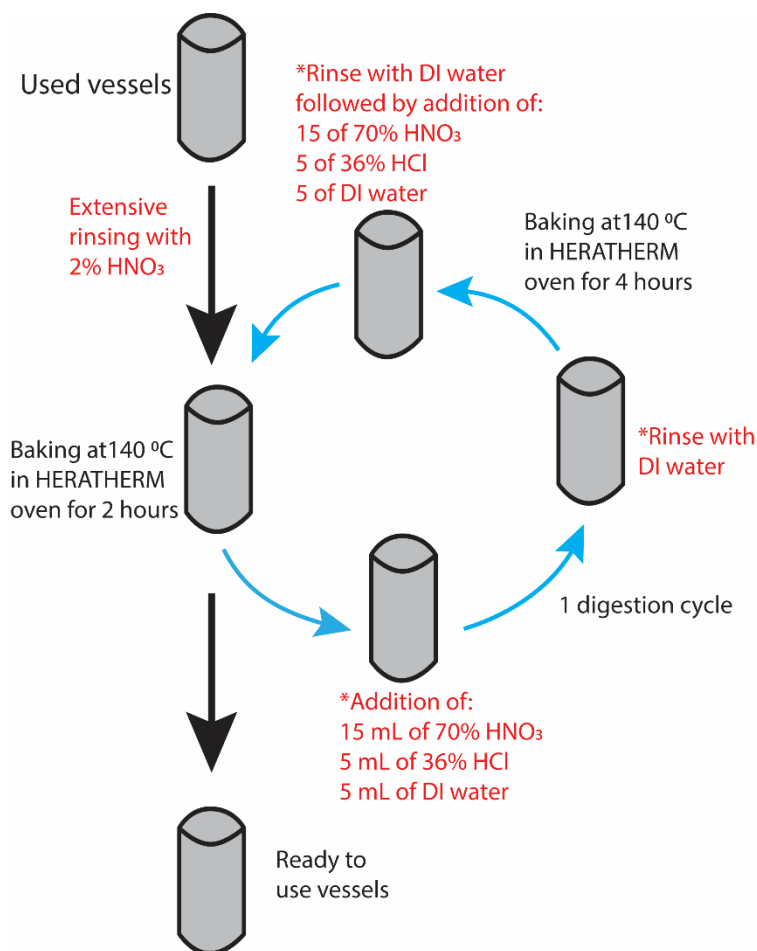


Figure 4 PTFE-TFM digestion vessels cleaning protocol.

4.4 ICP-OES method development

ICP-OES Qtegra software was used to optimize plasma conditions and resolve for spectral interferences. Selected wavelengths and plasma conditions are summarized in appendix C. Due to the wide ranges of concentrations for different elements, each sample from the MWD was subject to three dilutions (50, 1000 and 100,000 times) and triplicate injections were done for each dilution. In order to obtain high accuracy values, all quantified samples were computed using two calibration curves. Low calibration range extends from 1 to 300 µg/L to quantify low concentration elements (<300 µg/L) while high range calibration curve extended from 300 to 2000 µg/L for high concentration elements (>300 µg/L). Therefore, samples with concentrations below 300 µg/L were

quantified using low range calibration curve while samples higher 300 but less than 2000 µg/L were quantified using high range calibration curve.

Standards were freshly prepared in 2% HNO₃ solution using 68 certified elements standards (Inorganic Ventures, USA) for each run. Every time the ICP-OES system was used to analyze un-complexed HF containing samples, the system was reconfigured with HF resistant sample handling kit and the torch was aligned using 2 µg/mL standard Zn solution.

4.4.1 Data treatment

According to the International Organization for Standardization and commission directive 2009/90/EC, the limit of detection (LOD) is the lowest concentration at which an element of interest can be detected with reasonable statistical certainty while the limit of quantification (LOQ) is the lowest concentration that can be quantified with acceptable accuracy and precision (ISO 13530) ⁴³⁻⁴⁵. LOD is defined as 3 x SD and LOQ as 10 x SD where SD is calculated standard deviation. While it is convenient to use the limit of detection and quantification computed by Qtegra (ICP-OES software), the reported values reflect instrument detection limit and quantification, which assumes ideal conditions in their calculations ⁴⁶. Hence, manual calculations of all method LODs and LOQs using Excel spreadsheets was necessary. To reduce labor, a Virtual Basic Code was developed to compute all LODs and LOQs is presented in appendix D. All computed LODs and LOQs for each element are summarized in Appendix C.

The concentration of each element in each phone component was determined from the ICP results. On average, 500 ICP-OES injections per PCBA were necessary for the quantification of all elements of interest. As previously discussed, each smartphone component (i.e. PCBA) was divided over several digestion tubes. The digest from each tube was quantified separately and was treated as an independent sample. Below is a step by step demonstration, for Ag quantification as an example, of the adopted method.

Step 1:

$$[Ag]_{s1} = [Ag]_{\text{measured}} \times \text{Dilution factor} \quad (\text{Eq. 1})$$

Step 2:

$$\text{Mass of Ag(s1) (mg)} = [\text{Ag}]_{s1} \left(\frac{\text{ng}}{\text{mL}} \right) \times \text{Total digest volume (mL)} \times 10^{-6} \left(\frac{\text{mg}}{\text{ng}} \right) \quad (\text{Eq. 2})$$

Step 3:

$$\text{Total Ag mass in s1} = \sum_{s1}^{s_n} \text{Mass of Ag(s}_n) \quad (\text{Eq. 3})$$

Where $[\text{Ag}]_{s1}$ is the concentration of silver in sample 1 and s_n is the number of samples produced for each part. The process from Eq.1 to Eq.3 was repeated for every element in every studied smartphone component. It is important to note that total digest volume is the original digest volume obtained from the MWD without the addition of any DI water or acids.

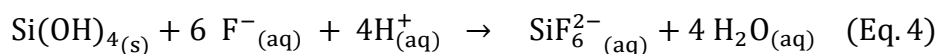
5. RESULTS AND DISCUSSIONS

This chapter will start by discussing method optimization procedure and then highlight the most important results to provide a better understanding of the evolution of smartphones metal content. Among the 60 different elements quantified in this study, 52 elements were identified as critical metals based on most recent metals environmental and supply criticality reports (see section 5.2).

5.1 Method optimization

Elemental analysis of waste electronic and electrical equipment has always been a challenge to the scientific community. The great diversity of elements and nature of sample poses significant challenges to the current digestion and comprehensive metals quantification technologies. As discussed in chapter 4, silicon material used in electronic devices necessitates the use of hydrofluoric acid for complete sample dissolution further complicating the analysis. In addition, current state of the art microwave assisted acid digestion technologies have a considerably low throughput, high labor and chemicals requirements. For these reasons, up to our knowledge, all studies reported in the literature include a sub-sampling step increasing the risks of cross contamination, dilution of certain low concentration elements and ultimately affecting the accuracy of collected data. For these reasons, an involved digestion and metals quantification method was developed in an attempt to accurately quantify all elements of interest in the selected smartphone parts. In the developed method, full smartphone parts (i.e. PCBs, back cameras and wireless charging chip) were considered and no sub-sampling step was necessary. Finally, full digestion of a high sample mass per digestion vessel, up to 1 gram, was achieved.

At a pH less than 4, dissolved silica polymerizes to form primary particles, which in turn flocculates and quickly precipitate out of solution potentially affecting the quality of obtained data⁴⁷. While the addition of HF might solve the issue (Eq. 4)⁴⁸, excess fluoride ion $[F^-]$ in solution could result in the formation of metal fluoride precipitate (Eq. 5)⁴⁹.





For this reason, an HF titration like method was developed to ensure that $[F^{-}]$ is stoichiometrically equivalent to completely dissolve silicon material while preventing potential loss of target elements as metal fluoride precipitate. Due to the wide range of silicon material used in different electronics samples, just enough amount of HF was experimentally determined to be (i.e. 2 mL 47-51% HF in 25 mL solution) a limiting reactant in reaction 1 (Eq. 4) in the acid digestion mixture, and hence preventing the formation of metal fluoride precipitate while still facilitating the digestion process. After three digestion cycles, the digest was removed, and all silicon precipitate was separated by decantation. Then, 1 mL of 70% HNO_3 was added to the collected precipitate followed by 0.25 mL increments addition of 47-51 % HF until a clear solution was obtained.

The developed method was validated by conducting a comprehensive recovery study. All elements of interest showed 100 ± 10 % recovery indicating no formation of metal fluoride precipitate. It is worth noting that since no silicon precipitate was observed in the recovery study samples, no further HF was added. However, since more HF was added to the digested samples, it was important to ensure that no metals were lost as metal fluoride precipitate and to understand matrix effect on metals quantification using ICP-OES. Hence, three PCBAs digest samples were randomly selected and spiked with 322.6 $\mu\text{g/L}$ concentration of each element from a standard solution. All elements of interest showed an acceptable recovery within 100 ± 10 % range expect for Silver (117.2%), Barium (88.6 %), Gallium (89.6 %), Tantalum (85.6 %), Titanium (83 %) and Tungsten (89.6 %). Although the above mentioned elements showed an off desired range recovery, they still fall in 100 ± 20 % range typically adopted in the literature for similar studies ^{11,20}. Furthermore, using yttrium as a method internal standard, the experimentally calculated dilution factors were 55, 1000 and 100,000 times. Hence, these dilution factors were adopted in all calculations done. A method blank was used to evaluate potential cross contamination and efficiency of adopted PTFE-TEM vessels cleaning protocol. No correction for obtained concentrations was done as all quantified elements in blank samples were below the limit of detection except for high concentration elements (i.e. Cu, Zn and Fe) showing less than 0.0001 % ($<10 \mu\text{g/L}$) of their actual concentration in the analyzed samples.

5.2 Elemental Composition of Studied Smartphones

Even though in the presented work we analyzed for 65 elements in all studied smartphone components, the discussion in the following sections will be limited to 52 elements identified as environmentally and nationally critical. In 2015, Graedel et al ⁵⁰ developed a criticality environmental implication (criticality EI) score from 0 to 100 ranking 62 elements based on their cradle to gate potential damage to ecosystems and human health. For the purposes of this work, elements having a criticality EI score of more than 30 were identified as environmentally critical elements. Furthermore, all studied elements that were identified in 2018 by the US Department of Interior and US Geological Survey (USGS) as nationally critical minerals for the US economy and national security are included in the following discussion ⁵¹. In assessing elements criticality, USGS methodology took into consideration elements supply chain vulnerability to disruption (i.e. natural disaster, conflict, resource nationalism) and importance to the manufacturing of a product. In addition, even though Cu, Fe and Zn were identified neither as environmentally nor nationally critical elements, they were included in the discussion due to their notably high concentrations in the studied devices. Finally, even though tin (Sn) was identified by USGS as a critical element, evolution of tin (Sn) concentration in the studied components will be discussed along with Cu, Fe and Zn due to its particularly high concentration the studied smartphone components.

5.2.1 Averaged Elemental Content (2010-2015)

5.2.1.1 PCBAs

Fig. 5 summarizes the average concentrations of all studied elements in all eight PCBAs. On average, 67.3% of a PCBA by weight was determined to be recoverable metals comparable to previously published work ¹¹. The highest concentration elements, Cu, Ni, Sn, Zn and Fe, accounted for 93.3% while REEs and platinum group elements (PGMs) collectively accounted for 0.53% of the total recoverable elements by weight. All regulated elements were determined to be in compliance with RoHS requirements where Pb, Cd and total Cr concentrations were found to be 78 µg/g, 2 µg/g and 30 mg/g respectively while mercury (Hg) was detected but not quantified ⁵². Over different smartphones generations produced between 2010 and 2015, PCBAs total metals content increased by 47% from 6.4 grams to 9.4 grams. Most of the elements quantified fall in the range of concentrations obtained are by similar work published by Bookhagen et al ²⁰ and Buechler

et al ¹⁹. However, it is important to note that in their work, quantifiable concentrations of cerium (Ce), thallium (Tl), Hg, rhodium (Rh), Praseodymium (Pr), Er, Holmium (Ho) and Terbium (Tb) were determined. Unfortunately, no conclusive comparison can be established with the results published in the literature given the differences in studied devices as well as adopted analytical methods.

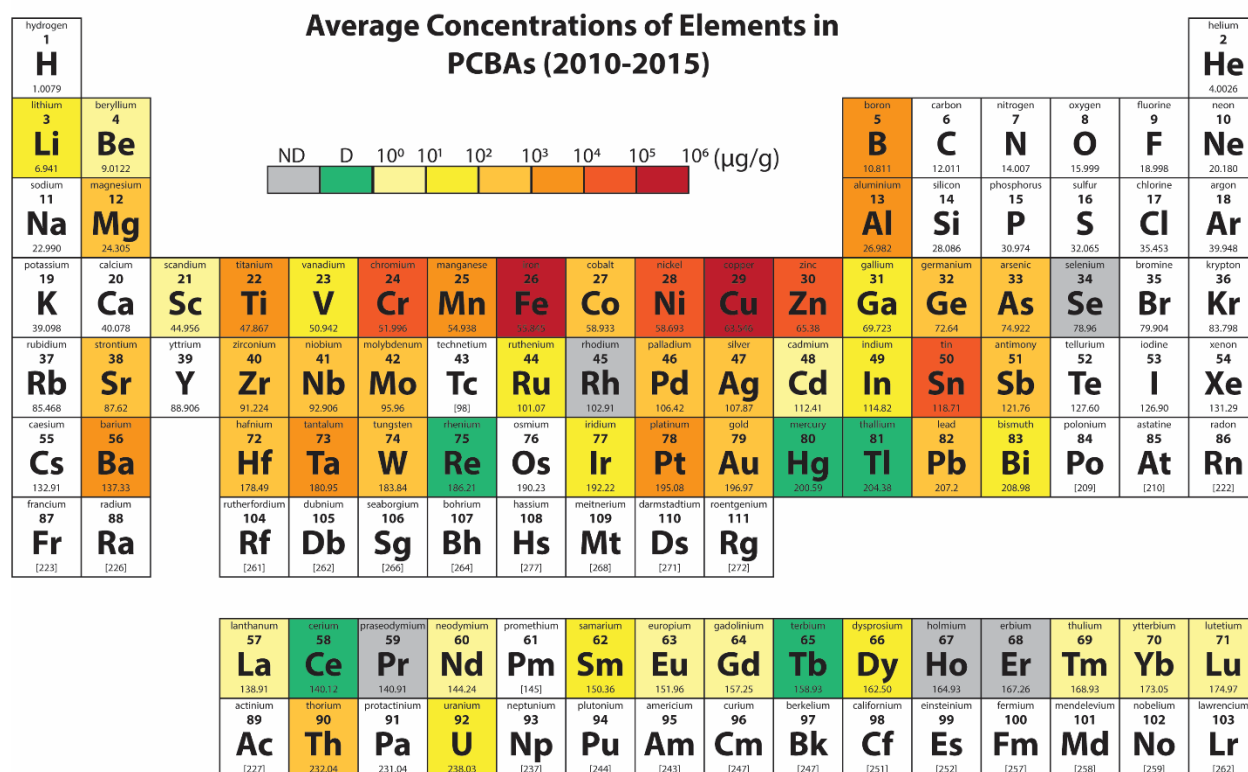


Figure 5 Average concentrations of elements in studied PCBAs (2010-2015) (μg/g of component).

5.2.1.2 Cameras

Total quantified metals in studied back cameras increased by 81.56 % from 0.58 g in S1 to 1.06 g in S8 back camera. By comparing the results presented in Fig.5 and Fig.6, significant differences and similarities in the elemental concentrations and composition between PCBAs and back cameras can be identified. Although back cameras are much smaller and have a very different function compared to PCBAs, their Cu and Fe concentrations fall in the same range. Furthermore, back cameras have higher concentrations of Nd, Pr, Zr, Au, Mo, lithium (Li), Tl, Mg, yttrium (Y) and Tb. REEs are specifically used in camera lens due to their ability to absorb ultraviolet light, magnetic and mechanical properties. For instance, Nd magnets are used in cameras for lenses autofocus feature, Pr is used as lens anti-reflection coating material and Y is used as an additive to lens glass improving its heat and shock resistance^{53–55}. On the other hand, back cameras showed lower concentrations of Ta which is mainly used in semiconductors due to its ductility and stability with temperature⁵⁶. In addition, back cameras showed lower concentrations of palladium (Pd), tungsten (W) and arsenic (As). Finally, Nb and germanium (Ge) were not detected in the studied back cameras.

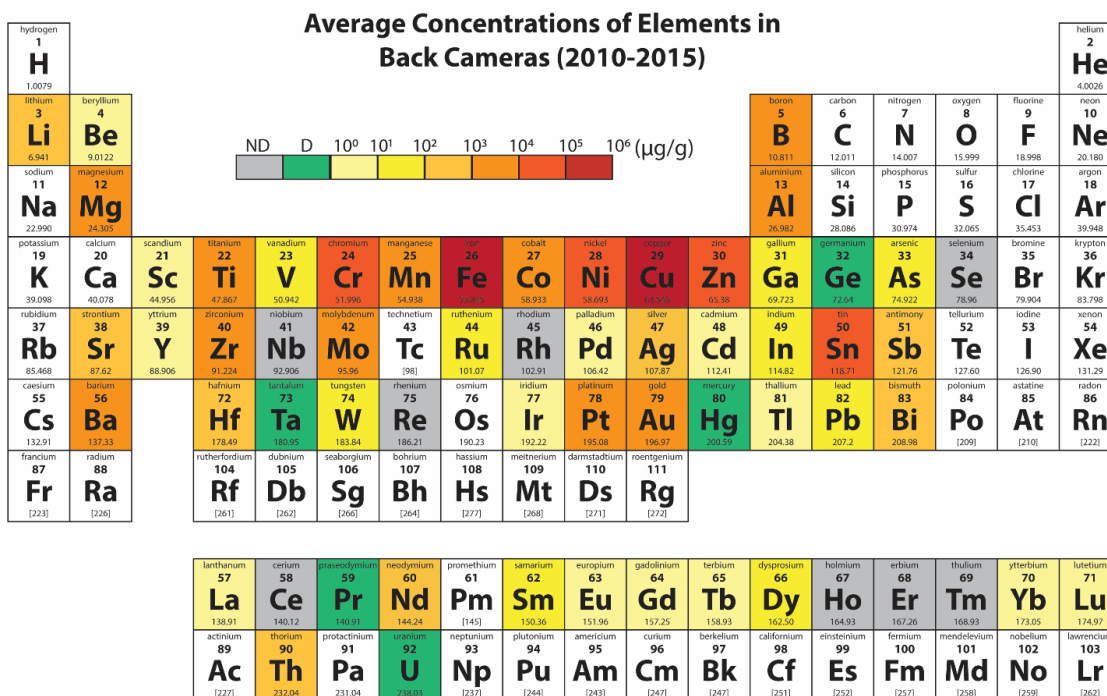


Figure 6 Average concentrations of elements in studied back cameras (2010-2015) (µg/g of component).

5.2.1.3 NFC/WC

The last component and latest technology introduced in the studied smartphones components is NFC antenna/wireless charging chip (NFC/WC). Similar to PCBAs and back camera composition, Cu and Fe concentrations were determined to be the highest concentration elements with similar concentration range (Fig. 7). On average, all quantified elements accounted for 84.06% of the total NFC/WC weight with 55.14 % and 36.64% of the quantified metals being Cu and Fe respectively. REEs and PGMs collectively accounted for 0.43% of the total quantified elements. Interestingly, five REEs (Gd, Nd, Lu, Y and Yb) were quantified while Tb was detected in NFC/WC. REEs are mainly used in wireless technology due to their strong magnetic properties

57.

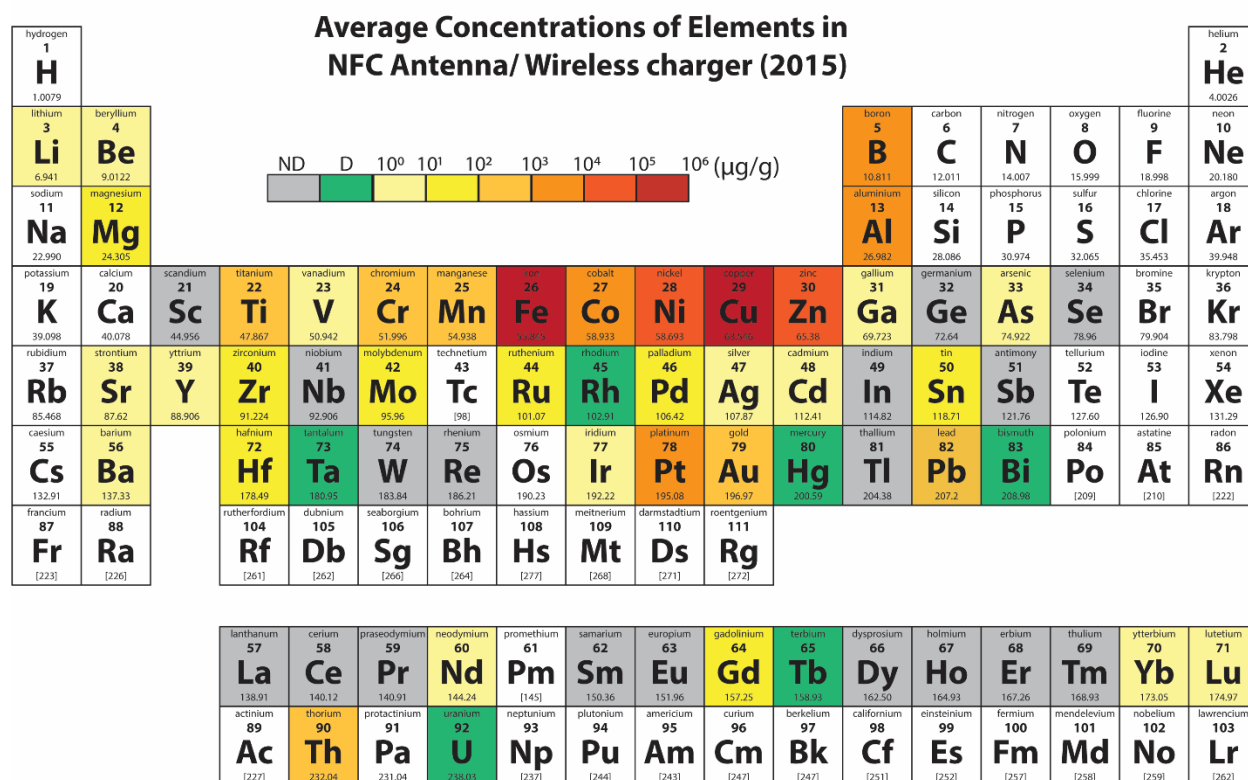


Figure 7 Average concentrations of elements in NFC Antenna/Wireless charger (2015) (µg/g of component).

5.2.2 Trend Over Time (2010-2015)

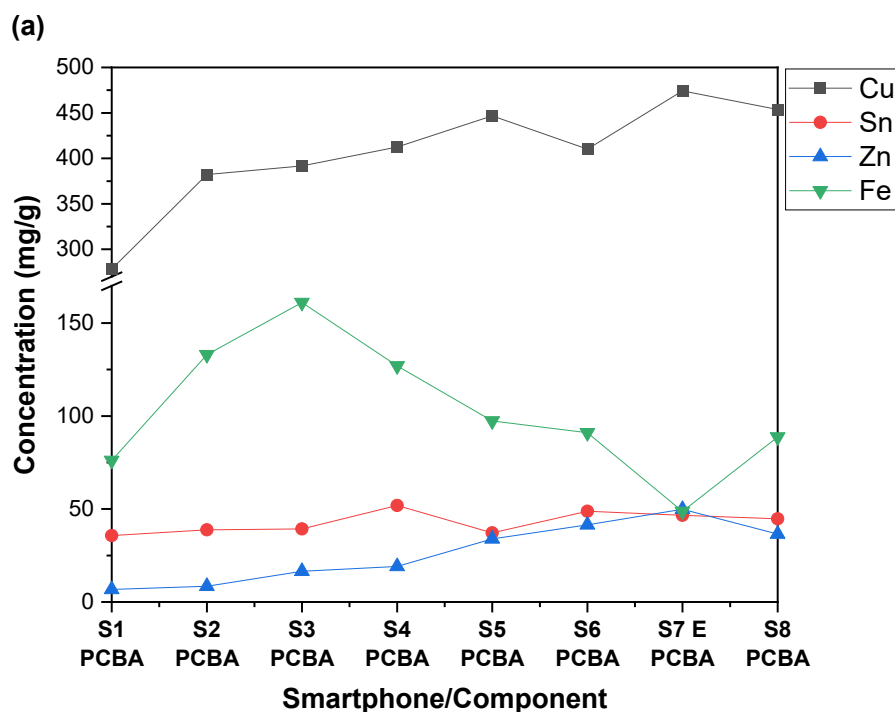
5.2.2.1 High Concentration Elements

As discussed in section 5.2, Cu, Zn and Fe are not classified as environmentally nor nationally critical but will briefly be discussed due to their high concentrations and use in electronics industry. Sn will be discussed in this section as well. Thanks to its excellent conductive properties, Cu is used as the main building block in most electronic devices essentially PCBAs. Steel, which is a mix of Fe and minute amount of carbon, is used to provide essential structural support allowing for smaller and more stable designs design capable of tolerating various mechanical shocks. Zn, in the form of zinc oxide, is a dielectric used for insulation in capacitors and semiconductors. Sn is used in the form of an alloy with other metals such as Pb, Cu, Ag and Au to connect electronic components in PCBAs in a process called soldering^{53,58}.

As presented in Fig. 8. (a), Cu and Sn concentrations increased in modern generation PCBAs indicating higher level of interconnections between different PCBAs components. Zn also followed an increasing trend from 6.78 mg/g S1 PCBA to a maximum of 49.89 mg/g in S7 PCBA then slightly decreased to 36.52 mg/g in S8 PCBA. Furthermore, Fe concentration increased from 76.15 mg/g to a maximum of 161.10 mg/g in S3 PCBA and then declined to a minimum of 48.76 mg/g in S7 PCBA.

As for back camera, even though a significant increment in Cu content can be identified with modern devices having higher Cu weight compared to their older counterparts, no significant trend in Cu concentration can be determined with a minimum concentration of 105.71 mg/g in S3 to a maximum of 357.66 mg/g S4 back camera (Fig. 8. (b)). However, Sn concentration decreased from 30.99 mg/g in S1 to a minimum of 8.92 mg/g in S4 then increased to a range of 14.80 to 17.43 mg/g in later camera generations. Nevertheless, it is important to note that total Sn content in cameras exhibits a different trend where it decreased from 33.65 mg in S1 to 7.44 mg in S3 followed by an increasing trend to reach 33.59 mg in S8 back camera. On the other hand, Zn followed an opposite trend to Sn where Zn concentration increased from 26.32 mg/g in S1 to 56.46 mg/g in S3 and then declined. As for Fe, no clear concentration trend can be identified yet total Fe content increased from 225.27 mg S1 to 420.97 S8 back camera.

Finally, given the limited number of NFC/WC samples tested, it is hard to discuss any significant trends. It is worth noting that the total quantified elements weight increased by 67.33% from 2.56 g in S6 and to 4.28 g S8 NFC/WC. However, even though no significant differences in Cu and Fe concentration between different devices can be determined, it can be clearly identified that higher Cu and Fe content was quantified in S8 2.57 g and 1.51 g compared to its older generation in S6 1.48 g and 0.69 g respectively, potentially to achieve higher charging capacity (Fig. 8. (C)). Furthermore, while Sn concentration increased from older generation to newer generation NF/WC, Zn concentration decreased significantly.



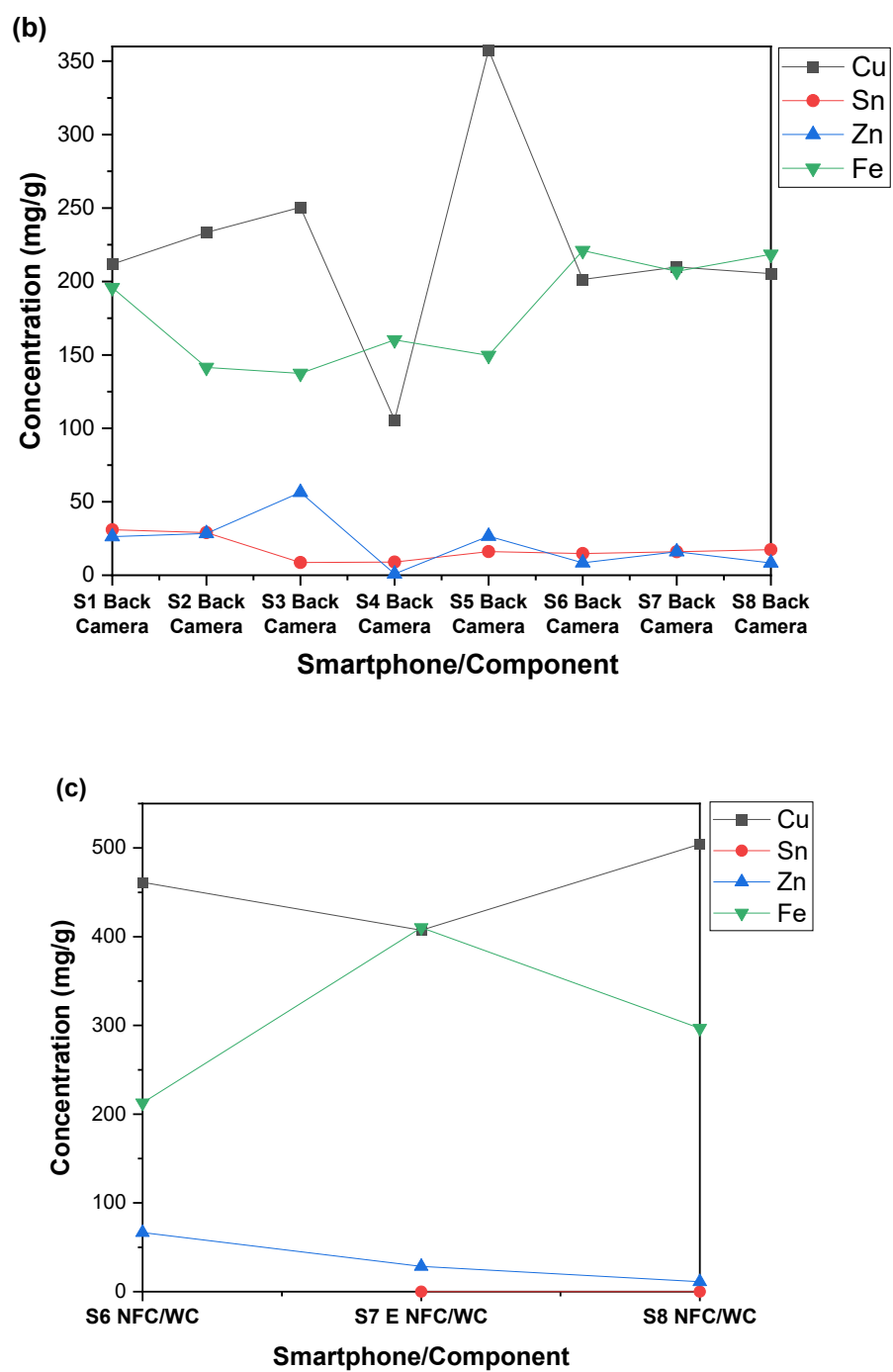


Figure 8 Evolution of Cu, Sn, Zn and Fe Concentrations in (a) PCBAs, (b) back cameras and (c) NFC/WC in mg/g of total component weight.

5.2.2.2 Environmentally Critical Elements

As discussed in the introduction of this section, elements having a criticality EI score of more than 30 were considered for the scope of this study. Hence, Ag, Au, U, Lu, Tm, Hg, Sc, Re and all five PGMs were determined to be environmentally critical elements. Elements (i.e. U, PGMs, Lu, Tm, Sc and Re) that were identified as environmentally, and nationally critical elements will be discussed in this section. The discussion in this section will focus on trends and changes in elements concentrations and content while further elaboration about their cradle to gate environmental impact can be found in section 5.3.

Copper group elements, Ag and Au, are used in electronics wiring due to their good conductivity and resistance to corrosion properties⁵⁹. Specifically, Au has a considerably higher resistance to oxidation but is less conductive than Ag. Both elements were proven to be critical for the electronics industry however due to higher Au prices, several manufacturers are actively trying to reduce their costs by substituting Au with other metal alloys such as Cu-Ag alloy⁶⁰⁻⁶². The obtained results show a similar trend where Ag concentration is increasing over different PCBAs generations while Au concentration is decreasing (Fig. 9. a). In addition, a similar trend for Au was observed in the analyzed smartphones back cameras where Au concentration is declining. No clear trend for Ag concentrations can be identified and it varied between 89.23 and 272.89 $\mu\text{g/g}$ (Fig. 9 b). However, the introduction of the new NFC/WC technology in 2015 required the addition of extra Au and Ag (Fig. 9 c).

Due to their durability, conductivity, resistance to oxidation and high temperature resistance, PGMs are very critical elements to our modern electronic applications. For instance, Platinum (Pt) and ruthenium (Ru) are essential for improved hard disks storage capacity, and Pd and Ir are widely used in ceramic capacitors and to control electrical flow^{63,64}. While Rh was detected, but not quantified, in only S7 NFC/WC, all other PGMs were quantified in all the studied components. On average, Pt only accounted for 86% while palladium (Pd), iridium (Ir) and ruthenium (Ru) were determined to be 9.5, 3.9 and 1.2 %, respectively, of total PGMs quantified in all PCBAs. Similar to Au trend, Pt concentration increased from S1 PCBA to reach a maximum of 2.28 mg/g and then declined to a minimum of 0.52 mg/g in S7 PCBA (Fig. 9 a). Furthermore, Pd followed an increasing trend like Ag with a maximum concentration of 132.97 $\mu\text{g/g}$ in S8 PCBA. Ru and Ir also followed a parallel trend showing a steep decline in concentration in S7 and

S8 PCBAs. As for PGMs concentrations in studied back cameras, Au and Pt showed an opposing trend where Pt concentration increased to reach a maximum of 931.87 $\mu\text{g/g}$ in S8 back camera (Fig. 9. b). In addition, Ru concentration was comparable among all back-camera generations and no clear trend can be observed. Although Pd was not quantified in earlier generation, S6, S7 and S8 back cameras showed a comparable concentration ranging between 20.32 and 25.91 $\mu\text{g/g}$. Furthermore, all back cameras showed a comparable concentration of Ir ranging between 4.54 and 12.82 $\mu\text{g/g}$. Pt and Ru concentrations in NFC/WC showed a slight increment peaking at S7 NFC/WC (Fig. 9. c). However, it is worth noting that their total content almost doubled between S6 and S7 NFC/WC. Pd, which was not quantified in S6 NFC/WC, was determined to be 6.99 and 45.17 $\mu\text{g/g}$ in S7 and S8 NFC/WC respectively. The increase of PGMs total content in NFC/WC indicate the need for stronger magnetic properties and hence faster charging capacity and better NFC connection.

Although the exact use of Lu in electronics is not very well documented in the literature, there are evidence proving the use of amorphous LaLuO_3 as an alternative dielectric in semiconductors ⁶⁵. In the obtained results, a minute comparable amounts of Lu were quantified in all studied parts. Due to its very low concentration, it hard to discuss a change in its trend. Nonetheless, the obtained results proof the consistent use of this very rare and expensive element in all the studied smartphone components.

Similar to Lu, Thulium (Tm) is another rare earth element with limited information about its use in electronics however few references report its application in high temperature superconductors ⁶⁶. Tm was either detected or quantified in all PCBAs at very low concentrations of less than 5.65 $\mu\text{g/g}$. No Tm was detected in all studied smartphone back camera or NFC/WC components.

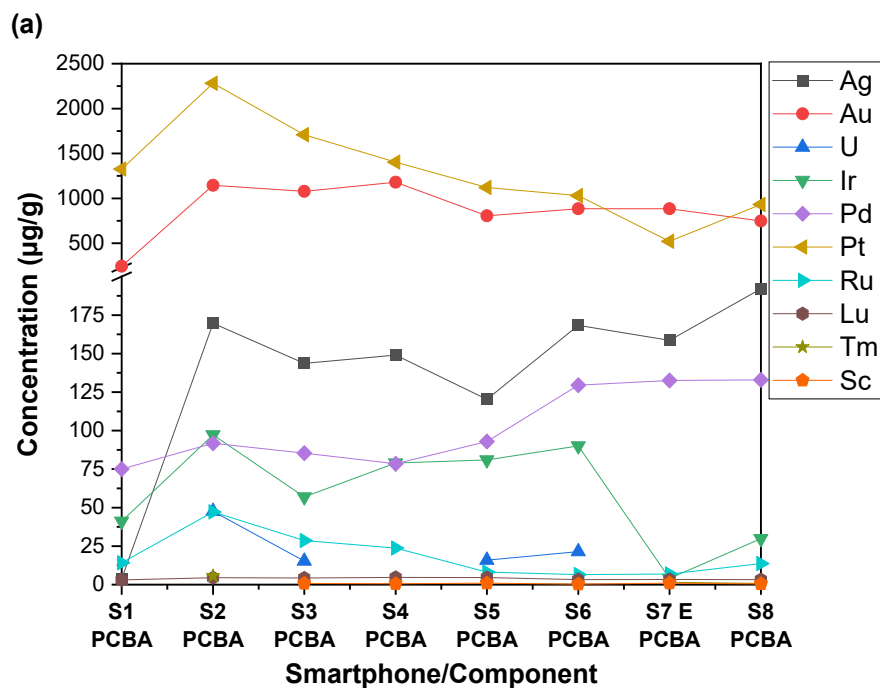
Hg is a regulated neurotoxin with well documented history of various uses in electronics ⁶⁷. From the obtained data, Hg seems to be of inevitable use in PCBAs since it was detected, but not quantified, in several samples including all studied components.

Scandium (Sc) was detected and quantified in most PCBAs and back camera samples at very low concentrations less than 2 $\mu\text{g/g}$. No clear trend for Sc use can be identified. Sc is mainly used in smartphones capacitors ⁶⁸.

Uranium (U) is a weakly radioactive naturally occurring element with no reported use in electronics, but rather its presence results in an error known in electronics industry as soft error ⁶⁹. The presence of a minute amount of U in most of the studied smartphones components could be the result of a contaminated supply of REEs, which are usually found in minerals with thorium (Th) and U ⁷⁰.

Rhenium (Re) is the last element in the identified environmentally critical elements. Re was only detected, but not quantified, in S2 and S6 PCBAs. Re is usually used as additive alloy with W and Mo to improve its resistance to wear and withstand corrosion ⁵³.

Fig. 10 summarizes the change in concentrations of environmentally critical elements in each studied component per smartphone model. As the graph shows, the concentration of environmentally critical elements in S1 PCBA increased to a maximum of 4.00 mg/g in S2 PCBA and then followed a decreasing trend. Likewise, the concentration of environmentally critical elements in back cameras decreased over different generations. However, the introduction of a new NFC/WC technology had a significantly high concentration ranging between 2.76 and 5.17 mg/g. Further quantification of the environmental implications on climate change and water depletion will be discussed in section 5.3.



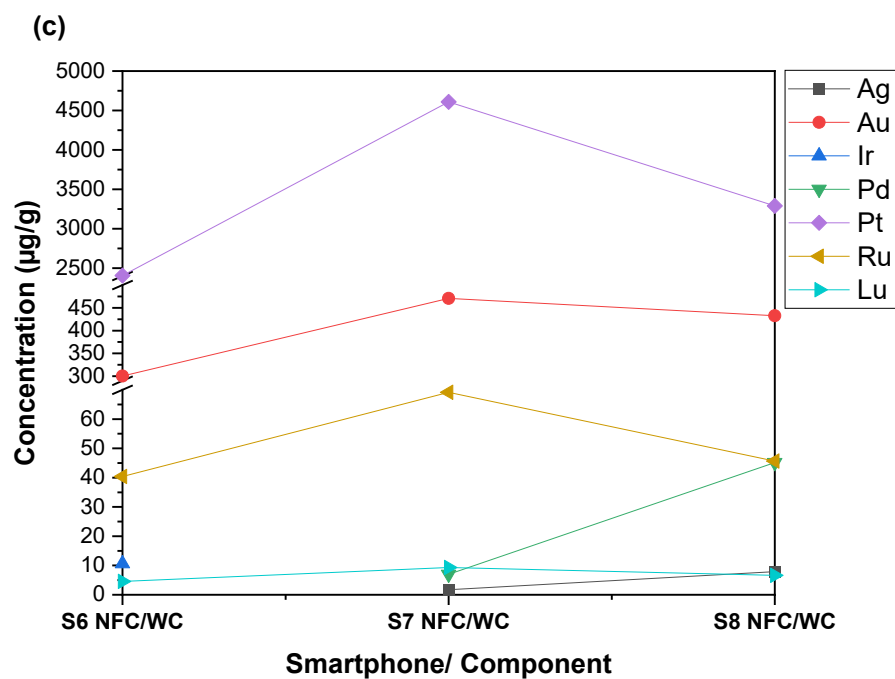
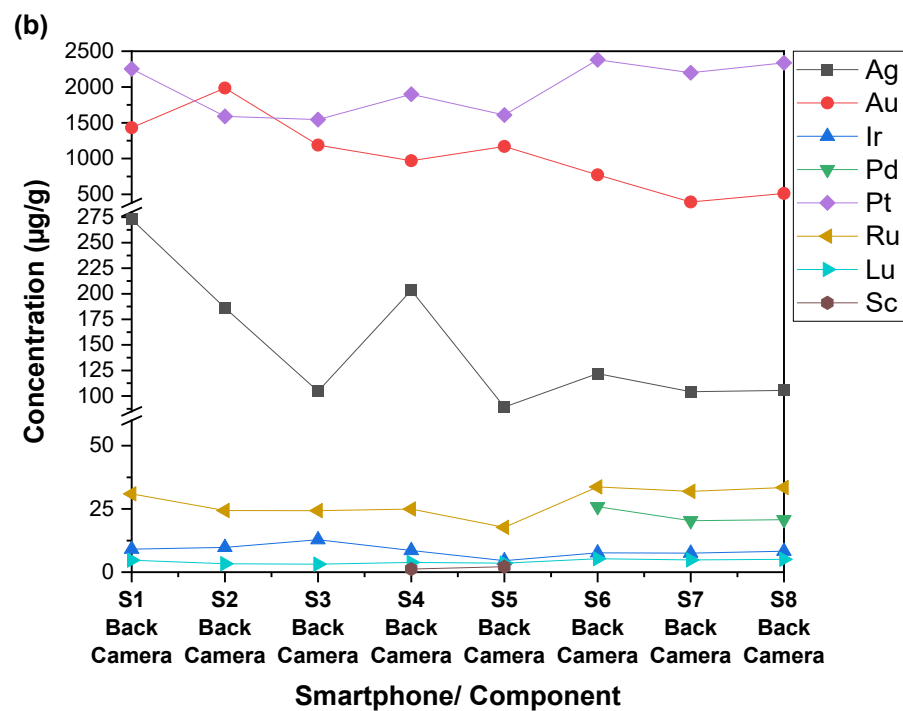


Figure 9 Evolution of environmentally critical elements Concentrations in (a) PCBAs, (b) back cameras and (c) NFC/WC in $\mu\text{g/g}$ of total component weight.

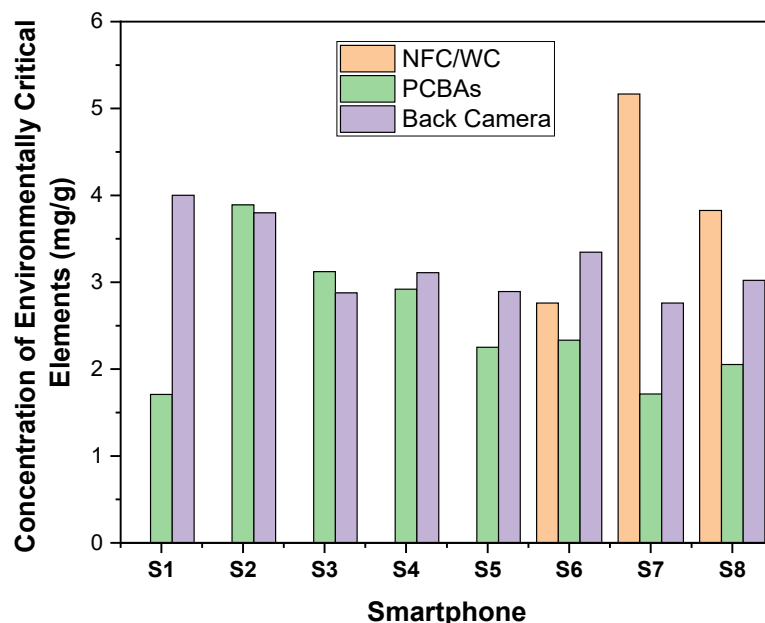


Figure 10 Evolution of total environmentally critical elements concentration in PCBAs, back cameras and NFC/WC in mg/g of total component weight.

5.2.2.3 Nationally Critical Elements

As previously discussed, in 2018, USGS identified a list of 47 metals including REEs and PGMs as critical metals. Among the list, only cesium (Cs), rubidium (Rb) and Tellurium (Te) were not included in this study due to instrument detection challenges. Briefly, it was not possible to identify interference free wavelengths and construct acceptable calibration curves for these elements on our ICP-OES system. This section will briefly discuss the change in high and low concentration USGS identified critical metals and will be concluded with a general summary about critical elements content in different smartphones generations.

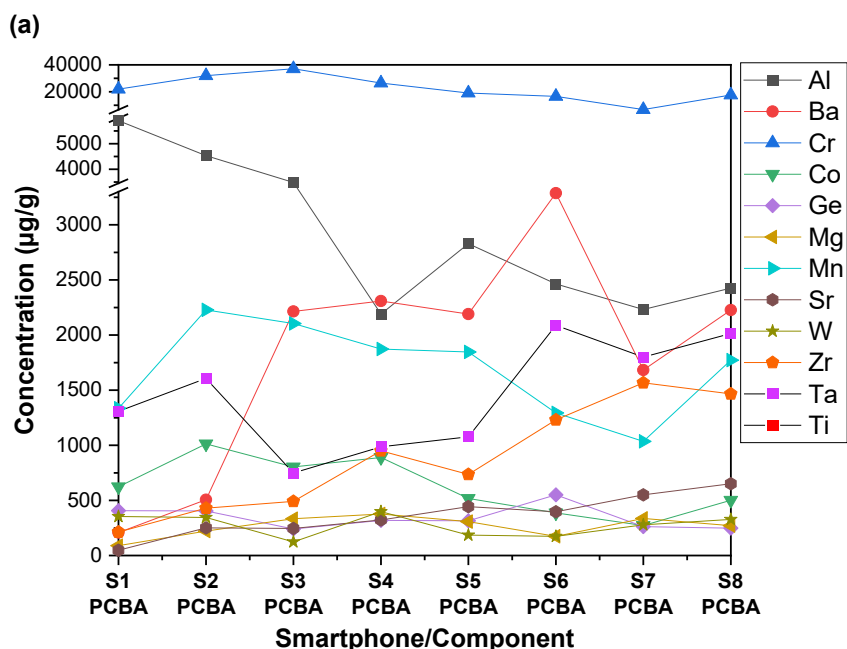
5.2.2.3.1 High concentration critical elements

Among all the USGS recognized critical elements, Aluminum (Al), Barium (Ba), Cr, Cobalt (Co), Germanium (Ge), magnesium (Mg), manganese (Mn), strontium (Sr), tungsten (W), zirconium (Zr), Tantalum (Ta), Titanium (Ti) and Sn were determined to be the highest concentration elements used in PCBAs. Sn was already discussed in section 5.2.2.2.

From Fig. 11. (a), it can be concluded that Al, Cr, Co and Ge concentrations in different PCBAs generations followed a declining trend as oppose to Mg, Mn, Sr and Zr which shows a significant increase in their concentrations. No clear trend for W concentration in PCBAs can be observed and its concentrations varied between 123.61 and 398.28 $\mu\text{g/g}$. It is important to note that Ba, Sr, Ta, Zr and Ti showed the highest concentration increase over all other metals.

On the other hand, as for the studied back cameras, Al and Sr concentrations exhibited an increasing trend over different generations while Ba and Mg concentrations increased then followed a decreasing trend. W concentration decreased significantly. Ge was not detected in S1 and S3 while it was detected, but not quantified, in all other studied samples. last and most importantly, Cr, Zr and Mn showed the highest increase in concentration among all other elements (Fig. 11. (b)).

Finally, as for the most recently introduced technology, NFC/WC, Al was the only element where its concentration decreased from S6 NFC/WC to S7 NFC/WC and then increased to a maximum of 2.17 mg/g in S8 NFC/WC, higher than in S6 NFC/WC. Mg, Mn, Sr and Co concentrations consistently decreased over different generations while Zr, Cr and Ba concentrations peaked in S7 NFC/WC. Ge and W were not detected in all three NFC/WC samples (Fig. 11 (c)).



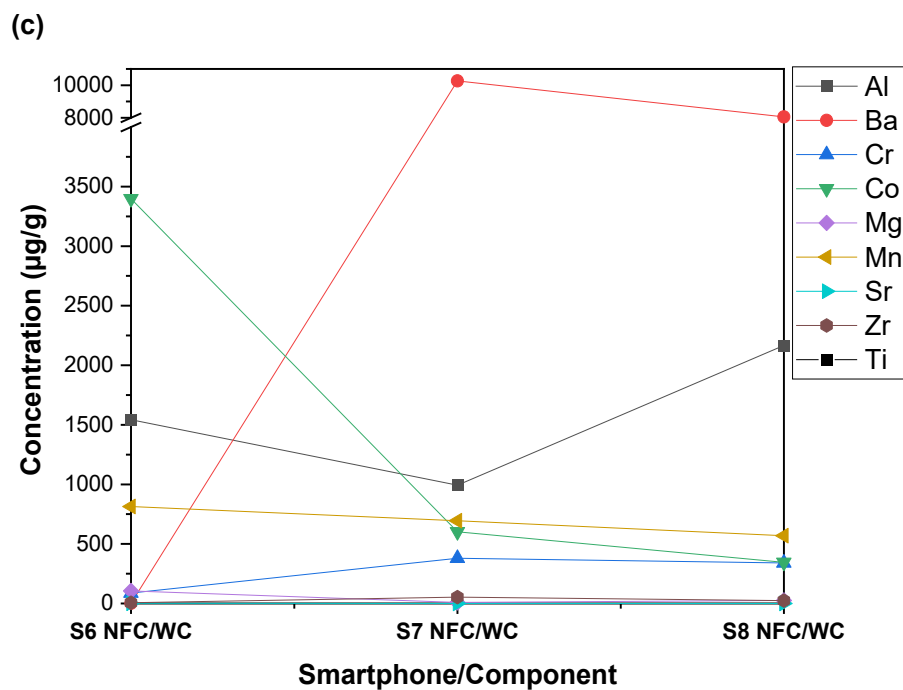
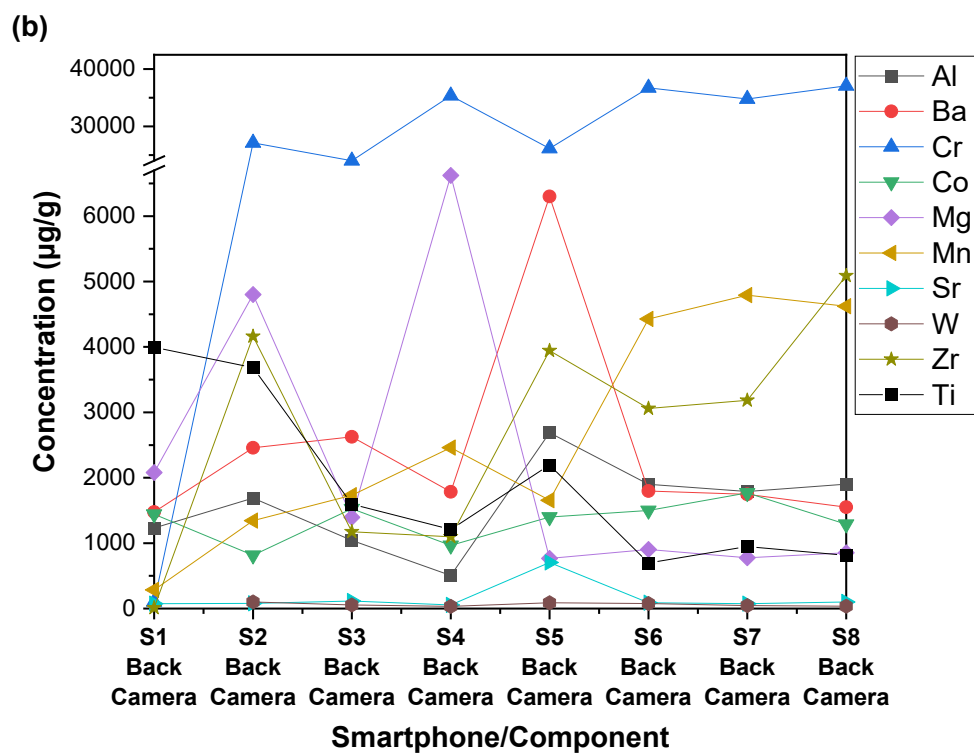


Figure 11 Evolution of high concentration of USGS identified critical metals in (a) PCBAs, (b) back camera and (c) NFC/WC in $\mu\text{g/g}$ of total component weight.

5.2.2.3.2 Low Concentrations Critical Metals

Low concentration USGS identified critical metals in the studied smartphones components included Antimony (Sb), arsenic (As), beryllium (Be), bismuth (Bi), gallium (Ga), indium (In), lithium (Li), niobium (Nb), vanadium (V) and hafnium (Hf).

As presented in Fig. 12 (a), Sb and Hf followed a similar change in concentrations over different PCBAs generations with the highest being 312.72 and 275.20 $\mu\text{g/g}$ respectively in S3 PCBA. The general concentration change profile for Be, In and V is declining in modern PCBAs while no clear trends for As, Bi and Ga concentrations can be determined. Niobium concentration decreased from 114.10 $\mu\text{g/g}$ S1 PCBA to be detected, but not quantified, in S2 PCBA and then increased significantly to peak at S7 PCBA with 415.67 $\mu\text{g/g}$. Li followed a trend similar to Nb where its concentration decreased from 40.24 $\mu\text{g/g}$ in S1 PCBA to a minimum of 9.98 $\mu\text{g/g}$ in S3 PCBA and then increased to maximum of 63.02 $\mu\text{g/g}$ in S7 PCBA. No significant trend in REEs concentrations can be identified where its concentration ranged between 102.88 and 278.29 $\mu\text{g/g}$.

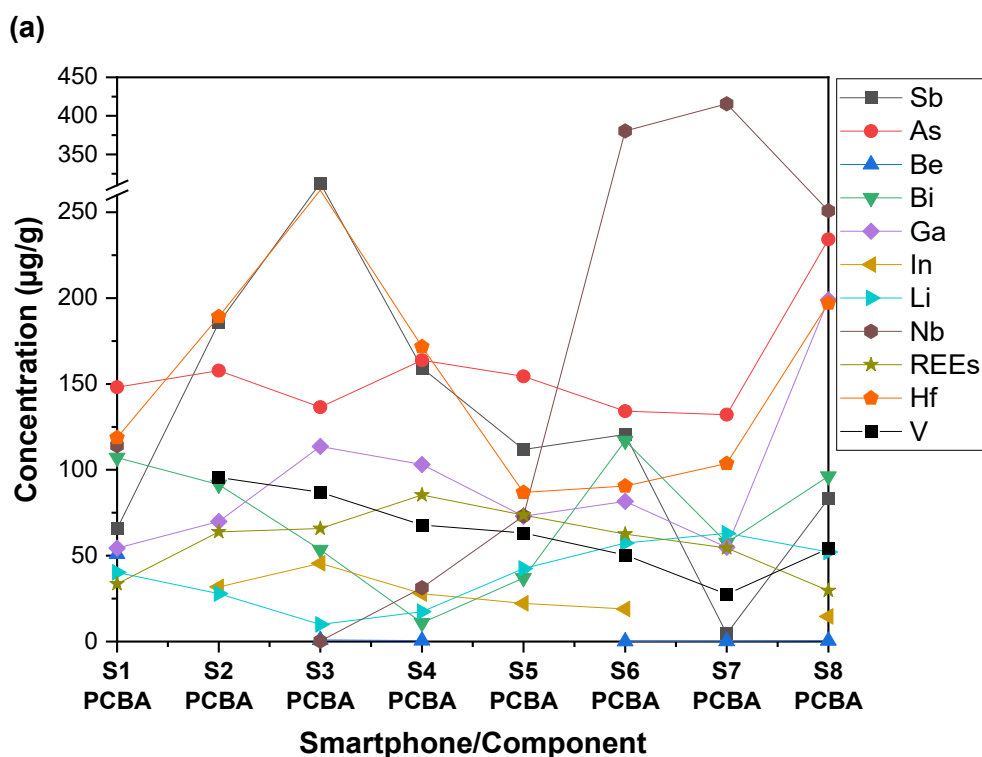
Although Sb was not detected in S1 and S2 back camera, it was quantified in later back camera generations with a concentration range between 140.52 to 378.23 $\mu\text{g/g}$ (Fig. 12 (b)). Hf exhibited the highest concentration increase among all other elements potentially due to its use in camera auto-focus sensor ⁷¹. Bi concentration decreased significantly in the latest back camera generations while As, In and V concentrations showed a constant increase to reach 32.66, 136.06 and 79.68 $\mu\text{g/g}$, respectively, in S8 back camera. Li concentration in all analyzed back cameras are comparable except for S5 possibly due to a change in the device design. No clear trend can be attributed to the change in REEs concentrations in different back camera generations. However, it appears to be slightly declining with a total concentration of 251.91 $\mu\text{g/g}$ in the latest generation back camera.

Sb, In and Nb were not detected in all three studied NFC/WC while Bi were only detected, but not quantified, in S8 NFC/WC respectively. Ga and V were not detected in S6 NFC/WC while quantified in the later devices with S8 NFC/WC having lower concentrations than S7 NFC/WC. Likewise, As was only detected in S6 but quantified in S7 and S8 NFC/WC with S8 having a lower As concentration than S7 NFC/WC. Li, REEs and Be showed a similar trend where their

concentration in S7 NFC/WC is higher than in S6 and S8, with the latter having higher concentrations than S6 NFC/WC (Fig. 12 (c)).

5.2.2.3.3 General Summary of USGS Identified Critical Elements

Fig. 13 summarize the evolution of USGS identified critical metals in all studied smartphones components. As presented in the graph, there's not much change in the concentration of nationally identified elements in PCBA with a concentration ranging from 73.59 in S7 PCBA to a maximum of 97.65 mg in S4 PCBA. As for the studied back cameras, a consistent increment in critical metals concentrations can be observed from 1.15 in S1 to 1.93 mg/g in S8 back camera. Finally, the addition of the new NFC/WC technology had a significantly high concentration of critical metals ranging from 7.07 to 8.46 mg/g.



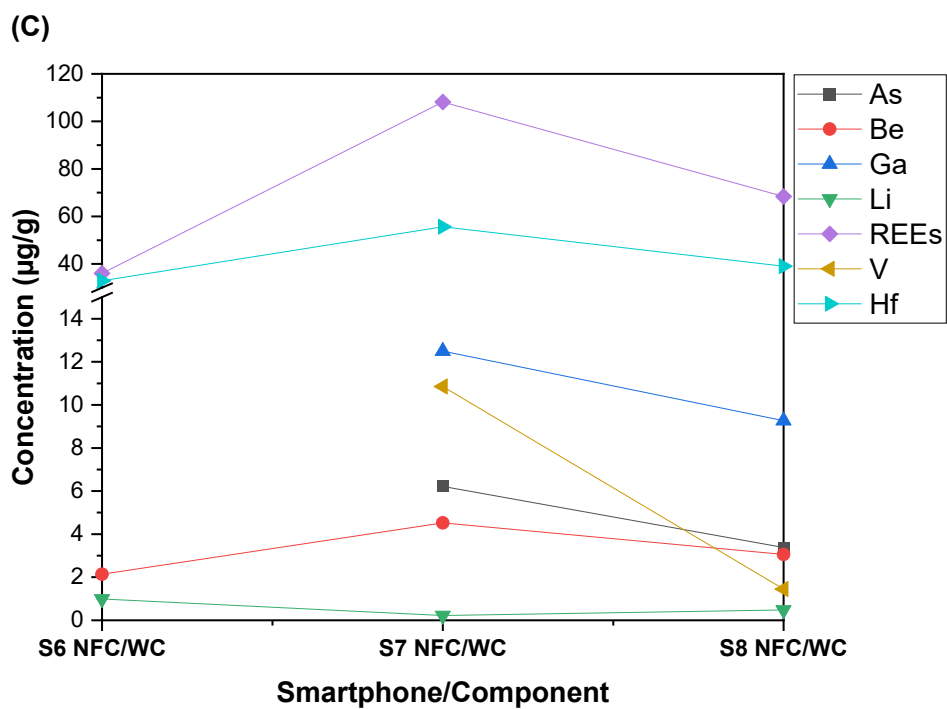
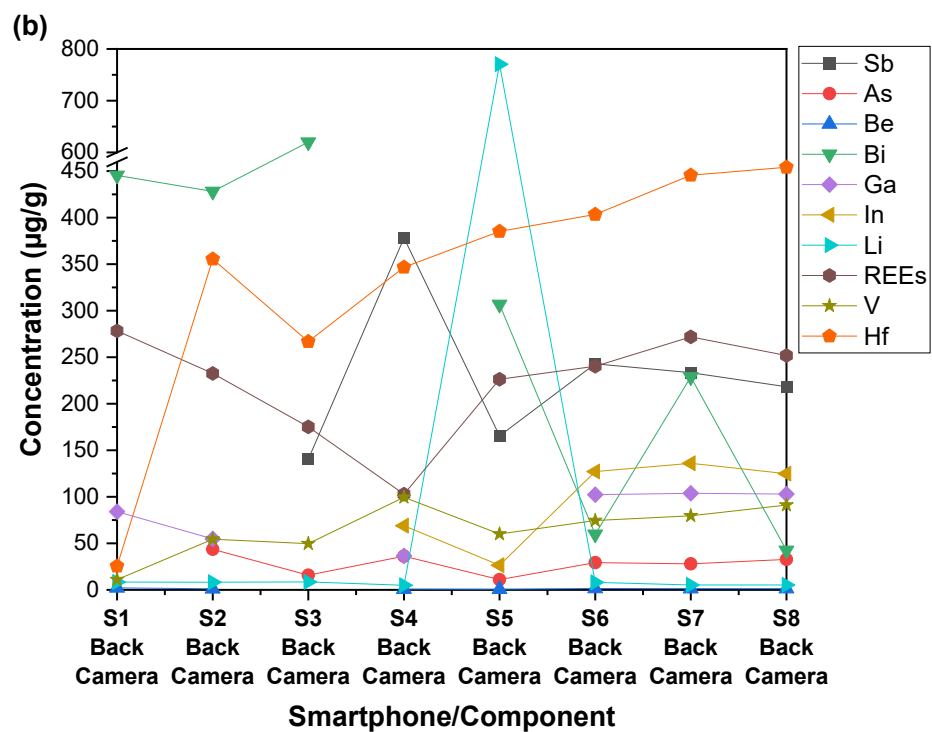


Figure 12 Evolution of low concentration of USGS identified critical metals in (a) PCBAs, (b) back camera and (c) NFC/WC in $\mu\text{g/g}$ of total component weight..

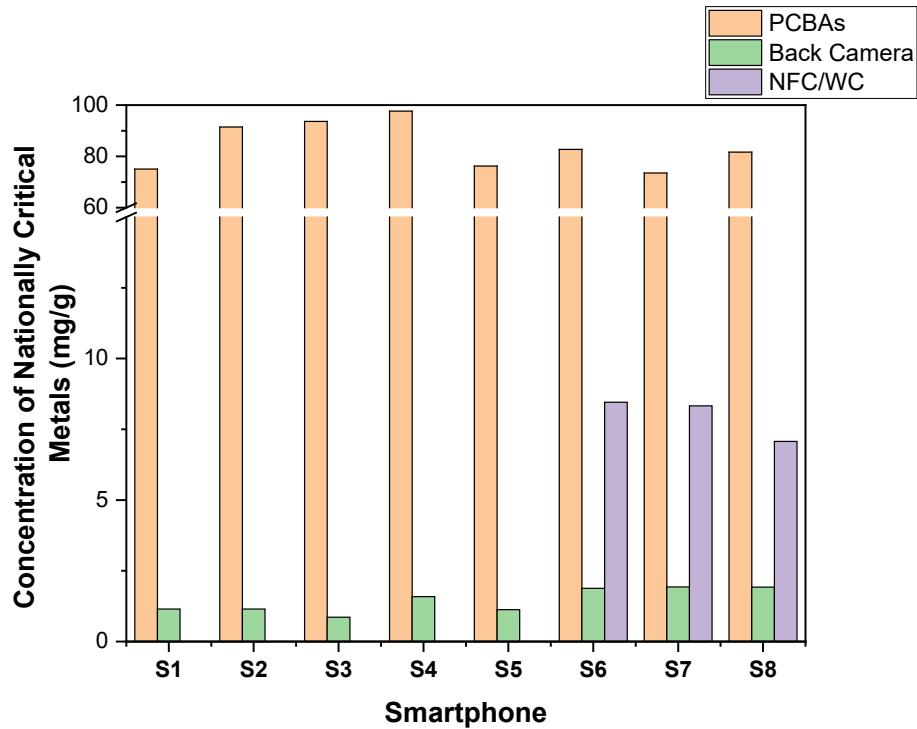


Figure 13 Evolution of total nationally identified critical metals concentration in PCBAs, back cameras and NFC/WC in mg/g of total component weight.

5.3 Environmental Impact of Smartphones Evolution

As noted in chapter 1, the environmental impact of the evolution of smartphones metals content is not fully understood mainly due to lack of information about the change in its composition over time. In this section, an attempt to estimate the cradle to gate environmental impact of metals used to manufacture the studied devices will be conducted. The scope of this work will focus on three main environmental categories which are climate change and water depletion. The life cycle inventory used to estimate selected environmental impacts was imported from table S5 in the supporting information provided by Graedel et al ⁵⁰ in their work titled “Criticality of metals and metalloids”. In their calculations, midpoint environmental impacts resulting from metals mining and refining per one kg of material output (cradle to gate) were computed using the ReCiPe 1.10 (World) method ⁷², taking into consideration various metals supply sources. Therefore, for the purposes of the presented work, the total environmental impact in one category was the result of multiplying the total quantified mass of a specific element by its

associated environmental impacts. A detailed calculation of all environmental impacts is available in appendix F.

5.3.1 Impact on Climate Change

Although total environmentally critical elements did not exceed 1.3% of the total quantified elements by mass, they contributed for at least 86.36 % of total CO₂ emissions related to mining and refining of all studied elements in all devices for all components. On average, Pt and Au accounted for 59.03 and 37.44% of total CO₂ emissions, respectively. As Fig. 14 shows, the total environmental impact per device increased from 371.49 in S1 to 639.16 g CO₂ eq in S2 and then declined to a minimum of 432.1 g CO₂ in S5 followed by spike in S6 to reach a maximum of 658.72 g CO₂ eq mainly due to the introduction of the new NFC/WC technology. As for elements used in camera manufacturing, no significant change was determined mainly due to minor changes in environmentally critical elements concentration in all studied back cameras. To estimate the cradle to gate total impact on climate change of all analyzed elements, sales data collected from several credible sources was used to estimate total impact of studied elements (Table 3). No separate sales data for S6 and S7 was available, hence their combined sales data was multiplied by the average CO₂ emission for each component. Therefore, the total estimated CO₂ eq produced by all documented units sold in the world is 150 thousand metric tons of CO₂ eq.

Assuming the latest studied model S8 produced in 2015 is a representative sample of all smartphones sold in 2019, the total CO₂ eq emission associated with the studied metals used in manufacturing only three components totals at 1 million and 106 tons of CO₂ eq globally and in USA, respectively. Using EPA Greenhouse Gas Equivalencies Calculator, 1 million tons of CO₂ eq is equivalent to fully charging approximately 36 times all 3.5 billion active smartphones in the world while 106 tons of CO₂ eq is equivalent to driving 90 times an average passenger vehicle from California to New York ⁷³.

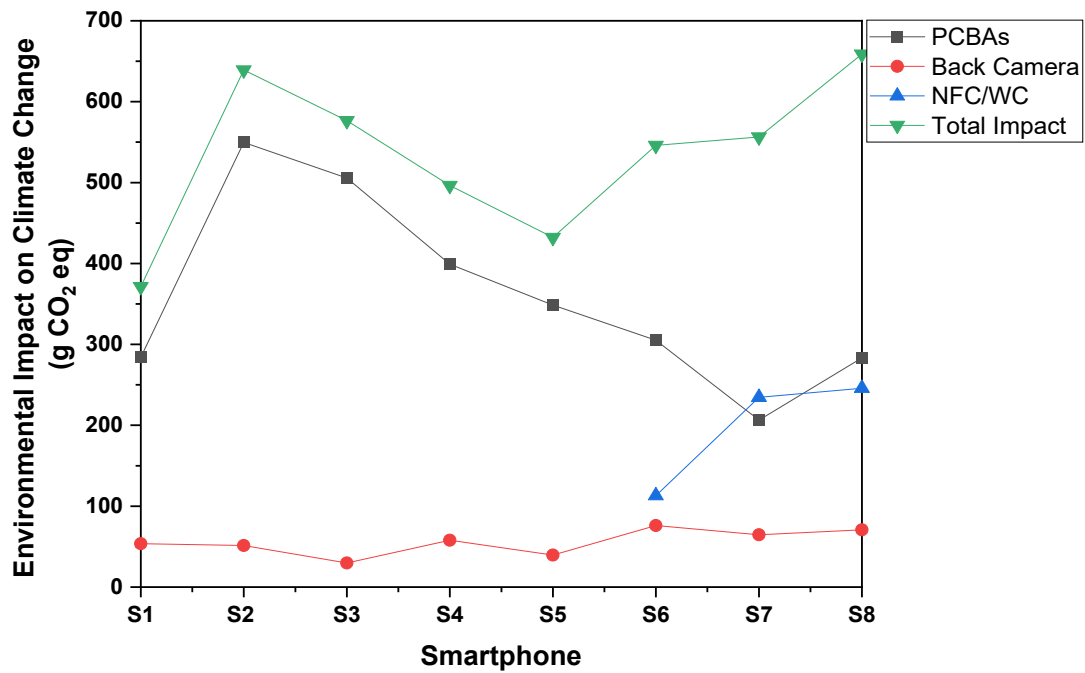


Figure 14 Evolution of total environmental impact on climate change for all the studied elements in PCBAs, Back Camera and NFC/WC.

Table 3 Calculated environmental impacts on climate change.

	Sales data	PCBAs	Back Camera	NFC/WC	Total impact
Devices	Million units sold	Thousand metric tons of CO ₂ eq			
S1/2010	2.4E+01 ⁷⁴	6.8E+00	1.3E+00	-	8.9E+00
S2/2011	4.0E+01 ⁷⁴	2.2E+01	2.1E+00	-	2.6E+01
S3/2012	7.0E+01 ⁷⁵	3.5E+01	2.1E+00	-	4.0E+01
S4/2013	8.0E+01 ⁷⁶	3.2E+01	4.6E+00	-	4.0E+01
S5/2014	1.1E+01 ⁷⁷	3.8E+00	4.3E-01	-	4.8E+00
S6 & S7/2015	4.5E+01 ⁷⁸	1.2E+01	3.2E+00	7.8E+00	2.5E+01
S8/2015	1.0E+01 ⁷⁸	2.8E+00	7.1E-01	2.5E+00	6.6E+00
Total	2.8E+02	1.1E+02	1.4E+01	1.0E+01	1.5E+02
USA sales in 2019	1.6E+02 ⁷⁹	4.6E+01	1.1E+01	4.0E+01	1.1E+02
Global Sales for 2019	1.5E+03 ⁸⁰	4.3E+02	1.1E+02	3.7E+02	1.0E+03

5.3.2 Impact on water depletion

A similar graph to the studied smartphones components impacts on climate change was obtained for water depletion (Fig. 15). The minute amount of environmentally critical elements accounted for most of the impact with Pt and Au accounting, on average, for at least 42.80 and 24.19 % of the total impact on water depletion for all components in all studied devices. As presented in Fig. 11, water depletion impact increased from 1.81 in S1 to 3.18 m³ in S2 followed by a decreasing trend to a minimum of 2.04 m³ in S5 and then spiked to 3.19 m³ in S8. The introduction of NFC/WC technology in S6 increased total environmental impact on water depletion significantly.

Assuming S8 device is representative of devices produced in 2019, equivalent to 4.8 km³ globally and 510 thousand m³ in USA fresh water were consumed to mine and process all quantified metals used in manufacturing only three smartphones components. To give a better illustration, 4.8 km³ could sustain a city as big as New York City for 3.5 years (Table 4).

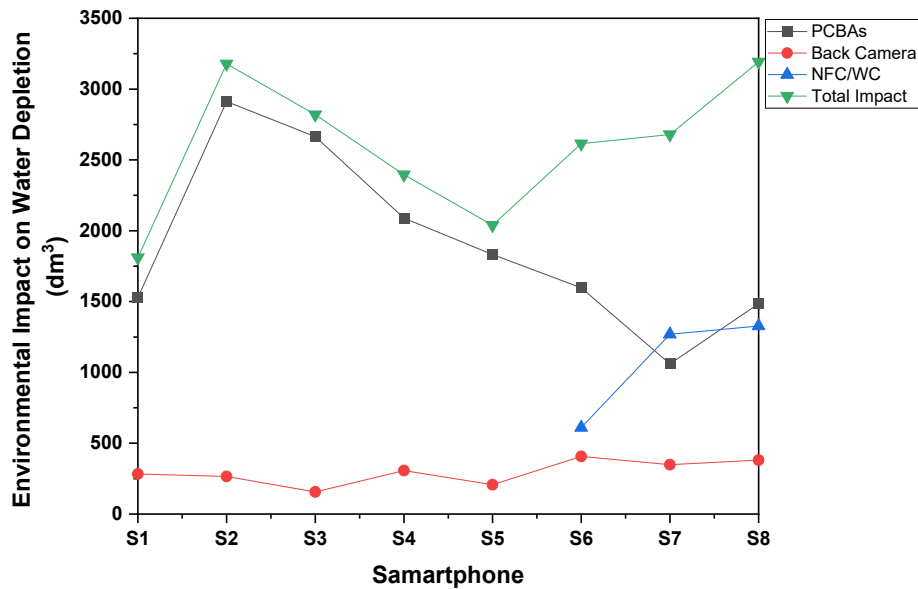


Figure 15 Evolution of total environmental impact on water depletion for all the studied elements in PCBAs, Back Camera and NFC/WC.

Table 4 Calculated impact on water depletion.

	Sales data	PCBAs	Back Camera	NFC/WC	Total impact
Devices	Million units sold	Thousand m3			
S1/2010	2.4E+01	3.7E+01	6.8E+00	-	4.3E+01
S2/2011	4.0E+01	1.2E+02	1.1E+01	-	1.3E+02
S3/2012	7.0E+01	1.9E+02	1.1E+01	-	2.0E+02
S4/2013	8.0E+01	1.7E+02	2.5E+01	-	1.9E+02
S5/2014	1.1E+01	2.0E+01	2.3E+00	-	2.2E+01
S6 & S7/2015	4.5E+01	6.0E+01	1.7E+01	4.2E+01	1.2E+02
S8/2015	1.0E+01	1.5E+01	3.8E+00	1.3E+01	3.2E+01
Total	2.8E+02	6.0E+02	7.6E+01	5.6E+01	7.3E+02
Total sales in 2019 USA	1.6E+02	2.4E+02	6.1E+01	2.1E+02	5.1E+02
Global sales in 2019	1.5E+03	2.3E+03	5.8E+02	2.0E+03	4.8E+03

5.3.3 Potential Resources Recovery

Metals recovery from spent electronics, especially smartphones, is not only important from a sustainability perspective but rather is great business with lots of potentials in a growing market. For instance, Chatterjee ⁸¹ estimated a total revenue up to 14.79 \$/kg of electronic waste recycled. To understand the change in metals value of different smartphones generations, total metals value per device for all studied components was computed using most the recent metals prices (Fig. 16). Detailed results about the calculations are available in the supporting information. With 160 million smartphones sold in 2019 and assuming that S8 is a representative device of the current smartphone's technology, the total addressable market value of metals reclamation from only three smartphone components at their end of life is estimated at 298.69 million USD in USA. The highest value elements were determined to be Au and Pt. More value could be recovered from other parts which include a significant amount of metals such as aluminum from frames, Nd from speaker magnets and others.

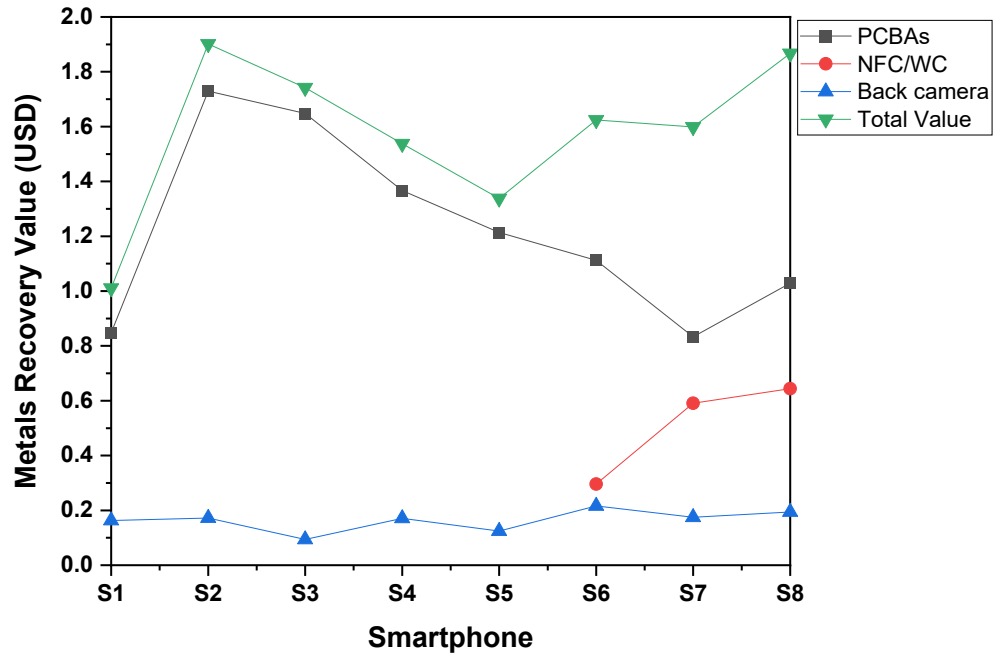


Figure 16 Evolution of recoverable metals value from spent PCBAs, Back cameras and NFC/WC.

6. CONCLUSIONS AND FUTURE WORK

A new titration like MWAD method was developed for the complete digestion of up 1 gram of electronic sample. The method was proven to be reliable and was successfully applied to different (1) smartphone components. (2) On average, 67.3% of a PCBA by weight was determined to be recoverable metals. The highest concentration elements, Cu, Ni, Sn, Zn and Fe, accounted for 93.3% while REEs and PGMs collectively accounted for 0.53% of the total recoverable elements by weight. (3) All regulated elements were determined to be in compliance with RoHS requirements where Pb, Cd and total Cr concentrations were found to be 78 µg/g, 2 µg/g and 30 mg/g respectively while mercury (Hg) was detected but not quantified. (4) Over different smartphones generations produced between 2010 and 2015, PCBAs total metals content increased by 47% from 6.4 grams to 9.4 grams. Furthermore, it was determined that the concentration of Cu, Zn, and Ag is increasing over time while Au and Pt concentrations are decreasing. (5) Although total environmentally critical elements did not exceed 1.3% of the total quantified elements by mass, they contributed for at least 86.36 % of total CO₂ emissions related to mining and refining of all studied elements in all devices for all components. (6) The total addressable market value of metals reclamation from only three smartphone components at their end of life is estimated at 298.69 million USD in USA. The highest value elements were determined to be Au and Pt. More value could be recovered from other parts which include a significant amount of metals such as aluminum from frames, Nd from speaker magnets and others. (7) The best proposed solution is to design smartphones with extended service life and adjust company's business model to recover their sales losses from software development and information technology.

Future work should use the reported data to perform cradle to grave life cycle analysis to provide a comprehensive illustration about the impact of smartphones development on various environmental impact categories. In addition, as presented in this work, estimating the environmental impact from only one smartphone component could be misleading as the introduction of other technologies could have a great impact on the obtained results. Finally, a resource efficiency index should be developed to take into account the improved functionality and resources used to manufacture the device.

APPENDIX B – PART 1

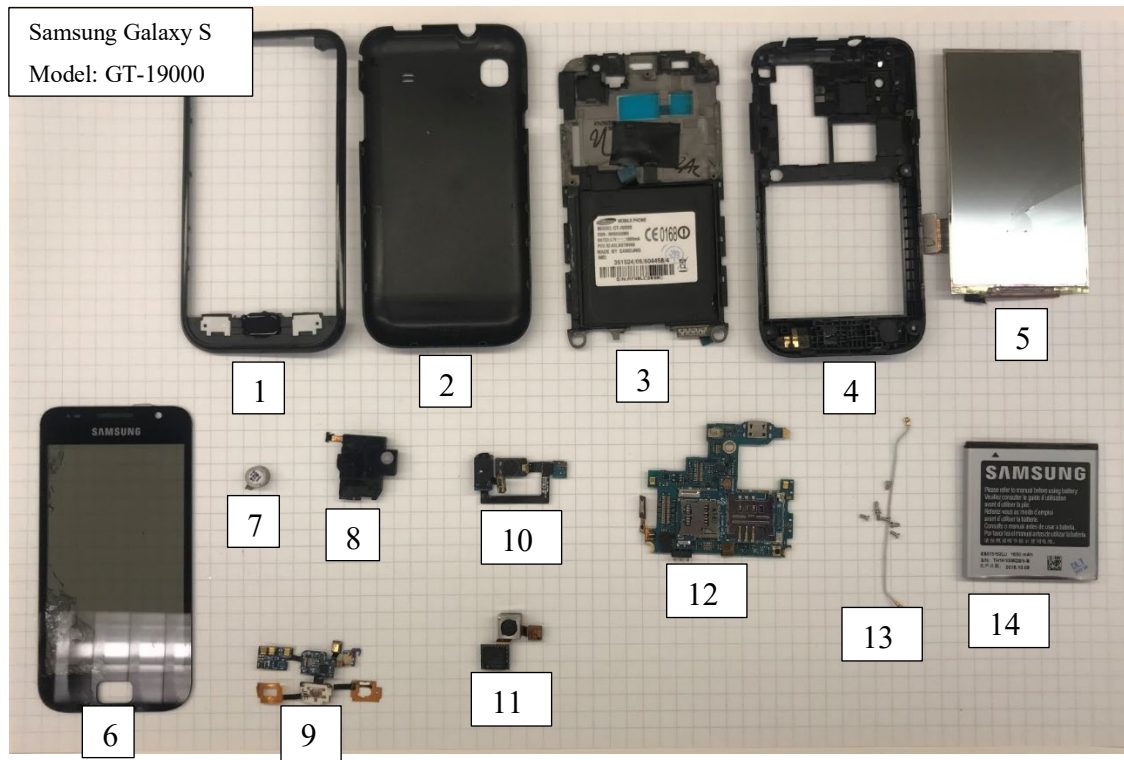


Figure 17 Samsung Galaxy S (Model: GT-19000). Release date: June 4, 2010.

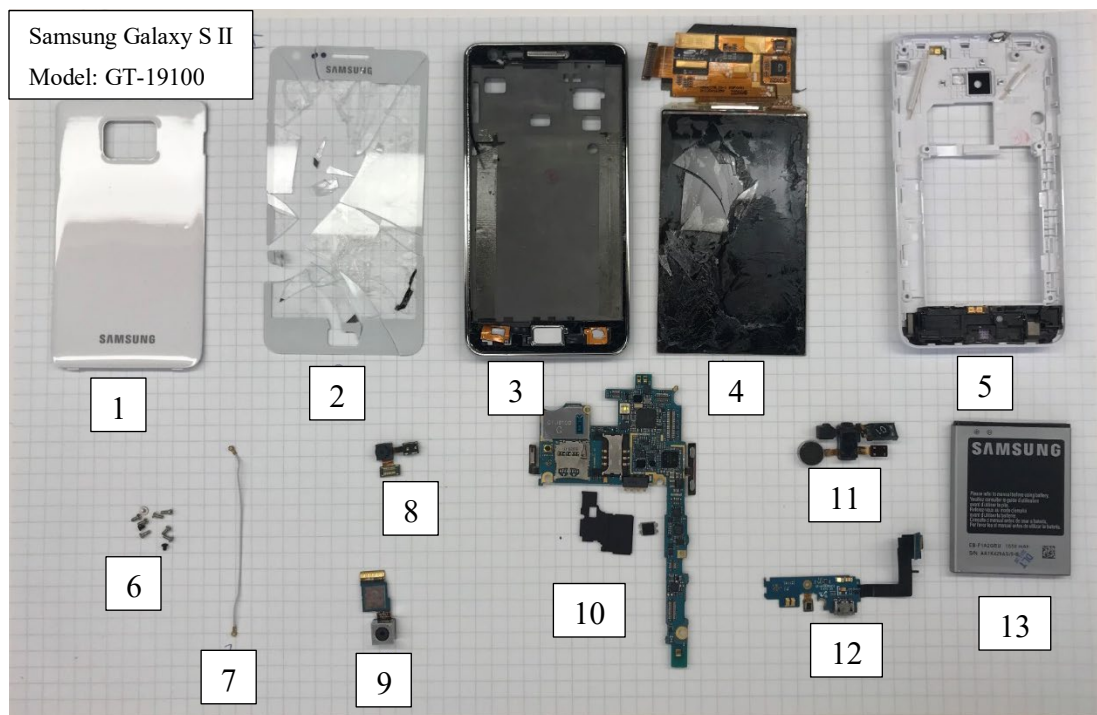


Figure 18 Samsung Galaxy S II (Model: GT-19100). Release date: May 2, 2011.

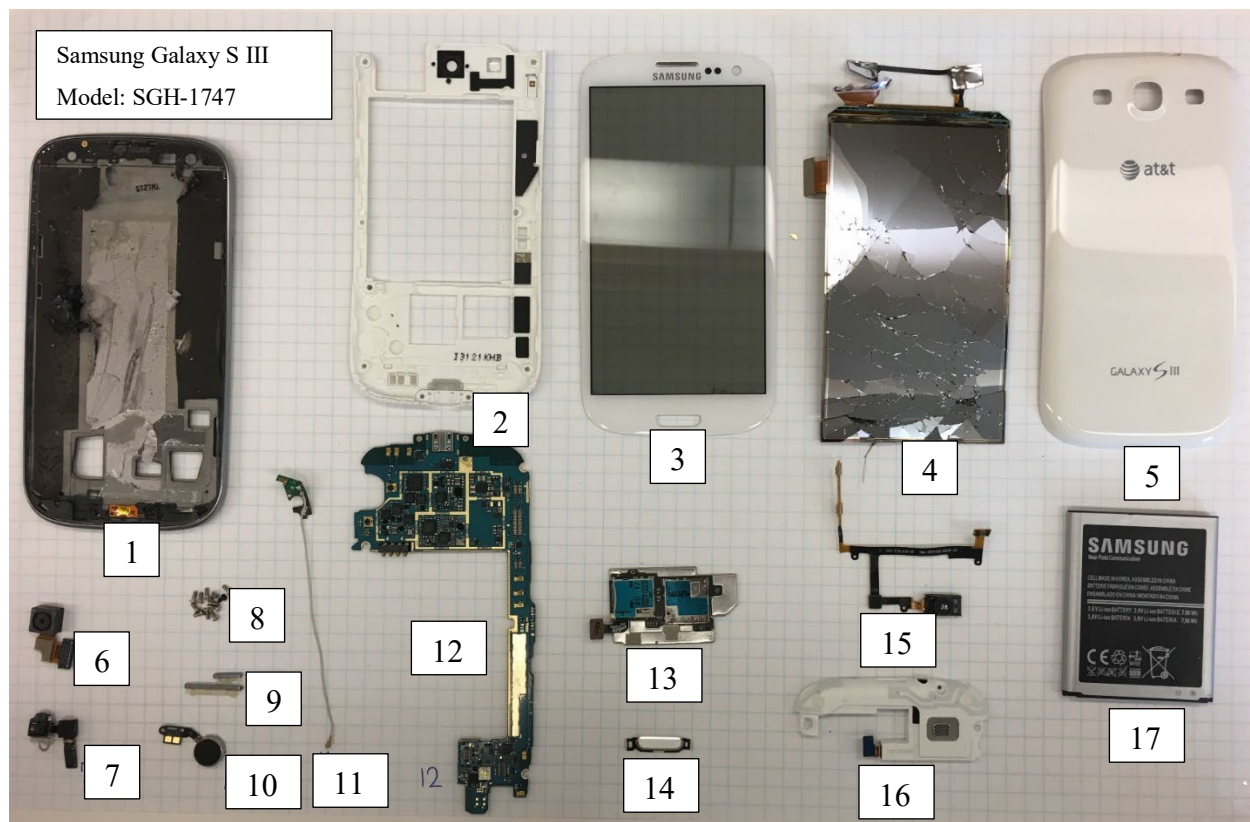


Figure 19 Samsung Galaxy S III (Model: SGH-1747). Release date: May 29, 2012.

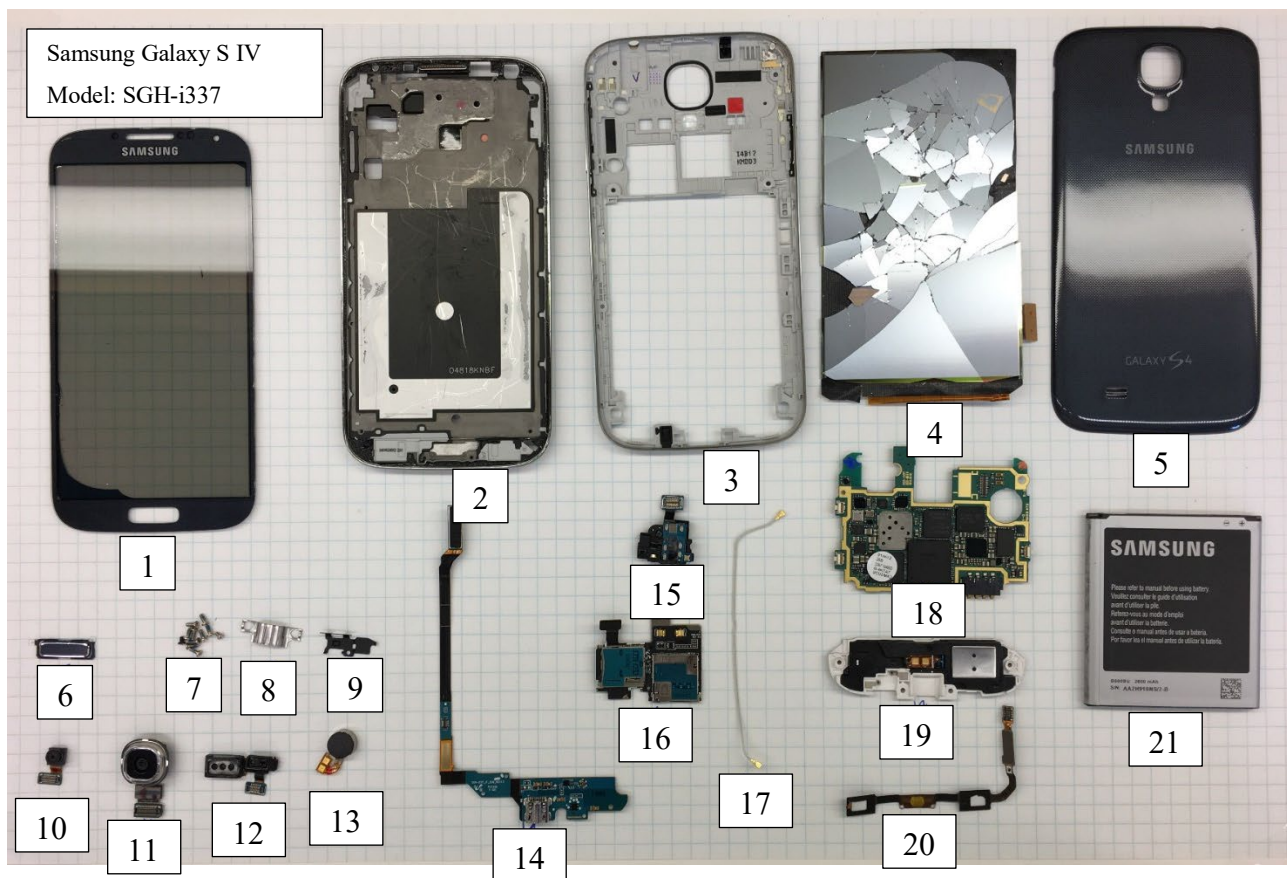


Figure 20 Samsung Galaxy S IV (Model: SGH-i337). Release date: April 27, 2013.

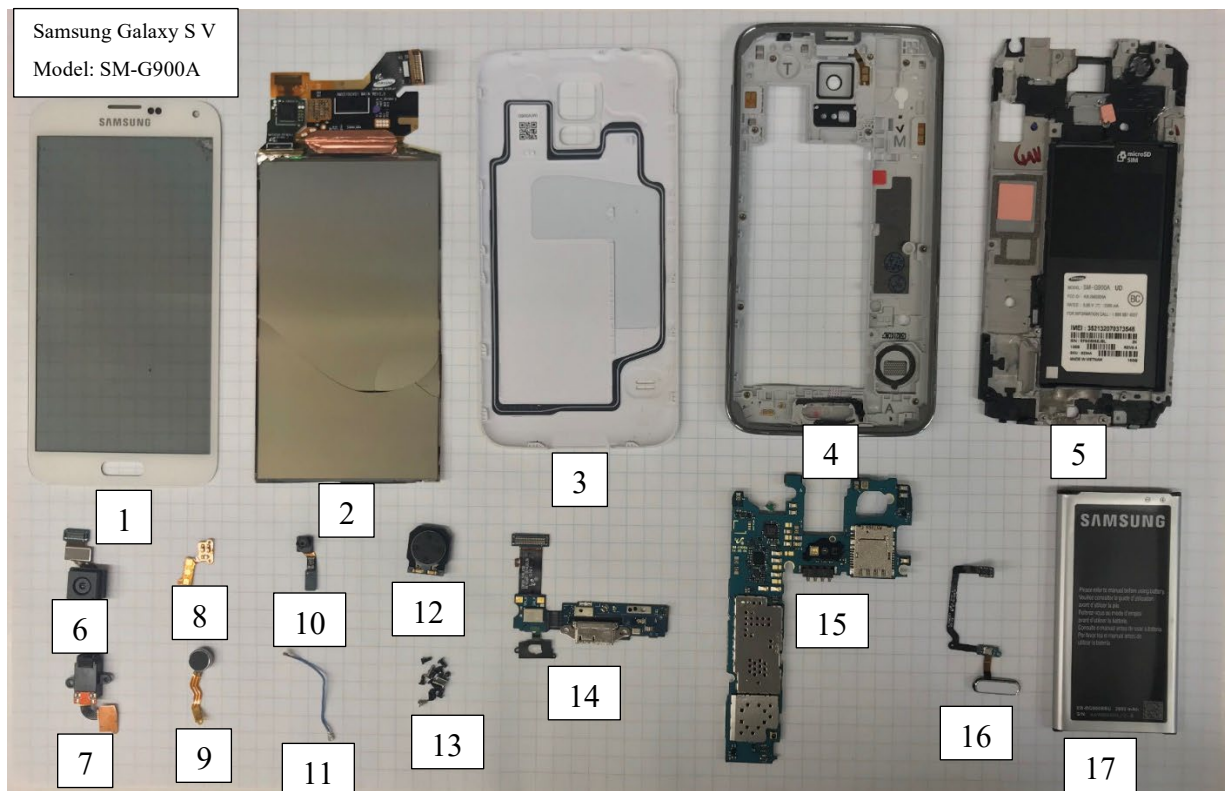


Figure 21 Samsung Galaxy S V (Model: SM-G900A). Release date: April 11, 2014.

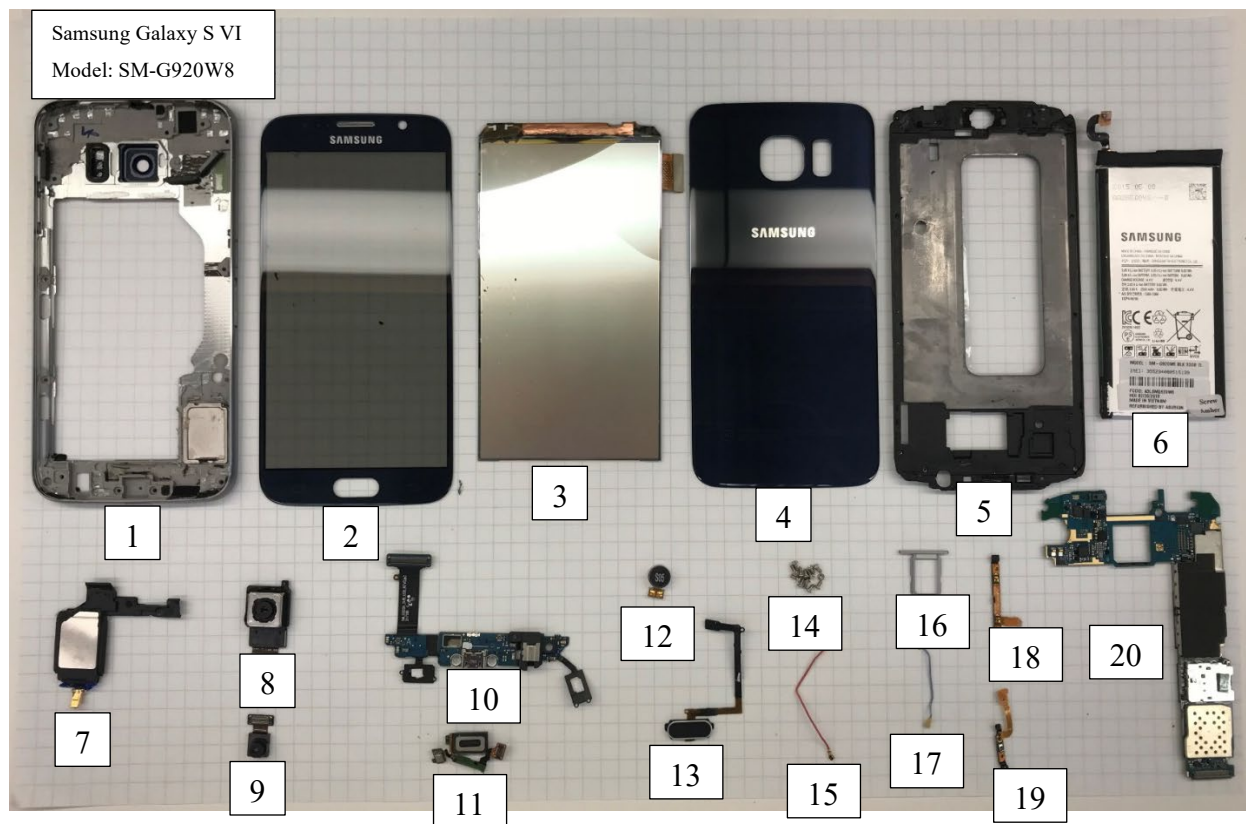


Figure 22 Samsung Galaxy S VI (Model: SM-G920W8). Release date: April 10, 2015.



Figure 23 Samsung Galaxy S VI (Model: Sm-G920W8). Release date: April 10, 2015.



Figure 24 Samsung Galaxy S VI Edge (Model: SM-G925A). Release date: April 10, 2015.



Figure 25 Samsung Galaxy S VI (Model: SM-G928VUD). Release date: August 21, 2015.



Figure 26 Samsung Galaxy S VI (Model: SM-G928VUD). Release date: August 21, 2015

APPENDIX C

Table 5 ICP-OES method parameters. Axial plasma view for all elements.

Element		Wavelength nm	Echelle Order	LOD (µg/L)	LOQ (µg/L)
Ag	Silver	328.068	103	1.7	5.7
Al	Aluminum	167.079	502	1.0	3.4
As	Arsenic	189.042	478	2.9	9.8
Au	Gold	242.795	139	2.3	7.6
B	Boron	249.773	135	1.1	3.6
Ba	Barium	455.403	74	0.0	0.1
Be	Beryllium	234.861	143	0.1	0.4
Bi	Bismuth	306.77	110	13.8	45.8
Ca	Calcium	184.006	483	0.5	1.8
Cd	Cadmium	226.502	449	0.3	1.1
Ce	Cerium	535.353	63	11.2	37.3
Co	Cobalt	228.616	447	0.7	2.5
Cr	Chromium	205.56	464	0.2	0.8
Cu	Copper	224.7	450	0.4	1.3
Dy	Dysprosium	353.17	95	0.4	1.5
Er	Erbium	323.058	104	1.8	5.9
Eu	Europium	381.967	88	0.1	0.3
Fe	Iron	239.562	141	1.0	3.4
Ga	Gallium	294.364	114	5.3	17.5
Gd	Gadolinium	342.247	98	0.9	3.0
Ge	Germanium	265.118	127	5.0	16.7
Hf	Hafnium	277.336	121	2.5	8.4
Hg	Mercury	184.95	482	1.0	3.4
Ho	Holmium	345.6	98	1.0	3.3
In	Indium	230.606	446	11.3	37.6
Ir	Iridium	212.681	458	1.8	5.9
K	Potassium	766.49	44	1.2	3.9
La	Lanthanum	379.478	89	0.5	1.8
Li	Lithium	670.784	50	0.1	0.2
Lu	Lutetium	261.542	129	0.1	0.3
Mg	Magnesium	279.553	120	0.01	0.3
Mn	Manganese	257.61	131	0.2	0.7
Mo	Molybdenum	202.03	467	0.5	1.8
Na	Sodium	589.592	57	0.5	1.8

Element		Wavelength nm	Echelle Order	LOD (µg/L)	LOQ (µg/L)
Nb	Niobium	316.34	106	0.9	3.0
Nd	Neodymium	406.109	83	2.6	8.6
Ni	Nickel	231.604	445	0.7	2.4
P	Phosphorus	178.284	489	3.9	12.9
Pb	Lead	182.205	485	4.6	15.2
Pd	Palladium	340.458	99	3.4	11.5
Pr	Promethium	390.844	86	2.0	6.8
Pt	Platinum	203.646	465	3.1	10.2
Re	Rhenium	197.312	471	0.6	2.1
Rh	Rhodium	343.489	98	3.5	11.7
Ru	Ruthenium	240.272	140	2.8	9.2
Sb	Antimony	206.833	463	2.6	8.7
Sc	Scandium	363.075	93	0.1	0.4
Se	Selenium	196.09	472	3.0	9.9
Si	Silicon	251.611	134	3.3	11.1
Sm	Samarium	442.434	76	1.4	4.7
Sn	Tin	189.989	477	0.7	2.4
Sr	Strontium	421.552	80	0.0	0.1
Ta	Tantalum	240.063	140	2.7	9.1
Tb	Terbium	350.917	96	1.9	6.5
Th	Technetium	274.716	123	4.3	14.4
Ti	Titanium	334.941	101	0.3	0.9
Tl	Thallium	190.856	477	2.2	7.2
Tm	Thulium	346.22	97	0.6	1.9
U	Uranium	409.014	82	35.3	117.7
V	Vanadium	292.402	115	0.7	2.4
W	Tungsten	209.86	461	6.2	20.5
Y	Yttrium	371.03	91	0.2	0.5
Yb	Ytterbium	328.937	102	0.1	0.4
Zn	Zinc	202.548	466	0.2	0.6
Zr	Zirconium	343.823	98	0.4	1.3

Table 6 ICP-OES operating parameters.

Parameter	Settings
RF Power, Watt	1270
Plasma Gas Flow Rate, L/min-1	13
Auxiliary Gas Flow Rate, L/min-1	0.5
Nebulizer Gas Flow Rate, L/min-1	0.5
Exposure Time	15 s (UV), 5 s (visible)
Spray Chamber	Duo Hydrofluoric acid
Nebulizer	Myra Mist

APPENDIX D

CODE I: this codes exports ICP-OES data for each element into a separate excel sheet in the same workbook. The code copies one column of 14 rows for a specific element and then does the same after moving 113 columns to the second injection of the same element.

```
Dim I As Integer, j As Integer, r As Integer, c As Integer, s As Integer
```

```
Sub Code_I()
```

```
c = 2
```

```
For I = 3 To 113
```

```
    Sheets.add.Name = Cells(3, I).Value
```

```
    Worksheets(Cells(3, I).Value).Range("A1:B14").Value =  
Worksheets("Sheet1").Range("A1:B14").Value
```

```
    For r = 3 To 1889
```

```
        c = c + 1
```

```
        For j = 1 To 14
```

```
            Worksheets(Cells(3, I).Value).Cells(j, c).Value = Worksheets("Sheet1").Cells(j, r  
+ I - 3).Value
```

```
        Next j
```

```
        r = r + 110
```

```
    Next r
```

```
    Worksheets(Cells(3, I).Value).Cells(1, c + 1).Value = "Average, ppb"
```

```
    Worksheets(Cells(3, I).Value).Cells(1, c + 2).Value = "StdDev.S"
```

```
    Worksheets(Cells(3, I).Value).Cells(1, c + 3).Value = "RSD, %"
```

```
    Worksheets(Cells(3, I).Value).Cells(1, c + 4).Value = "Recovery, %"
```

```
    Worksheets(Cells(3, I).Value).Cells(1, c + 5).Value = "Accuracy difference, %"
```

```
    Worksheets(Cells(3, I).Value).Cells(1, c + 6).Value = "LOQ, ppb"
```

```
    Worksheets(Cells(3, I).Value).Cells(1, c + 7).Value = "LOD, ppb"
```

```
c = 2
```

Next I
End Sub

CODE II: this code computes all necessary computations to calculate the limit of detection and quantification for each standard. Computations include average, standard deviation, percent relative standard deviation, percent accuracy, limit of detection and limit of quantification.

```
Sub Code_II()  
    Dim WS_Count As Integer  
    Dim I As Integer  
    Dim n As Integer, a As Double, b As Double  
    ' Set WS_Count equal to the number of worksheets in the active  
    ' workbook.  
    WS_Count = ActiveWorkbook.Worksheets.Count  
    ' Begin the loop.  
    For I = 1 To WS_Count  
c = 19  
n = 1  
For n = 1 To 8  
    Worksheets(I).Cells(n + 5, c + 1).Value =  
Worksheets(I).Application.WorksheetFunction.Average(Worksheets(I).Range(Worksheet  
s(I).Cells(n + 5, 3), Worksheets(I).Cells(n + 5, 18)))  
    Worksheets(I).Cells(n + 5, c + 2).Value =  
Worksheets(I).Application.WorksheetFunction.StDev_S(Worksheets(I).Range(Workshee  
ts(I).Cells(n + 5, 3), Worksheets(I).Cells(n + 5, 18)))  
    a = Worksheets(I).Cells(n + 5, c + 2)  
    b = Worksheets(I).Cells(n + 5, c + 1)  
    Worksheets(I).Cells(n + 5, c + 3).Value = a / b * 100  
    Worksheets(I).Cells(n + 5, c + 4).Value = Worksheets(I).Cells(n + 5, c + 1) /  
Worksheets(I).Cells(n + 5, c) * 100  
    n = n + 1  
Next n  
    I = I + 1  
Next I  
End Sub
```

```

Worksheets(I).Cells(n + 5, c + 5).Value = Worksheets(I).Cells(n + 5, c + 4) - 100
Worksheets(I).Cells(n + 5, c + 6).Value = 10 * Worksheets(I).Cells(n + 5, c + 2)
Worksheets(I).Cells(n + 5, c + 7).Value = 3 * Worksheets(I).Cells(n + 5, c + 2)
Next n
    ' Insert your code here.
    ' The following line shows how to reference a sheet within
    ' the loop by displaying the worksheet name in a dialog box.
Next I
End Sub

```

CODE III: this code visit ever active excel sheet and determine which standard is the best to estimate the limit of detection and quantification. Then, the selected standard is copied to one excel sheet to summarize all data instead of going manually to check every excel sheet for every element.

```

Sub Code_III()

    Dim WS_Count As Integer
    Dim I As Integer, n As Integer, m As Integer, l As Integer
    ' Set WS_Count equal to the number of worksheets in the active
    ' workbook.
    WS_Count = ActiveWorkbook.Worksheets.Count
    l = 7
    ' Begin the loop.
    For I = 1 To WS_Count
        m = 6
        For n = 6 To 13
            If Worksheets(I).Cells(n, 22) <= 10 And Worksheets(I).Cells(n, 23) <= 110
And Worksheets(I).Cells(n, 23) >= 90 Then

```

```

        Worksheets(I).Range(Worksheets(I).Cells(10 + m, 2), Worksheets(I).Cells(10
+ m, 27)).Value = Worksheets(I).Range(Worksheets(I).Cells(n, 1),
Worksheets(I).Cells(n, 26)).Value
        Worksheets(I).Cells(10 + m, 1).Value = Worksheets(I).Cells(3, 3).Value
        Worksheets("Sheet1").Range(Worksheets("Sheet1").Cells(10 + 1, 1),
Worksheets("Sheet1").Cells(10 + 1, 27)).Value =
Worksheets(I).Range(Worksheets(I).Cells(10 + m, 1), Worksheets(I).Cells(10 + m,
27)).Value
        l = l + 1
        m = m + 1
        n = n + 11
    Else
    End If
Next n
Next I
End Sub

```

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