An Introduction to Inductively Coupled Plasma Mass Spectroscopy (ICP-MS) and its Applications

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Abstract:- The inductively coupled plasma mass spectrometry (ICP-MS) owns the necessary ability to run elemental ultra-trace detection, as well as to elucidate temporally overlapping chromatographic peaks. In geochemistry, environmental and clinical studies of trace elements, ICP-MS plays a very important role in all its variants. In its versatility, ICP-MS has increased the scope of research as well as, together with new and improved methodologies for sample preparation, has changed the direction of interest and filled knowledge gaps in elemental and isotopic characterization. ICP-MS is the best detector with low detection limits, mass selectivity, large dynamic ranges, high sensitivities, isotope ratio capacities, and high throughput in traditional speciation analysis. With the aid of ICP-MS, the struggle to look for an outstanding form of quantification, such as drugs and proteomics, has come substantially close to an end. In short, ICP-MS will play a more and more significant role in pharmaceutical, biomedical, soil, clinical, forensic, and food research.

Keywords:- ICP-MS; Detection; Sample Preparation.

I. BACKGROUND OF ICP-MS

A. Fundamentals of ICP-MS

Inductively coupled plasma mass spectrometry (ICP-MS) has the superior detection capacities, commonly for the rare-earth elements, due to this characteristics, geochemical analysis labs were early adopters of ICP-MS technology. It was first introduced by R.S. Houk and colleagues in 1980, then put on the market in 1983 [1]. ICP-MS has been commonly used in many fields as well as one of the most important advances in analytical science nowadays. When the first commercial instrument appeared, the application that was first implemented into geological science research quickly spread to other areas, including chemical, clinical, nuclear, semiconductor, environmental, and research laboratories. This is particularly the case in the semiconductor industry, as ICP mass spectrometry is used as a method of analysis for high-purity material quality control, where demands grow with time. The method is also intended to be applicable to the study of trace quantities of hazardous metals, and ICP-MS is recently used with different environmental legislation giving response to the standards of stricter environmental and drainage. For special studies, ICP-MS can be combined with many types of sample separation or introduction techniques, which are included as capillary electrophoresis, high-performance liquid chromatography, laser-assisted sample introduction, gas chromatography, low-pressure chromatography, and so on [2]. ICP-MS has many benefits, including ICP Atomic Emission Spectroscopy, over other elemental research methods such as atomic absorption and optical emission spectrometry (ICP-AES) [3].

B. Operations of ICP-MS

ICP-MS is composed of ionization source, a sampling interface, ion lens, mass analyzer, and a sensitive detector [2]. A high temperature inductively coupled plasma (ICP) source is coupled to a mass spectrometer in an ICP-MS. The atoms of the elements in the sample are transformed by the ICP source to ions. The ions are then isolated by a mass spectrometer and detected. The Argon gas is used as a plasma source that flows through the ICP torch's concentric channels. The radio frequency (RF) load coil is connected to an RF generator. As power from the generator is supplied to the load coil, at the end of the torch, oscillating electrical and magnetic fields are created. Electrons are removed from the argon atoms when a spark is added to the argon flowing through the ICP torch, producing argon ions. In the oscillating fields, these ions are trapped and collide with other argon atoms, causing an argon discharge or plasma[4].

Usually, the sample is released into the ICP plasma as an aerosol, either by aspirating a liquid or dissolved solid sample into a nebulizer or by using a laser to directly turn solid samples into an aerosol [4]. When injected into the ICP torch, the sample aerosol is completely desolvated and the aerosol components are first transformed into gaseous atoms and then ionized at the end of the plasma atoms. The most significant characteristics of argon ICP plasma are the high temperature between 6000-10000 K, the ions produced are usually positive ions, M^+ or M^{2+}, and the capabilities of the detection technique that may differ with the sample introduction technique used. The ability to detect will differ with the sample matrix, which the degree of ionization that occurs in the plasma is affected or enable species to develop that may interfere with the determination of the analyte. Once the ions are formed from elemental species in the sample, they are then moved through the interface cones into the mass spectrometer [2].

The ions are separated when they reach the mass spectrometer by their mass-to-charge ratio (m/z). The most commonly used kind of mass spectrometer is the quadrupole mass filter. Four rods are arranged in this form (1 cm in diameter and 15–20 cm long). The alternating AC and DC

voltages are applied to opposite pairs of the rods in a quadrupole mass filter. The quadrupole mass filter is essentially a successive filter, with the settings varying at a time for each particular m/z. However, the voltages on the rods can be adjusted at a very quick rate. The outcome is that up to 2400 amu per second can be isolated by the quadrupole mass filter. That is why the ICP-MS quadruple is also known to have multi-elemental analysis properties at the same time. The ability to filter ions in their m/z enables ICP-MS to provide isotopic details since there are different masses of different isotopes of the same element. Once the ions are separated by their m/z, an effective detector must then detect or count them. The detector in ICP-MS is Dual Electron Multiplier. The main aim of the detector is to convert the number of ions that hit the detector into an electrical signal that can be measured using calibration standards and is correlated with the number of atoms in the sample of that element.

II. APPLICATIONS OF ICP-MS

ICP-MS is a plasma source with mass spectrometers in the same instrument to generate elemental and isotopic analytes. The ICP-MS has the ability to minimize matrix effects, multi-element capability, improved sub-nanogram per liter limits of detection (LODs), instrumentation robustness, and comfort offered by easy-to-use software. However, the matrix often poses a challenge to precise analysis in real sample analysis. In the case of high ion transfer spectrometers, this has been partly solved using advanced sample introduction techniques and solution dilution. In clinical, geo- and enviro analysis, and isotope research, ICP-MS plays a growing role in. It provides a simple way to assess the concentration levels of low-abundance elements and metal speciation by sub-nanogram per liter. It is irreplaceable to examine the influx of trace elements in hydrological processes, element movement in waste disposal deposits, soil horizons, aquifers, the aquatic ecosystem and biological uptake [5].

A. ICP-MS application in determining mercury (Hg) in soil

Mercury (Hg) is regarded as one of the most toxic contaminants correlated with its bioaccumulation properties and methylation processes in some biological systems [6].In certain parts of the environment, such as water, air, soil and sediment, mercury may be present. The presence of Hg in the soil can be caused by natural causes, such as geological sources, or by anthropogenic activities, such as the combustion of fossil fuels, industrial emissions and the use of fertilizers in agriculture [7, 8, 9, 10]. The background mercury level in the soil is very low, varying from 0.02 to 0.6 $\mu g\ g^{-1}$, depending on the form of soil[11].The need, along with its associated complexity, to define mercury in environmental samples is much more considered. Most methods require the decomposition of samples requiring the use of concentrated acids; this takes significant time and is responsible for the loss of analytes. A simple electrothermal vaporization (ETV) method combined with ICP-MS can be used to evaluate Hg by direct solid sample analysis [12].ICP-MS has a broad linear calibration range and a lower limit of detection (LOD) than atomic absorption spectroscopy (AAS), and is more

appropriate for evaluating Hg. The ETV system consists of a high-power glass chamber lamp fitted with solenoid valves to monitor the pyrolysis and vaporization processes of argon gas flow. The analyte vapor is collected in this method through a glass tube placed just above the sample, preventing the deposition of the analyte on the chamber wall and thereby reducing the memory effect. Soil analysis by ETV-ICP-MS prevents the use of reagents and the production of residues, which complies with the guidelines for green chemistry. The grounded samples are analyzed directly by ETV-ICP-MS. For both analysis methods, sampling, drying and grinding times are the same. Thus, the proposed method can be used for routine analysis, where the analysis time of around 60 s per sample, the threat of contamination, the loss of analytes and the generation of residues are considerably decreased matched with the techniques requiring sample extraction for the determination of Hg by nebulization-ICP-MS [11].

B. Whole blood selenium (Se) determination by ICP-MS

Selenium (Se) is an essential micronutrient for cardiovascular health and fertility, thyroid function and cancer prevention [13, 14, 15, 16].Se is integrated into manyseleno proteins and has antioxidant properties. Se concentrations vary greatly in human blood[17] and depend on either the regional availability of Se, which determines the content of the element in foodstuffs, or the supplementation of individual persons or farms[17, 18, 19, 20].Seafood, poultry, cereals and grains are among the richest sources of Se. The low intake of Se can increase certain cancers, increase cardiovascular disease incidence, Impairing the immune system, impairing development, improving thyroid dysfunction and impairing male fertility. Toxicity of Se, on the other hand, causes fatigue and harm to nervous system, tooth decay, gastrointestinal disorders, liver failure, loss of hair and nails, and skin lesions, [21].

ICP-MS has attracted much more attentions in recent years for calculating trace amounts of Se [22, 23]. Bunch and co-workers[21] successfully developed total whole blood Se analysis with a sample preparation using ICP-MS with a collision cell. Samples were easily collected from healthy adults (76 percent female) between 19 and 64 years of age after at least 8 hours. Whole blood aliquots (1 mL) were preserved at -70 °C in acid washed cryogenic vials before analysis. The ICP-MS calculation of Se was initially afflicted by polyatomic interference, which is an artifact of the ionization techniques used. Polyatomic interference usually accounts for the sample matrix, sample diluent, and/or inert gas used during ionization. Argon ($^{40}Ar_2^+$), which interferes with the most abundant isotope of selenium ($^{80}Se^+$), is an example of polyatomic interference [24].Improvements in technology, such as magnetic sector filters, improved resolution of mass spectrometry and reaction cells, have minimized the existence of interference. Not all interference can, however, be avoided. For example, Gadolinium, a contrast agent for MRI studies, is known to cause ICP-MS Se measurement interference with [25].

C. ICP-MS usage in determinig iodine in polyamides

Due to their low cost, mechanical strength, reusability, and thermal and chemical resistance, polyamides are widely used in the automotive industry [26].For example, these polymers are used for the housing of electronic devices that serve as pressure or temperature sensors in the exhaust gas and in the intake of gas for the motors. Several stabilizers, such as phenolic compounds, amines, but also metal derivatives, such as mixtures of copper (I) iodide and potassium iodide or bromide, are used to limit thermo-oxidative degradation of the polyamide[27].One of the most common is the mixture of CuI/KX (X = I or Br, but the use of thermal stabilizers containing CuI/KX might present a risk of corrosion in electronic devices as revealed by many studies and research in recent years, even without direct physical contact [28].

Digestion in the nitric acid medium and dilution of the resulting ammonia solution, followed by ICP-MS examination, can be used to assess the iodine in polyamides (PA). The 0.9 mg kg^{-1} quantification limit helps us to verify PA raw material pellets to certify their low iodine content. [28].ICP-MS is applied to calculate very low levels of iodine in polyamides in contrast to other analytical methods that can be used to assess the iodine content in polyamides, such as ion chromatography [29].It is also verified that the digestion method used in closed reactor using nitric acid medium, which is usually used in laboratories, may be used in ammonia medium prior analysis for polyamides providing a dilution of the digestion solution. It provides an easy alternative with absorbent solutions to combustion techniques (MIC, pyrolysis).For checking molded pieces, this technique can also be applied.This ensures that the iodine content in PA is very low, given the probablethreat of corrosion of the electronic components associated with the release of this element[28].

D. Usage of ICP-MS coupled with liquid chromatography for thallium analysis in tobaccos

Thallium (Tl) and its compounds have been described as potentially toxic to living things[30].The acute toxicity of Tl(III) to mammals, for instance, is greater than that of Hg(II), Cd(II) and Pb (II) [31].It is therefore of great importance to identify the species of Tl in environmental and biological samples. Thallium is mainly released into the environment as zinc, cadmium and lead processing waste, coal burning [32] and also as a result of its use in recent high-technology applications [33].Thallium determination is recorded in environmental samples such as serum, water and soil at the ng mL^{-1} level using a ratiometric phosphorescent probe [34].Dispersive solid phase micro extraction (DSPME) techniques are developed for the preconcentration and determination of thallium from a variety of samples [35, 36].Thallium is present in two oxidation states in the aquatic system, Tl(I) and Tl(l) (III). The two species of TL are toxic. However, Tl(III) is more poisonous and Tl(I) is less toxic and more stable.Due to successful soil extraction, tobacco produces high concentrations of Tl [37].

Highly sensitive analytical methods must be available to determine the Tl species in environment. Chen and colleagues[37] applied a rapid and simple ICP-MS coupled with a liquid chromatographic detector to the speciation study of thallium in tobacco and cigarette ash samples. Effluent from the column of the HPLC is supplied to the ICP-MS nebulizer for determination of Tl. Detection limits in the nanogram range can be reached for both Tl(I) and Tl(III) compounds based on peak height. The extraction of Tl from the ash sample is enhanced by the addition of HF. The tobacco extraction efficiency of Tl is between 98–110%. The HPLC-ICP-MS specification analysis of tobacco samples demonstrates a suitable agreement with the total Tl concentration achieved by ICP-MS analysis of fully dissolved samples. Consequently, the ICP-MS technique works well with better limits of detection and minor retention times in speciation of Tl species with good analytical feasibility.

E. ICP-MS application in determining trace antimony species in water

Antimony (Sb) is an omnipresent element which has long been commonly used in many industrial applications, such as batteries, semiconductors and fireproof textiles. Owing to its toxicity and biological effects, antimony has been identified a priority pollutant[38, 39, 40].The permissible limit of antimony approved by the US Environmental Protection Agency (EPA) in drinking water is 6 μg L^{-1}[10, 41].However, studies by speciation reported that the position of antimony inan environmental or biological system is critically dependent on its chemical forms[42].For instance, inorganic antimony species are more toxic than organic species, and inorganic trivalent or Sb(III) species are 10 times more toxic than Sb(V) species[43].

Manyanalytical techniques such as atomic absorption spectrometry [44], atomic emission spectrometry [45], atomic fluorescence spectrometry [46], and mass spectrometry [47], have been employed for the quantitative determination of antimony species. Nonetheless, the quantification of antimony species based on ICP-MS typically involves the use of a separation process before detection, as ICP-MS is unable to distinguish between the species of a given element [48]. In order to apply separation process, techniques such as solid phase extraction, liquid-liquid extraction and magnetic solid phase extraction (MSPE) using octyl-immobilized silica-coated magnetic Fe_3O_4 nanoparticles as an adsorbent combined with ICP-MS for speciation in environmental waters of Sb(III) and Sb(V), are applied. Sb(III) forms a hydrophobic complex of ammonium pyrrolidine dithiocarbamate (APDC) and is retained on nanoparticles of C8-Fe_3O_4/SiO_2, while Sb(V) remains a free species in an aqueous solution. At lower pH, hydrophobic APDC complexes are formed by both Sb species (total Sb), retained on the adsorbent. This suggested method is simple, reliable and sensitive and can be used in environmental waters without any pre-reduction or pre-oxidation activity for the speciation of Sb(III) and Sb(V)[49].

III. ADVANCES IN ICP-MS APPLICATIONS

A. Application of liquid chromatography couped to ICP-MS in determining arsenic species in fish

In nature, arsenic is found in numerous species that can be categorized as inorganic and organic arsenic. As (III) and As (V) are inorganic arsenic species, while p-hydroxyphenylarsonic acid (PHA), 4-aminobenzenearsonic acid (ASA), monomethylarsonic acid (MMA), arsenobetaine (AsB), and arsenocholine (AsC), are important organic arsenic species (NAPP) [50, 51, 52, 53].The species of arsenic originates from pollutants that are metabolized into many types of arsenic resulting from a number of industrial manufacturing methods, various household waste materials, animal drugs and fodder [54].Its toxicity varies because of its oxidation state, physicochemical properties and biological activities of different organisms [55].The inorganic arsenic species are highly toxic [56], with the most toxic and suspected human carcinogen being As (III) [57, 58]. Although the toxicity of As(V) is relatively high [59], organic arsenic is less harmful and is therefore known to be hypotoxic or non-toxic. However, arsenic species can be transformed by metabolism in the human body, and organic arsenic can be converted into other arsenic species in animals [51]. For instance, in chickens receiving fodder containing ROX, a variety of arsenic species can be identified. ROX can accumulate and turn in the animal, commonly used as an animal growth additive in fodder or as a medicine, resulting in waste water emissions that affect the environment[60].

Zhao and his colleagues [61] have established a profound, modest and fastprocess for the instantaneous analysis of 11 arsenic species in less than 17 minutes using high-performance liquid chromatography coupled with ICP-MS. The detection limit (LD) of the method was in the range of 0.11–0.59 g kg^{-1}. Repeatability values were in the range of 1.1–7.6% for spiked actual fish samples. Accuracy has been determined based on the analysis of spiked real fish samples at five concentration levels. The range of recoveries were 91–106%. In a pilot study, the validated method was used to analyze real fish samples, the main arsenic species present in the analyzed samples was organic arsenic particularly AsB, detecting only a trace amount of inorganic arsenic.

B. Analysis of polybrominated diphenyl ethers in mussels and fish usinggas chromatography coupled to ICP-MS

Polybrominated diphenyl ethers (PBDEs) have been on the market since the 1960s and are a category of chemicals. In various consumer products like electrical devices, plastics, construction materials and textiles, they have been commonly used as flame retardants [62]. PBDEs do not form chemical bonds with the flame retardant product matrix and can be easily leached into the environment during the manufacture and use or disposal of the products containing them [63, 64].PBDEs are seen in sediments, soils, surface water, waste sludge, outdoor or indoor air, house dust and biota, their occurrence has been demonstrated globally [65, 66, 67, 68].Samples taken from the deep ocean and remote locations in the Arctic [8] and Antarctic environments [69] can also be detected. PBDEs belong to a class of persistent organic contaminants that are hydrophobic, poorly degradable and appear to adsorb particulate matter, bioaccumulate in fatty tissues and bio-magnify across the food web.They are commonly found in various marine species and mammals [70], including humans, where blood, adipose tissue and breast milk have been detected. Studies have shown that exposure to PBDEs in laboratory animals and humans can cause adverse health effects, including disruption of growth and immune and endocrine (for example, thyroid hormone) systems, as well as neurodevelopmental delays [71, 72].The manufacture and use of technical penta-, octa- and deca-BDE mixtures has therefore been limited by EU law [73] and partly prohibited in the USA.

Soxhlet extraction[68, 74, 75], accelerated solvent extraction [76, 77, 78], ultrasound-assisted extraction [79] or microwave-assisted extraction [76, 80] have been used to extract PBDEs from fish and mussel tissue sample matrices in recent years. Using advanced instrumental techniques, the quality of PBDEs is evaluated with high sensitivity after extraction.Almost exclusively applied are those focused on gas chromatography (GC) separation of PBDEs [81] coupled with various highly developed detector systems, such as high resolution mass spectrometry [80, 82], negative chemical ionization mode of mass spectrometry [68, 79, 83] or electron capture detectors [75, 76, 77]. Alternatively, for the detection of GC-separated PBDEs, ICP-MS can be used [84].

Novak and his colleagues [86] determined six polybrominated diphenyl ether (PBDE) congeners, BDE 28, BDE 47, BDE 99, BDE 100, BDE 153 and BDE 154, by means of a sincere and sensitive analytical method based on gas chromatography coupled to ICP-MS in samples of mussel and fish tissue. They were washed with minimal solvent consumption bypassing the extract through a column filled with Florisil. PBDEs have been quantified by GC-ICP-MS in the organic phase. Strong agreement was reached between the results' defined and certified principles. The wet weight-based limits of detection (LODs) were in the ranges of 0.003–0.009 ng g^{-} for all six PBDEs samples. The recovery range was 94%–105%.

C. ICP-MS usage in determining ultra-trace plutonium isotopes in human urine

Plutonium is considered as extremely harmful Because of its chemical toxicity and the radioactivity of its major isotopes ^{239}Pu, ^{240}Pu, and ^{241}Pu. They have a strong affinity to accumulate long-term health risks in the liver and bones and thus posture once incorporated into the human body [87]. For instance, occupational exposure to Pu generally comes from inhalation [88, 89].It was also verified that during radiological incidents and events, Airborne Pu was released [90, 91].On June 6, 2017, 5 workers recently encountered internal radiation exposure due to inhalation of airborne Pu while testing nuclear fuel materials at a Japan Atomic Energy Agency (JAEA) nuclear research facility. Again, this accident highlighted the need for a rapid assessment of Pu's level of exposure for radiation protection and medical intervention purposes. Although biological dosimetry is usually used to assess external exposure, in vivo or in vitro bioassays can be used to evaluate internal contamination, particularly for alpha

and beta emitters, one of the simplest and most straightforward in vitro methods of urinalysis [92].

For the study of Pu isotopes (^{239}Pu, ^{240}Pu, and ^{241}Pu) in small-volume urine bioassays (20 mL and 100 mL) using a highly sensitive sector field-ICP-MS, Ni and colleagues [93] established a rapid method with enhanced 238U decontamination. This technique involves acid digestion, co-precipitation, extraction chromatography, and sector-field-ICP-MS measurement. Parameters that had a fair effect on analytical efficiency were extensively reviewed. The method obtained a high decontamination factor of ^{238}U (3.8×10^6) and the recovery of ^{242}Pu was stable with an average value of 72.7 ± 5.5% for 20 mL and 100 mL urine bioassays. The limits of detection for ^{239}Pu, ^{240}Pu, and ^{241}Pu by the method were in the range of 0.002–0.019 fg mL^{-1} for all urine samples.

IV. CONCLUSION

The inductively coupled plasma mass spectrometry (ICP-MS) owns the necessary ability to run elemental ultra-trace detection, as well as to elucidate temporally overlapping chromatographic peaks. In geochemistry, environmental and clinical studies of trace elements, ICP-MS plays a very important role in all its variants. In its versatility, ICP-MS has increased the scope of research as well as, together with new and improved methodologies for sample preparation, has changed the direction of interest and filled knowledge gaps in elemental and isotopic characterization. ICP-MS is the best detector with low detection limits, mass selectivity, large dynamic ranges, high sensitivities, isotope ratio capacities, and high throughput in traditional speciation analysis. With the aid of ICP-MS, the struggle to look for an outstanding form of quantification, such as drugs and proteomics, has come substantially close to an end. In short, ICP-MS will play a more and more significant role in pharmaceutical, biomedical, soil, clinical, forensic, and food research.

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REFERENCES

[1]. R. S. Houk, V. A. Fassel, G. D. Flesch, H. J. Svec, A. L. Gray, and C. E. Taylor, "Inductively Coupled Argon Plasma as an Ion Source for Mass Spectrometric Determination of Trace Elements," *Anal. Chem.*, vol. 52, no. 14, pp. 2283–2289, 1980.

[2]. J. Huang, X. Hu, J. Zhang, K. Li, Y. Yan, and X. Xu, "The application of inductively coupled plasma mass spectrometry in pharmaceutical and biomedical analysis," *J. Pharm. Biomed. Anal.*, vol. 40, pp. 227–234, 2006.

[3]. R. E. Wolf, Ph.D., Research Chemist, USGS/CR/CICT, March 2005.

[4]. H. Niu and R. S. Houk, "Fundamental aspects of ion extraction in inductively coupled plasma mass spectrometry," *Spectrochim. Acta B*, vol. 51, pp. 779–815, 1996.

[5]. I. J. Brenner, "Inductively Coupled Plasma Mass Spectrometry Applications," *Encyclopedia of Spectroscopy and Spectrometry, 3rd ed.*, pp. 229–235, 2017.

[6]. M. Sánchez-Báscones, J. M. Antolín-Rodríguez, P. Martín-Ramos, A. González-González, C. T. Bravo-Sánchez, and J. Martín-Gil, "Evolution of mercury content in agricultural soils due to the application of organic and mineral fertilizers," *J. Soils Sediments*, vol. 17, no. 4, pp. 927–935, 2017.

[7]. T. Zhong, D. Chen, and X. Zhang, "Identification of potential sources of mercury (Hg) in farmland soil using a decision tree method in China," *Int. J. Environ. Res. Public Health*, vol. 13, no. 11, 2016.

[8]. N. Mirlean, P. Baisch, I. Machado, and E. Shumilin, "Mercury contamination of soil as the result of long-term phosphate fertilizer production," *Bull. Environ. Contam. Toxicol.*, vol. 81, no. 3, pp. 305–308, 2008.

[9]. Z. Dai, X. Feng, C. Zhang, J. Wang, T. Jiang, H. Xiao, Y. Li, and G. Qiu, "Assessing anthropogenic sources of mercury in soil in Wanshan Hg mining area, Guizhou, China," *Environ. Sci. Pollut. Res.*, vol. 20, no. 11, pp. 7560–7569, 2013.

[10]. Y. Shan, M. Tysklind, F. Hao, W. Ouyang, S. Chen, and C. Lin, "Identification of sources of heavy metals in agricultural soils using multivariate analysis and GIS," *J. Soils Sediments*, vol. 13, no. 4, pp. 720–729, 2013.

[11]. W. Wohlmanna, V. M. Nevesa, G. M. Heidricha, J. S. Silvaa, A. B. da Costab, J. N.G. Paniza, and V. L. Dressler, "Development of an electrothermal vaporizer for direct mercury determination in soil by inductively-coupled plasma mass spectrometry," *Spectrochim. Acta - Part B At. Spectrosc.*, vol. 149, no. May, pp. 222–228, 2018.

[12]. F. G. Antes, E. Dullius, A. B. da Costa, R. F. Molz, J. N. G. Paniz, E. M. M. Flores, and V. L. Dressler, "Development of a vaporization system for direct determination of chlorine in petroleum coke by ICP-MS," *Microchem. J.*, vol. 109, pp. 117–121, 2013.

[13]. W. Saliba, R. El Fakih, and W. Shaheen, "Heart failure secondary to selenium deficiency, reversible after supplementation," *Int. J. Cardiol.*, vol. 141, no. 2, pp. e26–e27, 2010.

[14]. M. R. Safarinejad and S. Safarinejad, "Efficacy of Selenium and/or N-Acetyl-Cysteine for Improving Semen Parameters in Infertile Men: A Double-Blind, Placebo Controlled, Randomized Study," *J. Urol.*, vol. 181, no. 2, pp. 741–751, 2009.

[15]. M. Witkowski, J. Hubert, and A. Mazur, "Methods of assessment of magnesium status in humans: A systematic review," *Magnes. Res.*, vol. 24, no. 4, pp. 163–180, 2011.

[16]. M. B. Zimmermann and J. Köhrle, "The impact of iron and selenium deficiencies on iodine and thyroid metabolism: Biochemistry and relevance to public

health," *Thyroid*, vol. 12, no. 10, pp. 867–878, 2002.

[17]. G. Alfthan and J. Neve, "Reference values for serum selenium in various areas-evaluated according to the TRACY protocol," *J. Trace Elem. Med. Biol.*, vol. 10, no. 2, pp. 77–87, 1996.

[18]. G. Alfthan, M. Eurola, P. Ekholm, E. Venäläinen, T. Root, K. Korkalainen, H. Hartikainen, P. Salminen, V. Hietaniemi, P. Aspilab, and A. Aro, "Effects of nationwide addition of selenium to fertilizers on foods, and animal and human health in Finland: From deficiency to optimal selenium status of the population," *J. Trace Elem. Med. Biol.*, vol. 31, pp. 142–147, 2015.

[19]. J. L. Slavin, D. Jacobs, L. Marquart, and K. Wiemer, "The role of whole grains in disease prevention," *Journal of the American Dietetic Association*, vol. 101, no. 7. pp. 780–785, 2001.

[20]. K. H. Schulpis, T. Karakonstantakis, S. Gavrili, G. Chronopoulou, G. A. Karikas, G. Vlachos, and I. Papassotiriou, "Maternal - Neonatal serum selenium and copper levels in Greeks and Albanians," *Eur. J. Clin. Nutr.*, vol. 58, no. 9, pp. 1314–1318, 2004.

[21]. D. R. Bunch, W. Cieslak, and S. Wang, "Whole blood selenium determination by inductively coupled plasma mass spectrometry," *Clin. Biochem.*, pp. 4–7, 2017.

[22]. S. Chan, B. Gerson, R. E. Reitz, and S. A. Sadjadi, "Technical and clinical aspects of spectrometric analysis of trace elements in clinical samples," *Clin. Lab. Med.*, vol. 18, no. 4, pp. 615–629, 1998.

[23]. T. M. T. Sheehan and D. J. Halls, "Measurement of selenium in clinical specimens," *Ann. Clin. Biochem.*, vol. 36, no. 3, pp. 301–315, 1999.

[24]. A. M. Featherstone, A. T. Townsend, G. A. Jacobson, and G. M. Peterson, "Comparison of methods for the determination of total selenium in plasma by magnetic sector inductively coupled plasma mass spectrometry," *Anal. Chim. Acta*, vol. 512, no. 2, pp. 319–327, 2004.

[25]. L. Liu, K. Tamama, and O. M. P. Palmer, "Selenium overload?," *Clin. Chem.*, vol. 62, no. 4, p. 658, 2016.

[26]. J. Njuguna, Z. Mouti, and K. Westwood, "Toughening mechanisms for glass fiber-reinforced polyamide composites," *Toughening Mech. Compos. Mater.*, pp. 211–232, 2015.

[27]. A. I. Chernukhina and G. A. Gabrielyan, "Properties and Use of Chemical Fibers," *Fibre Chem.*, vol. 25, no. 6, pp. 30–34, 1994.

[28]. C. Devouge-boyer, S. Mouda, O. Gueguen, and S. Marcotte, "Talanta Determination of iodine in polyamide by inductively-coupled plasma/mass spectrometry," *Talanta*, vol. 189, no. July, pp. 568–572, 2018.

[29]. S. R. Krzyzaniak, R. F. Santos, F. M. Dalla Nora, S. M. Cruz, E. M. M. Flores, and P. A. Mello, "Determination of halogens and sulfur in high-purity polyimide by IC after digestion by MIC," *Talanta*, vol. 158, pp. 193–197, 2016.

[30]. G. Kazantzis, "Thallium in the environment and health effects," *Environ. Geochem. Health*, vol. 22, no. 4, pp. 275–280, 2000.

[31]. V. Cheam, "Thallium contamination of water in Canada," *Water Qual. Res. J. Canada*, vol. 36, no. 4, pp. 851–877, 2001.

[32]. A. K. Das, R. Chakraborty, M. L. Cervera, and M. De La Guardia, "Determination of thallium in biological samples," *Anal. Bioanal. Chem.*, vol. 385, no. 4, pp. 665–670, 2006.

[33]. A. L. J. Peter and T. Viraraghavan, "Thallium: A review of public health and environmental concerns," *Environ. Int.*, vol. 31, no. 4, pp. 493–501, 2005.

[34]. X. Lu, J. Zhang, Y. N. Xie, X. Zhang, X. Jiang, X. Hou, and P. Wu, "Ratiometric Phosphorescent Probe for Thallium in Serum, Water, and Soil Samples Based on Long-Lived, Spectrally Resolved, Mn-Doped ZnSe Quantum Dots and Carbon Dots," *Anal. Chem.*, vol. 90, no. 4, pp. 2939–2945, 2018.

[35]. Z. D. Firouzabadi, A. M. H. Shabani, S. Dadfarnia, and M. H. Ehrampoush, "Preconcentration and speciation of thallium by ferrofluid based dispersive solid phase extraction and flame atomic absorption spectrometry," *Microchem. J.*, vol. 130, pp. 428–435, 2017.

[36]. N. R. Biata, K. M. Dimpe, J. Ramontja, N. Mketo, and P. N. Nomngongo, "Determination of thallium in water samples using inductively coupled plasma optical emission spectrometry (ICP-OES) after ultrasonic assisted-dispersive solid phase microextraction," *Microchem. J.*, vol. 137, pp. 214–222, 2018.

[37]. W. T. Chen, S. J. Jiang, and A. C. Sahayam, "Speciation analysis of thallium in tobaccos using liquid chromatography inductively coupled plasma mass spectrometry," *Microchem. J.*, vol. 141, no. March, pp. 104–109, 2018.

[38]. Y. M. Nakamaru and J. Altansuvd, "Speciation and bioavailability of selenium and antimony in non-flooded and wetland soils: A review," *Chemosphere*, vol. 111, pp. 366–371, 2014.

[39]. R. Clough, C. F. Harrington, S. J. Hill, Y. Madrid, and J. F. Tyson, "Atomic spectrometry updates. Review of advances in elemental speciation," *J. Anal. At. Spectrom.*, vol. 29, no. 7, pp. 1158–1196, 2014.

[40]. S. L.C. Ferreira,W. N. L. dos Santos, I. F. dos Santos, M. M. S. Junior, L. O. B. Silva, U. A. Barbosa, F. A. de Santana, A. F. de S. Queiroz, "Strategies of sample preparation for speciation analysis of inorganic antimony using hydride generation atomic spectrometry," *Microchem. J.*, vol. 114, pp. 22–31, 2014.

[41]. S. Bagherifam, A. Lakzian, A. Fotovat, R. Khorasani, and S. Komarneni, "In situ stabilization of As and Sb with naturally occurring Mn, Al and Fe oxides in a calcareous soil: Bioaccessibility, bioavailability and speciation studies," *J. Hazard. Mater.*, vol. 273, pp. 247–252, 2014.

[42]. Y. Li, J. M. Liu, F. Han, Y. Jiang, and X. P. Yan, "Probing interactions of antimony species with DNA by short column capillary electrophoresis coupled with inductively coupled plasma mass spectrometry," *J. Anal. At. Spectrom.*, vol. 26, no. 1, pp. 94–99, 2011.

[43]. P. Li, Y. J. Chen, X. Hu, and H. Z. Lian, "Magnetic solid phase extraction for the determination of trace antimony species in water by inductively coupled plasma mass spectrometry," *Talanta*, vol. 134, pp. 292–297, 2015.

[44]. J. Tian, T. Huang, and J. Lu, "Speciation of Inorganic Antimony in Food and Water Samples by Flow Injection On-line Nano γ-Alumina Micro-column Solid-Phase Extraction Coupled with Slotted Tube Atom Trapping Flame Atomic Absorption Spectrometry," *Food Anal. Methods*, vol. 6, no. 4, pp. 1080–1089, 2013.

[45]. Y. Li, B. Hu, and Z. Jiang, "On-line cloud point extraction combined with electrothermal vaporization inductively coupled plasma atomic emission spectrometry for the speciation of inorganic antimony in environmental and biological samples," *Anal. Chim. Acta*, vol. 576, no. 2, pp. 207–214, 2006.

[46]. Z. Xing, B. Kuermaiti, J. Wang, G. Han, S. Zhang, and X. Zhang, "Simultaneous determination of arsenic and antimony by hydride generation atomic fluorescence spectrometry with dielectric barrier discharge atomizer," *Spectrochim. Acta - Part B At. Spectrosc.*, vol. 65, no. 12, pp. 1056–1060, 2010.

[47]. A. Calvo Fornieles, A. García De Torres, E. Vereda Alonso, M. T. Siles Cordero, and J. M. Cano Pavón, "Speciation of antimony(iii) and antimony(v) in seawater by flow injection solid phase extraction coupled with online hydride generation inductively coupled plasma mass spectrometry," *J. Anal. At. Spectrom.*, vol. 26, no. 8, pp. 1619–1626, 2011.

[48]. R. Miravet, E. Hernández-Nataren, A. Sahuquillo, R. Rubio, and J. F. López-Sánchez, "Speciation of antimony in environmental matrices by coupled techniques," *TrAC - Trends Anal. Chem.*, vol. 29, no. 1, pp. 28–39, 2010.

[49]. P. Li, Y. Chen, X. Hu, and H. Lian, "Talanta Magnetic solid phase extraction for the determination of trace antimony species in water by inductively coupled plasma mass spectrometry," *Talanta*, vol. 134, pp. 292–297, 2015.

[50]. T. Narukawa, K. Chiba, S. Sinaviwat, and J. Feldmann, "A rapid monitoring method for inorganic arsenic in rice flour using reversed phase-high performance liquid chromatography-inductively coupled plasma mass spectrometry," *J. Chromatogr. A*, vol. 1479, pp. 129–136, 2017.

[51]. Z. Yang, H. Peng, X. Lu, Q. Liu, B. Hu, R. Huang, G. Kachanoski, M. J. Zuidhof, and X. C. Le, "Arsenic Metabolites, Including N-Acetyl-4-hydroxy-m-arsanilic Acid, in Chicken Litter from a Roxarsone-Feeding Study Involving 1600 Chickens," *Environ. Sci. Technol.*, vol. 50, no. 13, pp. 6737–6743, 2016.

[52]. J. L. Todolí and M. Grotti, "Fast determination of arsenosugars in algal extracts by narrow bore high-performance liquid chromatography-inductively coupled plasma mass spectrometry," *J. Chromatogr. A*, vol. 1217, no. 47, pp. 7428–7433, 2010.

[53]. A. Terol, F. Ardini, M. Grotti, and J. L. Todolí, "High temperature liquid chromatography-inductively coupled plasma mass spectrometry for the determination of arsenosugars in biological samples," *J. Chromatogr. A*, vol. 1262, pp. 70–76, 2012.

[54]. I. Fiamegkos, F. Cordeiro, P. Robouch, D. Vélez, V. Devesa, G. Raber, J. J. Sloth, R. R. Rasmussen, T. Llorente-Mirandes, J. F. Lopez-Sanchez, R. Rubio, F. Cubadda, M. D'Amato, J. Feldmann, A. Raab, H. Emteborg, and M. B. de la Calle, "Accuracy of a method based on atomic absorption spectrometry to determine inorganic arsenic in food: Outcome of the collaborative trial IMEP-41," *Food Chem.*, vol. 213, pp. 169–179, 2016.

[55]. S. Hong, S. D. Choi, and J. S. Khim, "Arsenic speciation in environmental multimedia samples from the Youngsan River Estuary, Korea: A comparison between freshwater and saltwater," *Environ. Pollut.*, vol. 237, pp. 842–850, 2018.

[56]. A. Castro Grijalba, E. F. Fiorentini, L. D. Martinez, and R. G. Wuilloud, "A comparative evaluation of different ionic liquids for arsenic species separation and determination in wine varietals by liquid chromatography–hydride generation atomic fluorescence spectrometry," *J. Chromatogr. A*, vol. 1462, pp. 44–54, 2016.

[57]. B. Chen, X. Lu, S. Shen, L. L. Arnold, S. M. Cohen, and X. C. Le, "Arsenic speciation in the blood of arsenite-treated F344 rats," *Chem. Res. Toxicol.*, vol. 26, no. 6, pp. 952–962, 2013.

[58]. B. Sadee, M. E. Foulkes, and S. J. Hill, "Coupled techniques for arsenic speciation in food and drinking water: A review," *J. Anal. At. Spectrom.*, vol. 30, no. 1, pp. 102–118, 2015.

[59]. N. Ben Issa, V. N. Rajaković-Ognjanović, B. M. Jovanović, and L. V. Rajaković, "Determination of inorganic arsenic species in natural waters-Benefits of separation and preconcentration on ion exchange and hybrid resins," *Anal. Chim. Acta*, vol. 673, no. 2, pp. 185–193, 2010.

[60]. H. Peng, B. Hu, Q. Liu, Z. Yang, X. Lu, R. Huang, X. Li, M. J. Zuidhof, and X. C. Le, "Liquid chromatography combined with atomic and molecular mass spectrometry for speciation of arsenic in chicken liver," *J. Chromatogr. A*, vol. 1370, pp. 40–49, 2014.

[61]. F. Zhao, Y. Liu, X. Zhang, R. Dong, W. Yu, Y. Liu, Z. Guo, X. Liang, and J. Zhua, "Enzyme-assisted extraction and liquid chromatography-inductively coupled plasma mass spectrometry for the determination of arsenic species in fish," *J. Chromatogr. A*, vol. 1573, pp. 48–58, 2018.

[62]. M. Alaee, P. Arias, A. Sjödin, and Å. Bergman, "An overview of commercially used brominated flame retardants, their applications, their use patterns in different countries/regions and possible modes of release," *Environ. Int.*, vol. 29, no. 6, pp. 683–689, 2003.

[63]. C. A. De Wit, "An overview of brominated flame retardants in the environment, "Chemoshpere, vol. 46, no. 5, pp. 583–624, 2002.

[64]. I. Watanabe and S. I. Sakai, "Environmental release and behavior of brominated flame retardants," *Environ. Int.*, vol. 29, no. 6, pp. 665–682, 2003.

[65]. J. Cristale and S. Lacorte, "Development and validation of a multiresidue method for the analysis of polybrominated diphenyl ethers, new brominated and organophosphorus flame retardants in sediment, sludge and dust," *J. Chromatogr. A*, vol. 1305, pp. 267–275, 2013.

[66]. R. C. Hale, M. J. La Guardia, E. Harvey, M. O. Gaylor, and T. M. Mainor, "Brominated flame retardant concentrations and trends in abiotic media," *Chemosphere*, vol. 64, no. 2, pp. 181–186, 2006.

[67]. R. J. Law, C. R. Allchin, J. de Boer, A. Covaci, D. Herzke, P. Lepom, S. Morris, J. Tronczynski, and C. A. de Wit, "Levels and trends of brominated flame retardants in the European environment," *Chemosphere*, vol. 64, no. 2, pp. 187–208, 2006.

[68]. H. Wolschke, X. Z. Meng, Z. Xie, R. Ebinghaus, and M. Cai, "Novel flame retardants (N-FRs), polybrominated diphenyl ethers (PBDEs) and dioxin-like polychlorinated biphenyls (DL-PCBs) in fish, penguin, and skua from King George Island, Antarctica," *Mar. Pollut. Bull.*, vol. 96, no. 1–2, pp. 513–518, 2015.

[69]. S. Corsolini, N. Ademollo, T. Martellini, D. Randazzo, M. Vacchi, and A. Cincinelli, "Legacy persistent organic pollutants including PBDEs in the trophic web of the Ross Sea (Antarctica)," *Chemosphere*, vol. 185, pp. 699–708, 2017.

[70]. M. Frederiksen, K. Vorkamp, M. Thomsen, and L. E. Knudsen, "Human internal and external exposure to PBDEs - A review of levels and sources," *Int. J. Hyg. Environ. Health*, vol. 212, no. 2, pp. 109–134, 2009.

[71]. V. Lenters, C. Thomsen, L. A. M. Smit, B. A. G. Jönsson, H. S. Pedersen, J. K. Ludwicki, V. Zviezdai, A. H. Piersma, G. Toft, J. P. Bonde, G. Becher, R. Vermeulen, and D. Heederik, "Serum concentrations of polybrominated diphenyl ethers (PBDEs) and a polybrominated biphenyl (PBB) in men from Greenland, Poland and Ukraine," *Environ. Int.*, vol. 61, pp. 8–16, 2013.

[72]. B. Eskenazi, J. Chevrier, S. A. Rauch, K. Kogut, K. G. Harley, C. Johnson, C. Trujillo, A. Sjödin, and A. Bradman, "In utero and childhood polybrominated diphenyl ether (PBDE) exposures and neurodevelopment in the CHAMACOS study," *Environ. Health Perspect.*, vol. 121, no. 2, pp. 257–262, 2013.

[73]. EC, "Directive 2003/11/EC of the European parliament and of the council of February 6 2003 amending for the 24th time Council Directive 76/669/EEC relating to restrictions on the marketing and use of certain dangerous substances and preparations (pentabromodip," *Off J Eur Union OJ L*, vol. 16, no. 1, pp. 45–46, 2003.

[74]. M. D. Jürgens, A. C. Johnson, K. C. Jones, D. Hughes, and A. J. Lawlor, "The presence of EU priority substances mercury, hexachlorobenzene, hexachlorobutadiene and PBDEs in wild fish from four English rivers," *Sci. Total Environ.*, vol. 461–462, no. January 2009, pp. 441–452, 2013.

[75]. G. Poma, P. Volta, C. Roscioli, R. Bettinetti, and L. Guzzella, "Concentrations and trophic interactions of novel brominated flame retardants, HBCD, and PBDEs in zooplankton and fish from Lake Maggiore (Northern Italy)," *Sci. Total Environ.*, vol. 481, no. 1, pp. 401–408, 2014.

[76]. N. Tapie, H. Budzinski, and K. Le Ménach, "Fast and efficient extraction methods for the analysis of polychlorinated biphenyls and polybrominated diphenyl ethers in biological matrices," *Anal. Bioanal. Chem.*, vol. 391, no. 6, pp. 2169–2177, 2008.

[77]. I. Johansson, K. Héas-Moisan, N. Guiot, C. Munschy, and J. Tronczyński, "Polybrominated diphenyl ethers (PBDEs) in mussels from selected French coastal sites: 1981-2003," *Chemosphere*, vol. 64, no. 2, pp. 296–305, 2006.

[78]. T. Martellini, G. Diletti, G. Scortichini, M. Lolini, E. Lanciotti, A. Katsoyiannis, and A. Cincinelli, "Occurrence of polybrominated diphenyl ethers (PBDEs) in foodstuffs in Italy and implications for human exposure," *Food Chem. Toxicol.*, vol. 89, pp. 32–38, 2016.

[79]. K. Pozo, P. Kukucˇka, L. Vanˇková, P. Prˇibylová, J. Klánová, A. Rudolph, Y. Banguera, J. Monsalves, S. Contreras, R. Barra, and R. Ahumada, "Polybrominated Diphenyl Ethers (PBDEs) in Concepción Bay, central Chile after the 2010 Tsunami," *Mar. Pollut. Bull.*, vol. 95, no. 1, pp. 480–483, 2015.

[80]. P. Wang, Q. Zhang, Y.Wang, T. Wang, X. Li, L. Ding, and G. Jiang, "Evaluation of Soxhlet extraction, accelerated solvent extraction and microwave-assisted extraction for the determination of polychlorinated biphenyls and polybrominated diphenyl ethers in soil and fish samples," *Anal. Chim. Acta*, vol. 663, no. 1, pp. 43–48, 2010.

[81]. A. P. Vonderheide, "A review of the challenges in the chemical analysis of the polybrominated diphenyl ethers," *Microchem. J.*, vol. 92, no. 1, pp. 49–57, 2009.

[82]. J. Pulkrabová, J. Hajšlová, J. Poustka, and R. Kazda, "Fish as biomonitors of polybrominated diphenyl ethers and hexabromocyclododecane in Czech aquatic ecosystems: Pollution of the Elbe river basin," *Environ. Health Perspect.*, vol. 115, no. SUPPL1, pp. 28–34, 2007.

[83]. H. Fromme, W. Körner, N. Shahin, A. Wanner, M. Albrecht, S. Boehmer, H. Parlar, R. Mayer, B. Liebl, and G. Bolte, "Human exposure to polybrominated diphenyl ethers (PBDE), as evidenced by data from a duplicate diet study, indoor air, house dust, and biomonitoring in Germany," *Environ. Int.*, vol. 35, no. 8, pp. 1125–1135, 2009.

[84]. P. Novak, T. Zuliani, R. Milačič, and J. Ščančar, "Development of an analytical method for the determination of polybrominated diphenyl ethers in sewage sludge by the use of gas chromatography coupled to inductively coupled plasma mass spectrometry," *Anal. Chim. Acta*, vol. 915, pp. 27–35, 2016.

[85]. R. F. Swarthout, J. R. Kucklick, and W. C. Davis, "The determination of polybrominated diphenyl ether congeners by gas chromatography inductively coupled plasma mass spectrometry," *J. Anal. At. Spectrom.*, vol. 23, no. 12, pp. 1575–1580, 2008.

[86]. P. Novak, T. Zuliani, R. Milačič, and J. Ščančar, "Development of an analytical method for the determination of polybrominated diphenyl ethers in mussels and fish by gas chromatography—Inductively coupled plasma mass spectrometry," *J. Chromatogr. A*, vol. 1524, pp. 179–187, 2017.

[87]. D. M. Taylor, "Environmental plutonium in humans," *Appl. Radiat. Isot.*, vol. 46, no. 11, pp. 1245–1252, 1995.

[88]. J. H. Diel and J. A. Mewhinney, "Fragmentation of Inhaled ^{238}PuO$_2$ Particles in Lung," *Health Phys.*, vol. 44, no. 2, pp. 135–143, 1983.

[89]. E. H. Carbaugh, D. E. Bihl, and M. J. Sula, "Long-term follow-up of han-1, an acute plutonium oxide inhalation case," Radiat Pro Dosimetry, vol. 38, no. 1/3, pp. 99–104, 1991.

[90]. T. Shinonaga, P. Steier, M. Lagos, and T. Ohkura, "Airborne plutonium and non-natural uranium from the Fukushima DNPP found at 120 km distance a few days after reactor hydrogen explosions," *Environ. Sci. Technol.*, vol. 48, no. 7, pp. 3808–3814, 2014.

[91]. P. Thakur, S. Ballard, and R. Hardy, "Radiation release at the nations only operating deep geological repository - An independent monitoring perspective," *Environ. Sci. Technol.*, vol. 48, no. 21, pp. 12698–12705, 2014.

[92]. G. Li, "Metro-oriented multiservice transport platform," *Netw. Archit. Manag. Appl.*, vol. 5282, p. 112, 2004.

[93]. Y. Ni, J. Zheng, Q. Guo, W. Men, K. Tagami, and S. Uchida, "Rapid determination of ultra-trace plutonium isotopes (^{239}Pu, ^{240}Pu and ^{241}Pu) in small-volume human urine bioassay using sector-field inductively coupled plasma mass spectrometry," *Anal. Chim. Acta*, vol. 1000, pp. 85–92, 2018.