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Assessing the presence and health risks of potentially toxic metals in food: a comprehensive overview

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Cite this article: Mustatea G, Ungureanu EL. Assessing the presence and health risks of potentially toxic metals in food: a comprehensive overview. Explor Foods Foodomics. 2024;2:471–96. https://doi.org/10.37349/eff.2024.00047

Abstract

Food products can contain various substances, including essential nutrients, as well as non-nutritive elements and potentially toxic metals. Metal contaminants have the potential to accumulate within the food chain and, when they exceed safe thresholds, can be toxic to humans, leading to health issues. To mitigate health hazards caused by exposure to such harmful substances, accurate monitoring of metal concentrations in various food samples is crucial. Achieving this goal needs understanding the basic principles of various elemental analysis methods. Additionally, selecting the appropriate technique or combination of techniques is critical for obtaining accurate and relevant results. Various advanced analytical techniques, such as atomic absorption spectroscopy, flame emission spectroscopy, inductively coupled plasma-mass spectrometry (ICP-MS), and X-ray fluorescence (XRF) spectrometry, can be used for the quantification of heavy metals and metalloids in food. However, each method has its own limitations, and the accuracy depends on adequate sample preparation. This paper aims to provide a clear overview of commonly used methods and techniques for heavy metal detection in food products, addressing the advantages and limitations of each analytical technique. Additionally, it compares the most important performance parameters of the presented techniques, including the limit of detection (LOD), the limit of quantification (LOQ), recovery, and precision. Moreover, ensuring food safety involves conducting a thorough risk assessment analysis. By integrating risk assessment into the evaluation of heavy metals in food, it becomes possible to determine whether observed concentrations pose significant risks to human health. This step is imperative for establishing regulatory guidelines and implementing control measures to reduce or eliminate potential health risks. Incorporating risk assessment into the broader context of the review enhances its applicability in real-world scenarios, aiding policymakers, regulatory bodies, and researchers in making informed decisions regarding food safety standards and practices.

Keywords

Food contamination, potentially toxic metals, risk assessment, analytical techniques

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Introduction

Pollution with potentially toxic metals is a worldwide environmental problem that also poses a threat to human health [1]. Population growth and food demand lead to excessive toxic metal release into the environment, contaminating soil, water, and agricultural crops [2, 3]. There are various ways that potentially toxic metals enter the human body, including ingestion, skin contact, or inhalation [4]. Toxic metal contamination in food is a significant issue in the human body which necessitates the proper detection and monitoring of toxic metal accumulation in food crops, cereals, pulses, vegetables, fruits, and medicinal plants [4–6].

Special attention must be paid to some toxic metals such as Cd, Pb, Hg, or Ni present in foods in our daily diet. These metals which have no beneficial function can be toxic even at low concentrations [7]. The health effects of toxic metals depend on their specific type and form. Therefore, investigation of metal speciation in soil, food, and human samples is essential for understanding the associated health risks and factors such as bioavailability, toxicity, and biological responses [3].

To mitigate food contamination, the Food and Agriculture Organization of the United Nations (FAO), the World Health Organization (WHO), and the International Organization of Vine and Wine (OIV) have established guidelines for the regulation of these chemical contaminants in food products. Thus, these guidelines are outlined in documents such as the Codex Alimentarius, the Official Journal of the European Union [8], the International Code of Oenological Practices, and the Compendium of International Methods of Analysis of Wine and Must. Among these, As, Pb, Hg, and Cd have been prioritized in receive special attention and were included in the government monitoring and abatement programs [9].

The detection of heavy metals in various food raw materials, including grains, fruits, water, tea, and other processed agricultural products is an urgent necessity for ensuring food safety and quality that can only be achieved by using effective analytical methods [10]. The food industry faces a significant challenge in ensuring food safety and maintaining the levels of heavy metals in food at optimal levels. Beyond safety concerns, the presence of heavy metals in food can raise consumer fears and damage the reputation of food brands, leading to financial setbacks for the industry [11].

For these reasons, the objective of this review is to present the primary analytical methods involved in identifying potentially harmful metals in food products. The principles of selected techniques, benefits, drawbacks, and efficacy in detecting toxic metals were also presented. Additionally, the study includes a short analysis of their practical applications in assessing toxic metals from various food categories. Furthermore, the review includes a carcinogenic and non-carcinogenic risk (CR) assessment analysis for consumers posed by the concentrations of toxic metals found in food products.

The novelty of this study lies in the extensive array of analytical techniques employed to assess the degree of contamination in various food products. Furthermore, unlike other review studies, this review specifically examines the risk levels associated with heavy metal presence in food products.

Research methodology

The review protocol utilized to identify scientific articles was adjusted following the approach outlined by Anedda et al. [12]. The primary inclusion criteria consisted of (i) emphasis on detecting heavy metals in food products, (ii) studies detailing method validation and performance parameters, and (iii) studies involving health risk assessments (HRAs) of the detected heavy metals. Regarding data extraction, all pertinent studies were gathered and arranged into tables, which included details such as the metals investigated, the analytical techniques employed, the types and quantities of food products tested, the presentation of method performance parameters, the outcomes of HRA analyses, and the publication year.

Analytical techniques for the detection of potentially toxic metals

Various analytical methods have been reported for detection of harmful metals in food products, including inductively coupled plasma-mass spectrometry (ICP-MS), inductively coupled plasma-atomic emission

spectrometry (ICP-AES) [6, 13–16], inductively coupled plasma-optical emission spectrometry (ICP-OES) [16], laser ablation-inductively coupled plasma-mass spectrometry (LA-ICP-MS) [6], flame atomic absorption spectrometry (F-AAS), graphite furnace atomic absorption spectrometry (GF-AAS) [6, 15, 16], cold vapor-atomic absorption spectrometry (CV-AAS), hydride generation atomic absorption spectrometry (HG-AAS) [6], atomic fluorescence spectrometry (AFS) [6, 16], X-ray absorption spectroscopy (XAS) [6], energy dispersive X-ray fluorescence (EDXRF), total reflection X-ray fluorescence (TXRF) [15, 16], stripping potentiometry, anodic stripping voltammetry (ASV) [13, 16], differential pulse anodic stripping voltammetry (DPASV) [16], instrumental neutron activation analysis (INAA) [10], and X capillary zone electrophoresis [16].

The main challenges regarding the determination of harmful metals present in food samples are related to sample preparation, the presence of interferences, detection limits, and matrix effects. Given that toxic metals are present in very small concentrations in food, an efficient and reliable sample preparation method is very important to ensure that metals are not lost during this step [17].

Besides the target analyte, food samples can contain other elements that can interfere with the determination of toxic metals, potentially leading to inaccurate results. For this reason, careful sample preparation and the use of selective analytical techniques capable of detecting the element of interest can mitigate these interferences. As concerning the detection limits, toxic metals are present in very low concentrations, posing a challenge for conventional analytical techniques. To detect the ultra-trace metals at the parts per billion (ppb) level, techniques with high sensitivity, such as ICP-MS, are commonly employed. Due to the impact of the matrix effect on the efficiency of the analytical technique and the accuracy of results, it must be taken into account. The standard addition method is one of the primary methods that can be used to assess the matrix effect [17].

ICP-MS

ICP-MS is one of the widely successful used quantitative multi-element methods which can offer the possibility of a wide detection range of metals in foods with different matrix compositions [15, 18, 19]. Furthermore, ICP-MS is considered the preferred method for detecting heavy metal contents [6].

ICP-MS techniques need several components including a sample introduction system, ion source, interface, ion lens, mass filter, and an ion detector [6]. The principle of this process involves the use of an argon plasma source to dissociate the sample into its constituent atoms or ions [19]. In this stage, the liquid sample is nebulized with an effective nebulizer turning it into a fine aerosol, that is then carried with argon to the ICP torch. Within the plasma, the nebulized water matrix and chemical compounds evaporate, molecules dissociate into atomic constituents, and then ionized into positively single-charged ions. The next step is the extraction of single-charged ions from the argon plasma into the mass analyzers, which can be quadrupole, double-focusing sector field, and time of flight. Extracted ions are separated, in the mass analyzer, based on their mass-to-charge ratio or energy-to-charge ratio, especially in double-focusing SF instruments. The separated ion beams are detected by photomultiplier or Faraday cups. Among the various sample introduction systems developed for ICP-MS, liquid solution nebulization is the most common and cost-effective method [17, 18].

This technique can be used in combination with other analytical methods, for example, LA-ICP-MS, single particle-inductively coupled plasma-mass spectrometry (SP-ICP-MS), liquid chromatographyinductively coupled plasma-mass spectrometry (LC-ICP-MS), to facilitate the sample preparing process for the detection of forms and concentrations of different toxic metals as well as for isotope analysis in different matrix samples [6]. The significant number of ions generated, combined with very low backgrounds, provides excellent detection limits for most metals, typically in the parts per trillion (ppt) ranges [19]. The main benefits of this technique are related to excellent sensitivity, selectivity, accuracy, low detection limits, small sample volume, easy and simple sample preparation, wide linear range, multi-elemental analysis, the possibility of isotopic determination, capable of detecting minute levels, fast, allows for easy control of interferences [9, 15, 17, 18]. However, ICP-MS can have some drawbacks, such as the high cost of the equipment and laboratory setup, the cost of the high-purity gases needed, or the high level of expertise of the operators [9]. Besides this, another very important limit is related to the spectroscopic and non-spectroscopic multi-elemental interferences that can seriously affect its analytical efficiency [15]. This can be prevented by using the non-interfered isotope in case of multi-isotopic metals, by the subtraction of blanks, proper sample preparation, the use of mathematical correction, cold plasma conditions, by the use of collision or reaction cell technology, or by the use of high-resolution mass spectrometers that resolve metals and interferences [18]. Despite its challenges related to atomic and molecular isobaric interferences, multi-elemental interferences, and high cost, ICP-MS has been utilized for the determination of various toxic metals in a range of food items. These include fruits, vegetables, eggs, fish, cereals [20], processed seafood products [21], raw and processed rice, raw and processed chicken [22], and canned beef [23] (Table 1). Elevated levels were observed for As in fruits, vegetables, cereals, fish [20], and canned beef [23], Pb in fruits, vegetables, cereals, and fish [20], and for Cd in fruits, vegetables, cereals, and fish [20]. The concentrations of Cr, Ni, As, Cd, and Pb in all food groups (except chili), exceeded the maximum allowable concentration (MAC) of the tested metals in foods [20]. Additionally, the concentrations of Ad, Cd, Cr, Ni, and Pb, in canned food samples sold in Jordanian markets exceeded the permissible limits set by health organizations such as FAO/WHO [23]. Regarding the performance characteristics of this method, it demonstrated favorable detection and quantification limits for Cd, As, Pb, Sb, Mo, Se, Cr using ICP-MS, being between 0.00006 mg/kg and 0.0584 mg/kg (Table 2) [24–27]. In the case of Cd, the lowest limit of detection (LOD) was obtained by Mohamed et al. [25] and demonstrated for various certified reference materials (CRMs). The obtained regression coefficient of all investigated elements exceeded 0.990. Intermediate precision, as indicated by %RSD by using an internal reference material, ranged from 1.02% [26] to 1.717% [24]. Moreover, the CRMs used revealed improved recovery rates between 89.7 [25] and 108.7 [24]. Giraldo et al. [24] demonstrated that the method maintains accuracy and precision even at very low concentration ranges, between 0.00025–0.010 mg/kg. All these parameters suggest its suitability for the quantification of various toxic and trace metals in food products (Table 2).

ICP-OES

ICP-OES is a multi-element technique spectroscopic technique suitable for the detection of major, minor, and trace metals in different complex samples [19, 28]. The method is based on the spontaneous emission of photons from atoms and ions that have been excited in a radiofrequency discharge. Typically, samples are introduced into the plasma in liquid form. For this reason, solid samples are disintegrated by acid digestion prior to injection. However, gas and liquid samples can be directly injected into the instrument. The next step is a conversion of the sample solution into an aerosol, then sent into the center of the plasma which maintains a high atomization temperature of around 10,000 K. As the plasma generates free atoms in a gaseous state, adequate energy is often available to convert the atoms to ions which are promoted in excited states. The ionic excited state species may subsequently return to the ground state by emitting photons. The specific wavelength of these photons enables the identification of metals. The number of photons is directly proportional to the concentration of the element in the sample. Different sample introduction methods such as electrothermal vaporization (ETV) and laser ablation, as well as, nebulization or hydride generation (HG) which can be used for specific metals including arsenic, selenium, and antimony [19].

This method offers several important advantages represented by the high capacity for the simultaneous metals, its precise detection within short timeframes across wide concentration ranges, and the relatively low detection limits, which are typically lower than those obtained using GF-AAS [28]. This method displays some limitations due to spectral and non-spectral (also known as matrix) interference effects caused by concurrent metals in the sample. The spectral interferences can be corrected using the ICP-OES system software, while non-spectral interferences require optimizing and validating the method. Despite efforts to reduce non-spectral interferences, small matrix effects often persist, leading to inaccurate detection [28].

ICP-MS		
Fruits	Cr, Ni, Cu, As, Cd, Pb	0.06–5.4; 0.49–25; 0.11–32; 0.005–6.2; 0.004–1.1; 0.31–9.8
Vegetables $(n = 3)$	Cr, Ni, Cu, As, Cd, Pb	0.07–3.7; 0.07–10; 0.04–27; 0.005–6.3; 0.001–1.9; 0.06–13
Eggs (<i>n</i> = 2)	Cr, Ni, Cu, As, Cd, Pb	0.7–2.9; 0.10–9.1; 0.13–5.9; 0.009–0.96; 0.001–0.17; 0.005–0.77
Cereals $(n = 3)$	Cr, Ni, Cu, As, Cd, Pb	0.09–10; 0.04–10; 0.20–20; 0.01–7; 0.001–1.8; 0.06–11
Raw and processed rice (<i>n</i> = 6)	Mn, Fe, Cu, Zn, As, Cd, Pb, Se	4.7–5.4; 2.8–28.0; 1.3–1.8; 8.39–9.4; < 0.18–0.30; < 0.02; 0.02; 0.24–0.32
Fish (<i>n</i> = 3)	Cr, Ni, Cu, As, Cd, Pb	0.54–3.3; 0.09–20; 1.3–40; 0.01–7.1; 0.001–5.5; 0.06–4.0
Processed seafood products $(n = 9)$	Cu, Sn, Zn, Fe, Cd, Pb	1.87–26.33; 0.06–0.42; 9.98–64.58; 23.62–71.37; 0.02–0.31; 0.11–0.28
Canned beef ($n = 44$)	As, Cd, Cr, Cu, Ni, Pb, Zn	2.9 ± 1.4 ; 0.51 ± 0.02 ; 1.22 ± 0.63 ; 0.90 ± 0.02 ; 1.09 ± 0.70 ; 2.97 ± 0.60 ; 0.73 ± 0.73
Raw and processed chicken $(n = 9)$	Mn, Fe, Cu, Zn, As, Cd, Pb, Se	0.55–1.4; 14.7–19.8; 0.94–1.4; 11.4–22.7; < 0.18; < 0.02; 0.02–0.07; 0.67–0.76
ICP-OES		
Fruit juices (n = 36)	Al, Sn, As, Cd, Hg, Pb	0.065–1.039; 0.049–0.119; 0.001–0.018; 0.0008–0.003; 0.00035; 0.027–0.066
Canned fruit (n = 36)	Al, Sn, As, Cd, Hg, Pb	0.043–1.121; 0.071–0.0141; 0.001–0.019; 0.001–0.005; 0.00035; 0.470–0.910
Vegetables (n = 2)	As, Pb, Cd, Zn, Cu, Fe, Mn, Cr, Hg, Ni, Co	1.93–5.73; 3.63–7.56; 0.56–1.56; 23.53–24.50; 9.42–16.27; 85.10–490.46; 27.20–302.23; 1.49–4.63; 3.43–4.23; 1.86–4.13; 0.63–1.86
Honey (<i>n</i> = 25)	As, Cd, Cr, Pb, Ni, Zn, Cu	< 0.011; 0.001–0.125; 0.172–1.220; 0.117–1.627; 0.065–1.094; 0.122–6.638; 0.027–2.872
Chicken meat ($n = 50$)	Cd, Pb, As, Ni, Fe, Zn, Cu	0.004–0.010; 0.018–0.036; 0.005–0.012; 0.004–0.012; 5.37–7.25; 3.25–5.29; 0.41–0.54
Nuts (<i>n</i> = 14)	B, Co, Cr, Cu, Fe, Mn, Mo, Ni,	10.72-48.36; 0.0182-1.074; 0.1423-0.9261; 10.34-28.570; 30.99-87.03; 7.766-27.870; 0.0237-1.056; 0.1362-7.751;

Table 1. Investigation of potentially toxic metals content in food matrices through various analytical techniques

Concentration (mg/kg)

Tested food product Tested metals

F-AAS			
Raw meat (<i>n</i> = 63)	Fe, Cu	64.60–167.43; 83.07–99.48	[34]
Liver (<i>n</i> = 63)	Fe, Cu	94.26–1650.60; 77.51–473.99	[34]
Food additives (<i>n</i> = 11)	Fe, Mn, Cd, Co, Cr, Ni, Cu, Pb, Zn	3.133–6.683; 1.319–7.611; 0.005–0.023; 0.015–0.034; 0–0.134; 0.009–0.129; 0.273–3.047; 0.024–0.270; 0.575–1.360	[37]
GF-AAS			
Milk (<i>n</i> = 5)	Pb, Cd	0.004–0.008; 0.009–0.011	[<mark>39</mark>]
Cheese (<i>n</i> = 5)	Pb, Cd	0.003–0.010; 0.009–0.010	[<mark>39</mark>]
Eggs (<i>n</i> = 30)	Pb, Cd	0.005–0.990; 0.0008–0.690	[40]
Vegetables ($n = 5,785$)	Cd, Cr, Ni, Pb	< 0.001–0.340; < 0.005–0.463; < 0.005–1.900; < 0.005–0.661	[41]
Multifloral honey	Pb, Cd	< 0.003–0.360; < 0.001–0.0180	[40]
Raw meat (<i>n</i> = 63)	Cd, Cr, Pb, Ni	BDL-0.48; 0.46-3.15; 1.64-5.91; 3.55-7.74	[34]

0.6583-0.9791; 4.627-201.7; 33.99-59.33; 3.622-1516; 0.0828-0.2872; 0.0828-0.1231; 0.1278-0.5336

Se, Si, Zn, Al, As, Cd, Pb

Source

[20] [20] [20] [20] [22]

[20] [21]

[23] [22]

[29] [29]

[<mark>30</mark>]

[31] [32] [28]

Tested food product	Tested metals	Concentration (mg/kg)	Source
Liver (<i>n</i> = 63)	Cd, Cr, Pb, Ni,	0.65–15.98; 0.82–3.81; 2.79–81.87; 2.71–41.42	[34]
Edible seeds $(n = 10)$	Cd, Ni, Fe	0.039–0.254; 0.001–0.008; 0.038–0.147	[42]
Edible oils (<i>n</i> = 16)	Pb, Cu, Cr, Ni, Cd	< 0.013–0.019; < 0.016–0.022; < 0.025–0.033; < 0.009–0.013; 0.008–0.019	[77]
HG-AAS			
Milk (<i>n</i> = 5)	Hg	0.004–0.007	[39]
Cheese <i>n</i> = 5)	Hg	0.004–0.008	[39]
Vegetables ($n = 5,785$)	As, Hg	< 0.005–0.331; < 0.004–0.159	[41]
Rice (<i>n</i> = 13)	iAs, As (III), As (V), tAs	0.054–0.169, 0.030–0.158, 0.005–0.046, 0.083–0.258	[48]
Bread (<i>n</i> = 2)	As, Hg	3.404–6.453; 0.015–0.022	[4]
Sweets $(n = 5)$	As, Hg	3.404–12.280; 0.009–0.029	[4]
Wheat (<i>n</i> = 11)	As, Hg	0.05–0.295; 0–0.026	[4]
CV-AAS			
Milk (<i>n</i> = 5)	As	0.004–0.008	[39]
Cheese $(n = 5)$	As	0.005–0.007	[39]
Fisk (<i>n</i> = 11)	Hg	0.093–0.182	[50]
Canned fish (n = 11)	Hg	< 0.0005–0.199	[51]
Fruits (<i>n</i> = 269) EDXRF	Hg	0.0009–0.003	[52]
Milk and milk products $(n = 9)$	Mo, Pb	0.11–0.35; < 0.08	[58]
Raw and packed milk (<i>r</i> = 16)	r Cr, Mn, Ni, Cu, Zn, As, Cd, Hg, Pb, Fe	ND–0.225; 0.024–0.099; 0.058–0.107; 0.048–0.067; 0.486–1.253; 0.031–0.039; ND–0.025; ND–0.120; 0.023–0.056; 0.452–1.633 mg/L	[59]
Vegetables (n = 24)	Mo, Pb	0.05–0.10; 0.12–0.25	[58]
Leaf vegetables (<i>n</i> = 16)	Zn, Cu, Ni, Co, Fe, Mn, Cr, As, Pb	10.9–219.3; 1.5–11.6; 0.7–11.6; 0.3–0.47; 40.8–193.6; 0.26–868.5; 1.7–8.8; 0.09–1.4; 0.5–12.3	[60]
Pulses (<i>n</i> = 15)	Mo, Pb	0.77–3.18; 0.45–0.92	[58]
Pulses ($n = 3$)	Mn, Fe, Co, Ni, Cu, Zn, As, Rb, Zr, Mo, Ru, Ag, Cd, In	2.157–4.569; 19.454–81.445; 1.369–9.103; 1.991–2.568; 2.325–4.408; 2.308–6.059; 0.649–0.789; 1.055–2.945; 0.715–1.1 0.480–1.071; 0.332–1.477; 0.178–0.983; 0.302–0.675; 0.412–0.504	58; [<mark>61</mark>]
Eggs (<i>n</i> = 10)	Mo, Pb	0.15; 0.17	[58]
Fish (<i>n</i> = 27)	Mo, Pb	0.09–0.13; 0.11–0.15	[58]
Cereals ($n = 42$)	Mo, Pb	0.31–4.44; 0.11–0.82	[58]
Cereals $(n = 5)$	Mn, Fe, Co, Ni, Cu, Zn, As, Rb, Zr, Mo, Ru, Ag, Cd, In	1.8–2.169; 10.171–131.944; 2.513–14.433; 1.174–2.727; 2.323–3.765; 1.592–4.695; 0.474–1.174; 0.320–1.243; 0.462–1.1 0.412–1.296; 0.359–1.429; 0.178–0.983; 0.213–0.462; 0.435–0.733	16; [<mark>61</mark>]

Table 1. Investigation of potentially toxic metals content in food matrices through various analytical techniques (continued)

Tested food product	Tested metals	Concentration (mg/kg)	Source
Meat (<i>n</i> = 15)	Mo, Pb	0.05–0.10; 0.25–0.85	[58]
TXRF			
Rice (<i>n</i> = 10)	Ti, Cr, Mn, Fe, Ni, Cu, Zn, Rb, Sr, Ba, Pb	0.5–4.0; 0–1.6; 20–44; 13–33; 0.2–2.0; 1.7–3.1; 19–39; 0.6–35.2; 0.29–0.67; 0; 0.08–0.51	[62]
SRXRF			
Coriander leaf and seeds $(n = 2)$	Ti, Cr, Mn, Fe, Ni, Cu, Zn, As	110–150; 40–50; 80–230; 430–1380; 20–30; 140; 320–360; 10	[57]
ASV			
Cheese (<i>n</i> = 1)	Pb, Cd, Zn, Cu	0.014; 0.001; 0.586; 0.428	[13]
Yoghurt ($n = 1$)	Pb, Cd, Zn, Cu	0.007; 0.0009; 0.431; 0.399	[13]
Rice (<i>n</i> = 5)	Cd, Pb, Cu	0.00002–0.00005; 0.00005–0.0015; 0.00011–0.00044 mg/L	[69]
CSV			
Cheese (<i>n</i> = 1)	Se	0.0016	[13]
Yoghurt ($n = 1$)	Se	0.0012	[13]

Table 1. Investigation of potentially toxic metals content in food matrices through various analytical techniques (continued)

ICP-MS: inductively coupled plasma-mass spectrometry; ICP-OES: inductively coupled plasma-optical emission spectrometry; F-AAS: flame atomic absorption spectrometry; GF-AAS: graphite furnace atomic absorption spectrometry; HG-AAS: hydride generation atomic absorption spectrometry; CV-AAS: cold vapor atomic absorption spectrometry; EDXRF: energy dispersive X-ray fluorescence; TXRF: total reflection X-ray fluorescence; SRXRF: synchrotron radiation X-ray fluorescence; ASV: anodic stripping voltammetry; CSV: cathodic stripping voltammetry; BDL: below detection limit; ND: undetectable

Table 2. Performance parameters of various analytical techniques

Sample digestion	Metal	LOD	R²	Linear range (mg/kg)	LOQ	RSD _r /CV _r (%)	RSD _R /CV _R (%)	Precision (%RSD)	Measuring uncertainty (%)	Recovery (%)	Source
ICP-MS											
Microwave digestion	Cd	0.003 mg/kg	> 0.998	0.00025-0.010	0.005 mg/kg	n.r.	n.r.	1.7	0.033	95	[24]
Microwave digestion	As, Cd, Pb, Sb	0.0024–0.0092; 0.0001–0.0555; 0.0044–0.0151; 0.0008–0.0584 mg/kg	> 0.990	0.005–2.500	0.0078–0.0106; 0.0002–0.1851; 0.0147–0.0503; 0.0025–0.19405 mg/kg	n.r.	n.r.	n.r.	< 25	99.5–108.7; 95.3–100.7; 89.7–97.2; 92.5–102.4	[25]
Dry ashing, wet digestion, microwave digestion	Mo, Se, , Cr	0.00006; 0.00013; 0.00006 mg/kg	> 0.9996	n.r.	0.00021; 0.00044; 0.00021 mg/kg	n.r.	n.r.	1.02; 1.27 1.18	; n.r.	98.7; 99.1; 98.4	[26]
Wet digestion	Pb, Cd,	0.0024; 0.0012; 0.0028	> 0.9994	n.r.	0.0072; 0.0037; 0.0084	n.r.	n.r.	n.r.	n.r.	103.89; 101.21;	[27]

Sample digestion	Metal	LOD	R ²	Linear range (mg/kg)	LOQ	RSD _r /CV _r (%)	RSD _R /CV _R (%)	Precision (%RSD)	Measuring uncertainty (%)	Recovery (%)	Source
	As	mg/kg			mg/kg					96.99	
ICP-OES											
Microwave digestion	Cd	0.034 mg/kg	> 0.998	0.001–0.005 (I); 0.010–0.050 (II); 0.100–0.500 (III)	0.043 mg/kg	n.r.	n.r.	2.3	0.079 (I); 0.047 (II); 0.034 (III)	91	[19]
Microwave digestion	As, Cd, Hg, Pb	0.00100; 0.00005; 0.00035; 0.00200 mg/kg	0.9891 (Cd); 0.9899 (Hg); > 0.99 (AS, Pb)	0.0003–1.200 (As, Cd, Hg); 0.0012–1.200 (Pb)	0.00330; 0.00016; 0.00117; 0.00660 mg/kg	n.r.	n.r.	n.r.	n.r.	94; 98; 101; 105	[33]
Dry ashing, wet digestion, microwave digestion	Mo, Se, , Cr	0.00091; 0.00589; 0.00444 mg/kg	> 0.9996	n.r.	0.00303; 0.01960; 0.01480 mg/kg	n.r.	n.r.	n.r.	n.r.	109.4; 40.9; 0	[26]
Wet digestion	Al, Hg	0.0040; 0.0021 mg/kg	n.r.	n.r.	0.0121; 0.0063 mg/kg	n.r.	n.r.	n.r.	n.r.	94.73; 97.30	[27]
F-AAS											
Wet digestion	Cd, Pb	0.004; 0.04 mg/L	0.9991; 0.9998	0.01–1.0; 0.10–2.0	0.01; 0.1 mg/L	1.36; 6.03	n.r.	1.33; 6.35	n.r.	95.39–103.24; 87.32–92.51	[39]
Microwave digestion	Zn, Fe	0.090; 0.130 mg/kg	> 0.997	0.0002–0.005; 0.0001–0.002	n.r.	n.r.	n.r.	n.r.	n.r.	88; 90	[44]
Wet digestion	Fe, Zn, Mn, Cu, Cr, Ni, Cd, Pb	0,167; 0.073; 0.026; 0.026; 0.030; 0.067; 0.030; 0.063 mg/kg	> 0.99	n.r.	0.557; 0.244; 0.068; 0086; 0.100; 0.233; 0.100; 0.210 mg/kg	n.r.	n.r.	n.r.	n.r.	96; 98; 93; 94; 87; 104; 96; 100	[38]
Wet digestion	Fe, Mn, Cd, Co, Cr, Ni, Cu, Pb, Zn	0.3813; 0.2975; 0.0150; 0.1696; 0.1505; 0.0518; 0.1974; 0.4823; 0.0209 mg/kg	> 0.997	0.5–10; 0.4–7.0; 0.02–0.4; 0.4–4.0; 0.1–2.0; 0.1–2.0; 0.3–4.0; 2.5–10; 0.1–10	1.2825; 0.9959; 0.0499; 0.5654; 0.5019; 0.1727; 0.6581; 1.5951; 0.0698 mg/kg	n.r.	n.r.	n.r.	n.r.	n.r.	[37]
GF-AAS											
Microwave digestion	Pb, Cr, Cd	0.065; 0.01; 0.11 mg/kg	0.9996 (Pb, Cd); 0.9998 (Cr)	2–40; 2–16; 0.25–4.0	0.22; 0.03; 0.38 mg/kg	8.7; 8.76; 8.75	8.86; 9.96; 8.65	n.r.	12.42; 11.48; 4.43 %	94.63; 93.97; 101.63	[45]
Microwave digestion	Cd, Cr, Cu, Mn,	0.00014; 0.00109; 0.00301; 0.00897;	> 0.997	0.0005–0.005 (Cd); 0.002–0.050 (Cr);	n.r.	n.r.	n.r.	n.r.	n.r.	96.5; 100; 98.9; 111; 79.4; 100	[44]

Table 2. Performance parameters of various analytical techniques (continued)

Sample digestion	Metal	LOD	R ²	Linear range (mg/kg)	LOQ	RSD _r /CV _r (%)	RSD _R /CV _R (%)	Precision (%RSD)	Measuring uncertainty (%)	Recovery (%)	Source
	Ni, Pb	0.0102; 0.00048 mg/kg		0.005–0.050 (Cu, Mn, Ni); 0.001–0.020 (Pb))						
Microwave digestion	Pb, Cd, As	0.000008; 0.000002; 0.0000003 mg/kg	n.r.	n.r.	0.000025; 0.000006; 0.00001 mg/kg	1.87; 3.88; 2.77;	n.r.	n.r.	n.r.	103.8; 90.1; 97.8	[43]
Microwave digestion	Pb, Cd, Cr	0.078; 0.010; 0.022 mg/kg	> 0.997	0.015–0.075; 0.001–0.006; 0.004–0.020	0.156; 0.021; 0.044 mg/kg	4.90–9.12	6.69–9.11	n.r.	15.8; 12.6; 11.8	90.40–97.73; 98.0–104.4; 92.40–92.80	[46]
HG-AAS											
Dry ashing, microwave digestion	As	0.00017 mg/kg	0.9981	0.0005–0.005	0.00058 mg/kg	0.35	n.r.	7.5	1.22	97.5	[39]
Microwave digestion	As, Hg, Se	0.0011; 0.0033; 0.00316 mg/kg	> 0.997	0.002–0.050 (Se, As); 0.0005–0.010 (Hg)	n.r.	n.r.	n.r.	n.r.	n.r.	114; 77; 106	[44]
Microwave digestion	Hg	0.0000033 mg/kg	n.r.	n.r.	0.000001 mg/kg	4.84	n.r.	n.r.	n.r.	98.8	[43]
Wet digestion	Hg	0.02 mg/kg	> 0.994	0.04–0.87	0.04 mg/kg	19.6	34.2	n.r.	n.r.	92–118	[49]
CV-AAS											
Microwave digestion	Hg	0.0173–0.0284 mg/kg	1.0000	0.0010-0.0160	0.0575–0.0948 mg/kg	7.58	6.08	n.r.	8.96	95.56–107.98	[15]
Microwave digestion	Hg	0.0049 mg/kg	0.999	0.001–0.030	0.0157 mg/kg	2.38–12.70	3.16–13.27	n.r.	n.r.	94–104	[55]
Microwave digestion	Hg	0.000118 mg/L	> 0.99	0.001–0.005 mg/L	0.000394 mg/L	1.5–3.0	1.7–4.2	n.r.	n.r.	90.1–105.8	[54]
Wet digestion	Hg	0.0001 mg/kg	0.9994	0.00005–0.010	0.0003 mg/kg	n.r.	n.r.	n.r.	n.r.	90.78	[53]
Wet digestion (TXRF)	Pb, As, Cr, Hg	0.00059; 0.00041; 0.00057; 0.00075 mg/L	0.9999; 0.9999; 0.9999; 0.9999; 0.9996	0.0019–0.100; 0.0013–0.100; 0.0019–0.100; 0.0025–0.100	0.00195; 0.00135; 0.00190; 0.00250 mg/L	3.31; 1.59; 5.11; 1.71	3.26; 1.96; 5.27; 4.77	n.r.	n.r.	91–108	[66]
Wet digestion (TXRF)	Fe, Zn, Cu, Mn, As	0.00016-0.00040; 0.00008-0.00023; 0.00007-0.00013; 0.00009-0.00030; 0.00005-0.00007 mg/kg	n.r.	n.r.	0.00049–0.00085; 0.00022–0.00065; 0.00016–0.00042; 0.00069–0.00100; 0.00016–0.00025 mg/kg	2.10–9.54; 4.01–9.04; 5.33–9.16; 2.51–11.05; 6.41	n.r.	n.r.	n.r.	61.73–82.12; 79.58–99.65; 73.78–82.68; 83.86–99.41; 93.90	[64]

Sample digestion	Metal	LOD	R ²	Linear range (mg/kg)	LOQ	RSD _r /CV _r (%)	RSD _R /CV _R (%)	Precision (%RSD)	Measuring uncertainty (%)	Recovery (%)	Source
Wet digestion (HDXRF)	As, Cd, Ni, Pb, Sn, Zn	0.072; 0.070; 0.502; 0.063; 0.033; 4.383 mg/kg	0.9961; 0.9995; 0.9991; 0.9617; 0.9980; 0.9748	0.24–10; 0.23–30; 1.67–5; 0.21–1; 0.11–12; 14.62–150	0.242; 0.233; 1.672; 0.208; 0.108; 14.611 mg/kg	0.64; 0.23; 0.81; 3.78; 4.15; 0.13	0.85; 0.75; 1.81; 4.12; 6.23; 1.43	n.r.	n.r.	96; 113; 94; 96; 108; 88	[65]
ASV											
Dry ashing	Pb, Cd	0.025: 0.025 mg/kg	0.9714; 0.9660	0.025–0.250; 0.025- 0.250	0.1595; 0.1557 mg/kg	n.r.	n.r.	n.r.	n.r.	n.r.	[71]
Wet digestion	Zn, Cd, Pb, Cu	0.00005; 0.00012; 0.00025; 0.00004 mg/kg	0.999; 0.9969; 0.9915;	0.0001–0.500; 0.0003–0.220; 0.0005–0.200;	0.0001; 0.0003; 0.0005; 0.0001 mg/kg	n.r.	n.r.	n.r.	n.r.	95; 96; 97; 98	[8]
Dry ophing		0 00072: 0 00106 malka	0.9989) n r		D r	.	.	D r	[70]
Dry ashing	PD, Cu	0.00072, 0.00106 mg/kg	0.9965, 0.9968	0.005-1.0, 0.005-1.0	/ 11.1.	11.1.	11.1.	11.1.	11.1.	11.1.	[70]
Dry ashing	Pb, Cd	0.02055; 0.02512 mg/kg	0.9367; 0.9442	0.040–0.090; 0.020–0.100	0.06226; 0.07612 mg/kg	n.r.	n.r.	n.r.	n.r.	n.r.	[72]
CSV											
Wet digestion	Se	0.00014 mg/kg	0.9965	0.0004–0120	0.0004 mg/kg	n.r.	n.r.	n.r.	n.r.	91	[13]

Table 2. Performance parameters of various analytical techniques (continued)

n.r: not reported; RSD_r: relative standard deviation for repeatability; CV_r: coefficient of variation for repeatability; RSD_R: relative standard deviation for reproducibility; CV_R: coefficient of variation for reproducibility; ICP-MS: inductively coupled plasma-mass spectrometry; ICP-OES: inductively coupled plasma-optical emission spectrometry; F-AAS: flame atomic absorption spectrometry; GF-AAS: graphite furnace atomic absorption spectrometry; HG-AAS: hydride generation atomic absorption spectrometry; CV-AAS: cold vapor atomic absorption spectrometry; XRF: X-ray fluorescence; TXRF: total reflection X-ray fluorescence; HDXRF: high-definition X-ray fluorescence; ASV: anodic stripping voltammetry; CSV: cathodic stripping voltammetry; LOD: limit of detection; LOQ: limit of quantification; R²: coefficients of determination

ICP-OES, as a multi-element method, has been used to evaluate various toxic metals in different food products, such us fruit juices, canned fruits [29], vegetables [30], honey [31], chicken [32], and nuts [28] (Table 1). It was demonstrated that in 97.22% of fruit juice samples, Pb concentration exceeded the Codex limit of 50 µg/kg, while in all canned fruit samples, it remained below the legal limit of the Codex standard (1000 µg/kg) [29]. Additionally, Sn levels in all samples were below the Codex legal limit, with fruit juices at 100 mg/kg and fruit preserves at 250 mg/kg. Hazelnut samples showed the highest Al contamination, especially given that some studies suggest an upper limit of 6 mg per day for Al intake, beyond which toxicity can occur [28]. Alarmingly higher concentrations of As, Pb, Cd, Cr, and Hg were also detected in both tomato and cabbage samples analyzed [30]. Certain Pb concentrations in honey samples exceeded standard levels, while Cd levels were below recommended limits [31]. The highest metal concentrations were obtained in liver samples [32]. Conversely, the lowest levels of Cd, Cu, Fe, Ni, and Zn were detected in meat samples, while gizzard samples showed the highest small amount of Pb. The high levels of heavy metals in the liver can be attributed to their role in the detoxification and storage of heavy metals to substantial levels [32].

The performance parameters of this method are detailed in Table 2. The limits of detection and quantification varied between 0.00005–0.034 mg/kg and 0.00016–0.043 mg/kg, respectively. As shown in Table 2, Karimi et al. [33] achieved regression coefficients between 0.9891 and 0.9899 for Cd and Hg, using a concentration range of 0.0003–1.200 mg/kg. Intermediate precision and precision, expressed as %RSD, using an internal reference material, ranged from 0.961% to 4.104%. Recovery percentages for tested elements by using different CRMs varied between 94.73 [27] and 109.4 [26]. It should be noted that Khan et al. [26] achieved significantly low recovery values for Se. For Cd, the recovery percentage was approximately 92%, slightly lower than those obtained for Cd using ICP-MS with the same reference material [24]. Extended uncertainty demonstrated by Giraldo et al. [24] for Cd analysis was less than 1% for all three concentration ranges (0.001–0.005 mg/kg, 0.010–0.050 mg/kg, and 0.100–0.500 mg/kg). These findings indicate the suitability of this method to quantify the potentially harmful metals in food products.

Atomic absorption spectrometry

Atomic absorption spectrometry (AAS) is one of the earliest commercially developed methods for the elemental analysis of multi-elements (both metals and metalloids) in all types of samples (environmental, biological, industrial, etc.), through the absorption of characteristic spectral lines by atomic vapors generated from a substance [6, 14]. This technique consists of five primary components: a light source, an atomization system, a spectroscopy system, a detection system, and a display unit. The operating principle can be simplified as follows: the atomizer transforms the liquid sample into atomic vapor under high temperatures; atomic vapor irradiated by using a light source, has the capability to absorb radiation at a specific wavelength for each element; the spectroscopic system distinguishes between different spectral lines; the content of the element to be measured in the sample is proportional to the amount of light absorbed [6, 14].

Based on the atomization device used, AAS can be classified into: GF-AAS, F-AAS, CV-AAS, and HG-AAS. Hence, proper digestion techniques are essential for the maximal extraction of specific metals from different samples [6]. Among these techniques, F-AAS and GF-AAS are commonly utilized in many analytical laboratories [9]. Although newer techniques for heavy metal detection have been developed, AAS continues to be a potent tool in analyzing elemental metals in plants and conducting trace analysis, primarily due to the multiple benefits, like high selectivity, accuracy, sensitivity, low interferences, good repeatability, low price, easy to operate, and fastness, which can be used for an extensive range of analyses [6]. Regarding the drawbacks, compared with ICP-OES, ICP-AES, or ICP-MS, AAS technologies can offer single-element analysis, offer a restricted analytical range, involve the use of flammable gases, and require a higher sample volume [9, 14].

F-AAS

The flame technique is considered a proper technique due to its simplicity and speed, making it suitable for determining metals at part per million (ppm) concentration levels from samples with ample analyte content [14, 19]. Also, it is one of the most widely used methods utilized for detecting trace metal ions and is preferred when analyzing a limited number of metals in a sample [17].

F-AAS offers air-acetylene and/or nitrous oxide flame atomizers. The sample, introduced into the flame, as an aerosol by the nebulizer, is dissociated into constituent atoms, which partially absorb the electromagnetic radiation in the ultra-violet visible spectroscopy (UV/Vis) part of the spectrum. This technique cand be used to assess the concentrations of trace metals directly in various samples [18, 19].

The main drawback of F-AAS analysis for solid samples is related to the sample pretreatment process, which is often time-consuming and problematic. This step often involves challenges such as incomplete dissolution, precipitation of insoluble analytes, loss of metals during heating, and contamination. The overall concentration of the analyte can be assessed after acid digestion or alkali fusion. Although microwave-assisted sample dissolution is commonly used, it can cause some challenges, including cost, short lifespan of digestion vessels, risk of explosions, potential losses and contamination, extended cooling periods, limited sample throughput, corrosion of microwave components, and the need for constant

supervision during digestion, which are exaggerated during trace metals analysis. The optimal method for analyzing solid samples would involve eliminating the sample dissolution, through minimizing sample preparation and enhancing analytical results [18]. Although F-AAS is generally considered to be free from interferences, some distinct spectral and non-spectral interferences can appear during the process [14]. This can be achieved through the use of an appropriate modifier mixture and carefully optimized pyrolysis and atomization temperatures, which can mitigate background absorption resulting from the complex matrix [18]. However, the main drawback of F-AAS is its restriction to single-element detection and the range of linear responses, despite its ability to provide good precision for many metals [9].

Contrary to the presented challenges, this technique is considered advantageous, due to its relative simplicity and low cost of equipment [17] and low operation costs, good analytical performance [14, 17]. The F-AAS technique provides rapid analysis, typically within 10–15 seconds per sample, and demonstrates excellent precision in terms of repeatability [19].

F-AAS has been successfully applied for determining heavy metals from various matrices. However, certain metals such as As and Zr may pose some challenges for F-AAS analysis because the equipment can't provide such a high temperature to induce complete atomization [19]. F-AAS can be used without prior analyte pre-concentration and is frequently employed to measure low concentrations of metals such as Al, Ca, Co, Cr, As, Cd, Cu, Fe, Mn, Ni, Pb, and Zn [17]. F-AAS has been utilized to assess the levels of trace metals in raw meat, liver [34], and food additives [35] (Table 1). The samples analyzed showed that the concentrations of Cd exceeded the MAC, except for Sonali chicken muscle meat. In addition, the levels of Cr, Pb, Ni, and Cu in the tested samples exceeded the MAC threshold [34]. The increased levels of chromium in poultry muscle could be attributed to the use of feed derived from tannery waste, which usually contains high levels of chromium. Iron levels in food additives are below the threshold set by FAO and WHO in 2009 (20 mg/kg). Also, the concentrations of Co, Ni, and Zn in all samples remain below the permissible limit defined by FAO and WHO in 1984. In contrast, the content of Mn in all food additive samples, except sumac, exceeds the permissible limit established by FAO and WHO in 1984 (> 4 mg/kg) [34]. This method is an accepted and widely used method for determining various trace metal ions from a great variety of food matrices and is highly recommended due to its relative simplicity and cost-effectiveness [35].

The performance parameters of this technique are detailed in Table 2. The detection and quantification limits ranged from 0.004–0.4823 mg/kg and 0.01–0.1727 mg/kg, respectively [36, 37]. The correlation coefficients for all investigated elements were above 0.99. The technique demonstrated improved recovery values for the elements studied, ranging from 87% to 104% according to Al-Massaedh et al. [38]. Notably, the method also showed enhanced regression coefficients and recovery values even at low concentration ranges (0.00001–0.005 mg/kg) compared to higher concentration ranges (0.01–10 mg/kg) investigated by Eka et al. [36] and Jasim et al. [37]. This method demonstrated sufficient accuracy and precision for the determination of these heavy metals in various food products, as demonstrated by acceptable recovery rates and low RSD values.

GF-AAS

The graphite furnace technique involves a high level of automation compared to other AAS techniques [14]. GF-AAS represents a suitable atomization method for assessing analyte concentrations in samples with precision at the ppb level [19]. The LOD for most metals, obtained through this technique typically falls in the micrograms per liter (μ g/L) or ppb range [14]. Although initial studies highlighted potential interferences, the GF-AAS technique become a highly reliable routine technique for trace metals analysis. The attractive characteristic of the graphite furnace is its capability for direct analysis of solid samples. In this case, the nebulization system that simplifies the introduction of solid material into the atomizer is absent [14]. In this method, samples are mixed with matrix modifiers prior to atomization processes. The utilization of matrix modifiers serves to stabilize the analyte and increase the volatility of the matrix, thus reducing chemical interference and improving the sensitivity of this method. The atomization process involves vaporizing the sample and dispersing it in a graphite tube (atomizer), a small cylindrical chamber

constructed of graphite. The graphite tube is heated to various temperatures in several steps, which include drying, calcination, and atomization, to remove the solvent and matrix components and to atomize the remaining sample. The atomized sample remains in the tube for a long time, increasing sensitivity. Afterward, the sample vapors are exposed to a beam of light, which excites the atoms present. The light absorbed by the atoms is then captured by a detector, and the intensity of light absorption is used to determine the concentration of the element in the sample [14, 17]. Many components of equipment required for GF-AAS and F-AAS are similar. Both methods use the same light source, background correction system, monochromator or polychromator line isolator, photomultiplier or charge-coupled device detector, and readout system. The main distinction lies in the atomization of the sample: GF-AAS uses a graphite furnace, while F-AAS uses an acetylene/air flame. GF-AAS is particularly advantageous for direct analysis of solid materials due to the lack of a nebulization system, which simplifies the addition of solid samples to the atomizer. In addition, GF-AAS operates at significantly higher atomization temperatures, up to 3000 K, distinguishing it from F-AAS [17, 19]. GF-AAS is the most widely used analytical tool for trace metal analysis due to several advantages, including cost-effectiveness, simplicity, substantial accuracy, higher sensitivity, lower detection limits, and relatively short analysis time. In addition, GF-AAS allows the removal of sample matrices by adding the matrix modifier prior to analyte atomization, providing greater flexibility for the analysis of samples with complex organic matrices [15]. The graphite furnace system is also suitable for the determination of metals in different matrices [14]. GF-AAS revealed excellent detection limits for most metals despite the small sample size of 20 μ L required for analysis [19]. Nevertheless, the method does have its drawbacks, including a restricted working range, slow analysis, and high cost [19]. Moreover, a graphite furnace is approximately 100-1000 times more sensitive compared with F-AAS under the same radiation sources [9], which involves supplementary costs for graphite furnace purchase. As examples of its application, GF-AAS has been used to analyze the content of toxic metals in milk, cheese [39], eggs, multifloral honey [40], vegetables [41], raw meat, liver [34], edible seeds [42], and edible oils [43]. As indicated in Table 2, high levels of Cd were detected in liver samples [34], and of Pb in raw meat and liver [34]. The concentrations of Pb and Cd in eggs exceeded the limits stipulated by Chinese regulations of 0.2 µg/g, and 0.05 µg/g, for Pb and Cd, respectively [40]. In contrast, Pb concentrations in honey were lower compared to the Chinese regulation of $1 \mu g/g$. Pan et al. [41] demonstrated that only 0.25% of samples for Cd and 1.56% for Pb were higher than the MAC values. It was demonstrated that the levels of Cd found in both whole pumpkin and roasted and raw sunflower seed samples exceeded the maximum acceptable limit of 100 µg kg⁻¹ for grains established by the Codex Alimentarius Commission [42]. The results presented in Table 2 indicated excellent linearity ($R^2 > 0.997$) of the calibration curves at various concentration levels for different toxic metals, reflecting the high accuracy and reliability of the obtained results. The LOD and limit of quantification (LOQ) values ranged from 0.0000003 mg/kg to 0.11 mg/kg and 0.000001 mg/kg to 0.38 mg/kg, respectively [43]. The coefficient of variation (%CV) for repeatability and reproducibility ranged from 4.90 to 9.12 and 6.69 to 9.11, respectively, indicating good precision of the method. The recovery percentages varied between 79.4% and 111% [44], suggesting accurate measurement capabilities. The measurement uncertainty demonstrated by Hossain et al. [45] and Ullah et al. [46] ranged between 4.43 and 15.8, underscoring the reliability of the method (Table 2).

HG-AAS

HG-AAS stands as one of the common methods for measuring arsenic levels from different sample types. This technique is a powerful approach which involves chemical reagents possessing characteristic properties of metalloid metals [47]. In HG, a reducing agent such as sodium borohydride (NaBH₄) and hydrochloric acid (HCl) are typically used to transform metalloids from aqueous solutions into volatile hydrides [48]. These hydrides are then transported using an inert gas stream to the atomizer, which is typically a heated quartz cell in F-AAS [47]. Within the quartz cell, the hydrides are converted into gaseous metalloid analyte atoms in the presence of a source lamp, and a signal is generated by measuring the amount of light absorbed [19]. The degree of the reaction depends on the conditions, but all of the inorganic arsenic iAs in a solution can be transformed into arsine (AsH₃) and transferred to the vapor phase [48]. By using the specificity of HG in various reaction media, iAs speciation can be performed. For example, the

specific iAs can be quantified by pre-reducing inorganic As(V) (by using ascorbic acid and potassium iodide) or oxidation of As(III) to As(V) (by using hydrogen peroxide). This selective HG approach has been previously employed in arsenic speciation in several kinds of samples (e.g., biological tissues, food, and drinking water) [48].

The primary benefits of HG-AAS technique are related to the simplicity, low detection limits for hydride-forming metals and mitigated matrix effects, and fast measurement (30–50 seconds per sample) [19, 47]. Regarding the limitations of the method, these are primarily associated with interferences within the matrices. Various studies have highlighted interferences such as transition metals, mutual hydride-forming metals, and the conditioning of the quartz cell surface, which can minimize the effectiveness of the HG-AAS technique. Besides this, the HG-AAS technique is restricted to certain metals, such as As, Bi, Sb, Se, Te, Ge, and Sn which are able to form volatile hydrides [47]. The accuracy of the results is influenced by various parameters, including the valence of the analyte, gas pressures, acid concentration, and cell temperature. Additionally, to achieve high-quality data in this technique high-skill operators are required [19]. Despite its limitations, HG-AAS has been utilized to evaluate the content of Hg in milk and cheese [39], As and Hg in vegetables [41], As in rice [48], and As and Hg in bread, sweets, and wheat [4]. Higher levels of As were observed in bread (3.404–6.453 mg/kg) and sweets (3.404–12.280 mg/kg) [4]. Regarding Hg, increased concentrations were found in vegetables (up to 0.0159 mg/kg) [41], compared to the levels of Hg from other food matrices presented in Table 1.

The limits of detection and quantification ranged between 0.0000033–0.02 mg/kg and 0.000001–0.04 mg/kg, respectively [43, 49]. The regression coefficient obtained for various concentration ranges (0.0005–0.87 mg/kg) was higher than 0.994. The method's repeatability ranged from 0.35% to 19.6%, and the precision was 7.5%. Accuracy, evaluated by analyzing various CRMs, revealed recovery values between 92% and 118% [49]. The results presented in Table 2 demonstrate that this method is valid and reliable for detecting various toxic metals, such as As, Hg, and Se.

CV-AAS

CV-AAS is employed for the determination of metals capable of forming hydrides or volatile species. This technique uses a chemical vapor generation system which is applied for various samples [18]. Presently, this method is considered the most sensitive and reliable technique for determining very low concentrations of mercury by AAS. The LOD for mercury with this method is approximately 0.02 μ g/L, being an alternative option for achieving even lower detection limits. The cold vapor technique can provide higher sensitivity compared to conventional flame AAS [14]. Mercury has a unique characteristic that allows its vapor to be measured at room temperature [19].

CV-AAS is a flameless AAS technique used for mercury assess, based on the absorption of radiation at 253.7 nm by mercury vapor. Mercury is initially reduced to its elemental state using a strong reducing agent such as NaBH₄ or stannous chloride. Subsequently, the mercury vapor is driven by an argon carrier gas to the absorption cell (atomizer), positioned in the light path of the AAS equipment [19]. Direct transfer of volatile compounds to the atomizer can increase the sensitivity of the method by eliminating additional steps before atomization [18].

This technique is considered advantageous due to the use of large sample volumes that contain a greater amount of mercury atoms that improve sensitivity [14]. Additionally, this method is characterized by low detection limits, rapid measurements (30–50 seconds per sample), and minimal interference [19].

The primary limitation of this method is related to its specificity to mercury determination, due to the incapability of other metals to achieve a volatile-free atomic state at room temperature through chemical reduction [14]. Additionally, the analytical procedures can be laborious and involve high consumption of chemical reagents [19].

However, CV-AAS was utilized to assess the presence of toxic metals in milk and cheese [39], fish [50], canned fish [51], and fruits [52]. Elevated levels were observed for Hg in fish (0.093–0.182 mg/kg) [50] and canned fish (< 0.0005–0.199 mg/kg) [51] compared to other matrices listed in Table 1. Mercury levels in

the fish samples were below the maximum permissible limits set by the WHO, which specify levels of less than 0.5 μ g/g wet fresh weight [50]. Furthermore, these levels were lower than those imposed by Regulation 2023/915 [8]. Mercury concentration in the majority of fish species was below the 0.5 mg/kg (500 ng/g) limit recommended by the FAO/WHO, based on wet weight [51]. The levels of Pb, Cd, As, Hg, and Sn detected in the examined fruits were below the established limits [52].

The proposed method exhibited linearity in the concentration range of 0.00005–0.0948 mg/kg [53], with coefficients of determination (R²) exceeding 0.99. Recoveries from fortified samples or CRMs ranged from 90.1–107.98% [54], with repeatability and reproducibility expressed as RSD between 1.5–12.70% and 1.7–13.27%, respectively [54, 55]. The LOD and LOQ values ranged between 0.0001–0.0284 mg/kg and 0.0003–0.0948 mg/kg, respectively [53]. Perelonia et al. [15], demonstrated an expanded relative uncertainty of less than 8.96%. These results confirmed the accuracy and performance of the method.

X-ray fluorescence

X-ray fluorescence (XRF) is a spectrochemical method used for both identification of elemental composition and quantitative analysis of diverse inorganic materials. The obtained results can be presented as atom percent or weight percent. The needed quantity of sample for chemical analysis depends on the method employed, and the instrumentation, ranging from a few tens of milligrams (approximately 40 mg) to around 12 g [56]. XRF is a physical phenomenon that takes place when high-intensity X-ray radiation generated by an X-ray tube interacts with the sample. Furthermore, this radiation can displace one or more tightly bound electrons from the inner orbitals, leading to the atom becoming unstable. Electrons from outer shells promptly fill the resulting vacancies in the lower orbitals, releasing energy in the form of X-rays. Since the energy levels of electrons vary for each element, the energy of the XRF peak can be linked to a specific element [17, 19]. The energy distribution is measured by an energy-dispersive detector, which can assess the metals present in the sample and their relative concentrations [17]. XRF is an elemental analysis technique that covers o wide range of metals, from sodium to uranium, from various matrices and typically requires minimal sample preparation [19]. XRF spectrometers are commonly used to detect metals with atomic numbers from 4 (beryllium) to 92 (uranium), detecting concentrations ranging from 0.1 μ g/g to high percentage levels [17]. The XRF spectrometer includes a radiation (X-ray) source, sample chamber, detector, and computer for data processing [19]. XRF is an advantageous and reliable method used for obtaining detailed elemental information due to its non-destructive nature and continuous readings. The optimized operational parameters cand improve the detection limits and the detection efficiency. Compared with multi-element techniques like ICP-MS/ICP-OES, XRF can offer also, other important advantages, like including minimal sample preparation for solid samples non-destructive analysis, increased overall speed, reduced generation of hazardous waste, and lower operational costs [17].

The sensitivity of XRF depends on factors such as the energy of the incident radiation, instrument geometry, and detector efficiency. Precision in XRF measurements is limited by the nature of detected photons. Also, detection limits are influenced by instrument sensitivity and the background level of the sample matrix. The lack of robustness in calibration methods contributes to substantial systematic errors, that can be significant when the analyzed quantities are very small [18]. Based on the XRF principle, polarized X-ray fluorescence (PXRF), TXRF, or high-definition X-ray fluorescence (HDXRF), synchrotron radiation X-ray fluorescence (SRXRF) was developed. The PXRF and TXRF methods revealed improved peak-to-background ratios. In this case, an electron from the inner orbitals of the target atoms can be rejected after its exposure to photons or charged particles (electrons or ions) with energies higher than the binding energy of the bound inner electrons. TXRF uses radiation that is incident on the tested samples, at an angle below the critical angle, ensuring the complete reflection back [17]. SRXRF is a highly efficient method due to its ability to detect multiple metals, precision, sensitivity, minimal sample preparation requirements, and relatively short analysis time [57]. EDXRF technique was used to evaluate the levels of trace elements in milk and milk products [58, 59], vegetables [60], leafy vegetables [60], pulses [58, 61], eggs, fish [58], cereals [58, 61], and meat [58]. Elevated concentrations were found for Pb in leafy vegetables (0.5-12.3 mg/kg) [60] and for As in leafy vegetables (0.09-1.4 mg/kg) [60] and cereals [61] (Table 1). Additionally, the levels of Fe, Ni, and Cd in both food and plant samples exceeded the WHO/FAO permissible limits, while the concentrations of As, Mo, and Co exceeded the permissible limits only in the plant samples [61]. TXRF and SRXRF techniques were involved in the detection of various toxic and trace metals from rice [62] and coriander leaf and seeds [57]. The highest lead concentration detected in pulses was below the maximum permissible limit [58]. The accumulation of Zn, Mn, Cr, As, and Pb in the studied vegetables exceeded the maximum tolerable levels recommended by the Joint FAO/WHO Expert Committee on Food Additives (1999) [63]. In contrast, the levels of copper, iron, cobalt, and nickel were below the required limits [60]. The findings for Fe, Cu, Zn, and Pb were within the safe limits established by WHO/FAO [61].

Table 2 presents excellent analytical performance in validating the XRF method for detecting various heavy metals. The LODs ranged from 0.00005 mg/kg to 4.383 mg/kg, with corresponding LOQs from 0.00016 mg/kg to 14.611 mg/kg [64, 65]. Calibration curves showed good linearity for all metals ($R^2 > 0.999$) using the TXRF method [64], although the linearity was lower for the HDXRF technique [65]. Wang et al. [65] and Beltrán et al. [66] demonstrated excellent accuracy, with percent recoveries ranging from 91% to 108% for real and spiked samples. Nurhain et al. [64] reported lower recovery values between 61.73% and 99.65%. The repeatability and reproducibility of this technique, expressed as RSD, were between 0.13–11.05% and 0.75–6.23%, respectively. These results indicate that the XRF technique is a valuable tool for detecting heavy metals in food products [67].

Stripping voltammetry

Stripping voltammetry (SV) is a useful electroanalytical technique involved in trace metal detection and quantification. This method involves two main steps. In the first step of electrolysis/deposition, the analyte accumulates through faradic processes (anodic or cathodic) or non-faradic processes (adsorptive), at the surface of the working electrode over a specified period. The time of this preconcentration phase depends on the concentration of the analyte in the solution. In this way, lower element concentrations require longer accumulation times until a sufficient amount of sample is on the electrode surface. Accumulation increases with time rather than with the concentration of the element in the sample, allowing extremely low detection limits to be achieved. The first preconcentration phase is followed by a stripping step, in which the previously accumulated metal is released into the solution by applying an anodic potential. The resulting current during the stripping process is directly proportional to the metal concentration in the water sample. In the electrolysis step, the analyte of interest and the other metals that can be reduced at this deposition potential are reduced at the working electrode. When a low deposition potential is used under acidic conditions, hydrogen is generated at the surface of the working electrode by proton reduction, while oxidants are produced at the auxiliary electrode. Hydrogen production presents challenges because it can block the electrode surface, compromise reproducibility, and increase the noise level of voltammograms, but the new equipment contains a rotating electrode to avoid the problem of hydrogen bubble obstruction [18]. The advantages of this technique include remarkably low detection limits, high sensitivity, and the capability to detect trace metals in different oxidation states. Additionally, the portability of instrumentation, rapid analysis capabilities, and relatively low costs for basic instrumentation and operation should also be mentioned [18, 19]. SV also facilitates the analysis of speciation, because the deposition of different oxidation states of a given element usually occurs at distinct potentials [67]. As concerning the limitations of this technique, one issue is related to the presence of its toxic soluble salts released by the mercury film electrode [18]. Besides this, thin film mercury electrodes may provide lower LOD [19]. For this reason, nonmercurial electrodes like electropolymerized polymer film, boron-doped diamond, bismuth, antimony, as well as silver or gold electrodes can be used as alternatives to the mercury electrode. The detection of multiple metals by stripping analysis poses challenges due to overlapping potential peaks in the narrow potential range where metals undergo reduction or oxidation processes. However, there are methods for the simultaneous detection of arsenic, copper, lead, and mercury in the presence of oxygen using differential pulse ASV with a vibrating gold microwire electrode, allowing analysis without the need for deoxygenation. This aspect simplified the stripping process and reduced the measurement time. Under acidic conditions, the applicability of SV is constrained at relatively high

deposition potentials because of the interfering effects of the hydrogen generation at the working electrode [18].

Depending on the nature and direction of the preconcentration and stripping phases, voltammetry can be anodic, cathodic, and adsorptive SV. Besides these, other less common stripping methodologies are used which include potentiometric stripping analysis (which, although not a voltametric technique, is based on similar deposition mechanisms as SV) and abrasive SV [68]. Concerning SV methodologies, ASV and CSV were employed for the analysis of diverse harmful and trace metals in cheese, yogurt [13], and rice [69]. The findings of these studies revealed decreased concentrations of the examined metals. Most of the metal concentrations analyzed were below internationally accepted limits, indicating no health concern [13].

Table 2 highlights the excellent analytical performance of the ASV and CSV methods for detecting various heavy metals. In the case of ASV methods, the LODs ranged from 0.00005 mg/kg to 0.02512 mg/kg, with corresponding LOQs from 0.0001 mg/kg to 0.500 mg/kg. Calibration curves exhibited good linearity for all metals ($R^2 > 0.990$) [70], except the results obtained by Palisoc et al. [71, 72], which obtained coefficients of regression between 0.9367 and 0.9714. As concerning the accuracy of the method, Shahbazi et al. [13], demonstrated excellent percent recoveries for Zn, Cd, Pb, and Cu ranging from 95% to 98%. The obtained results demonstrated the suitability of this method for the quantification of potentially toxic metals [13]. Regarding the CSV method, Shahbazi et al. [13] demonstrated enhanced performance parameters for the detection of Se. The LOD and LOQ were 0.00014 mg/kg and 0.0004 mg/kg, respectively, within a linear range of 0.0004 mg/kg to 0.120 mg/kg. Also, the method also proved its accuracy with a recovery rate of 91% [13]. Due to the complex matrix of the samples, it is evident that no single analytical technique can be employed to determine all metals present in the sample. One of the primary criteria for selecting an analytical method is related to the LOD, because AAS and XRF methods enable determination at the ppm level, ICP-OES and GF-AAS permit analysis at the ppb level, and only ICP-MS can detect very low concentrations in the ppt range. Another important criterion is the capability of the technique to analyze multiple metals simultaneously. ICP-MS, ICP-AES, and ICP-OES are multielement techniques, compared with AAS, which is limited in terms of multielement analysis, but is cost-effective and requires less maintenance compared to other techniques. Besides this, attention must be given to non-spectral and spectral interferences in measurements conducted by techniques such as ICP-AES, ICP-MS, and AAS. For this reason, the samples must be subjected to digestion or at least dilution processes to reduce the presence of interfering compounds before analysis [17].

Sample digestion is a critical step in elemental analysis due to the risk of contamination and analyte loss, which can lead to systematic errors. Traditional dry ashing and wet digestion are commonly used procedures for organic matter digestion in samples. Effective sample digestion procedures can reduce the chances of significant loss or contamination. Dry ashing methods often result in significant loss or contamination and are therefore unsuitable for analyzing minor and trace elements like Mo, Se, and Cr. In contrast, wet digestion methods, such as using a heating block or microwave, yield good recoveries and are considered effective for sample preparation [26]. Errors during sample preparation can be minimized by using appropriate ashing methods, proper digestion acids, and high-purity acids [17].

Regarding wet digestion, the results presented by Helal Uddin et al. [73], revealed that using HNO₃ and HCl in a 1:3 ratio was the most efficient digestion method. It provided significantly higher recoveries (P < 0.05) for all metals compared to using HNO₃ alone or HNO₃ and HClO₄ in a 2:1 ratio. The recovery values obtained by Akinyele and Shokunbi [74] from both dry-ashed and wet-digested samples were nearly quantitative (> 90%), except for chromium analysis, where recoveries were around 80%. In most spiked samples, the obtained results demonstrated that dry-ashed samples had slightly higher recovery rates. Based on these results, the authors consider the dry ashing method can be more sensitive than the wet digestion method. Additionally, they recommend the dry ashing method for four reasons: it is cost-effective, involves fewer risks associated with chemical usage, requires simple equipment (muffle furnace) that is easy to handle, and achieves better recovery in the samples [74].

Yang et al. [75] demonstrated that microwave-assisted digestion yielded improved recovery values for CRMs compared to dry ashing and wet digestion methods, due to the several advantages over conventional wet ashing and dry ashing procedures, which were more time-consuming and complicated without providing any additional benefits in digestion efficiency. The microwave digestion procedure is simpler, more effective, faster, and less prone to contamination [75]. As shown in Table 2, microwave-assisted digestion was the most commonly used technique across all analytical methods, likely due to its numerous advantages.

The levels of heavy metals in food products are affected by various factors, such as the type and variety of plants, their bioavailability, cultivation methods, environmental conditions, and their ability to bioaccumulate [9]. In addition, post-harvest practices, including storage, packaging, and cooking techniques, play a significant role. Practices such as washing after harvest usually remove metal contaminants, while cooking can either decrease or increase metal content [76]. The high concentrations of As, Pb, Cd, Cr, and Hg detected in both tomato and cabbage samples were associated with high levels of these metals in agricultural soil [30].

Contamination observed in fruits can be correlated with soil and water contamination during growth, water use during processing, equipment safety failures, and potential migration of heavy metals from packaging [29]. Similarly, increased levels of toxic metals found in milk and milk products could be attributed to increased soil and water exposure to lead sources near hazardous waste sites [39]. In addition, the geographical region of the tested samples affects the concentrations of harmful or trace metals. Certain metals showed higher concentrations in the Eastern region due to the presence of more industries there [31]. Similarly, heavy metal content in rural samples was high compared to urban samples [4]. Also, the highest levels of mercury were detected in imported dried apples compared to those from local sources [52].

Moreover, the information provided in Table 1 highlights the importance of monitoring food composition and establishing regulations and thresholds for contaminants in globally traded foods. This effort aims to ensure food safety and promote a healthy diet [42].

Risk assessment of potentially toxic metals from food products

The quality of food has received significant attention due to its impact on nutrition and human health. The presence of essential and toxic metals in food products is crucial, as their concentrations can have both positive and negative effects on human health [77]. The HRA proposed by the U.S. Environmental Protection Agency (US EPA) is a valuable tool that offers a comprehensive methodology to evaluate the potential health risks associated with exposure to specific chemical contaminants. This approach involves the evaluation of various parameters, including the dose of exposure and the assess of both non-CRs and CRs. Non-carcinogenic analysis represents the probability of adverse health effects resulting from exposure to a particular contaminant within a defined period and involves the hazard quotient (HQ) and hazard index (HI)/total hazard quotient (THQ) parameters. CR estimates the probability of an individual developing a type of cancer during the lifetime after exposure to the potential carcinogen [78]. Estimated daily intake (EDI) of Fe, Zn, Cu, Sn, Pb, and Cd concentrations from processed seafood products are lower than the imposed tolerable daily intake (TDI) values. As a result, both the non-carcinogenic (HQ and THQ) and CR analyses indicated no risk to consumer health [21].

EDI values of As, Cd, Pb, Cr, Mn, Ni, Cu, and Zn from fruits and vegetables were below the maximum tolerable daily intake (MTDI) values. Exception Mn and Cu, the values of HQ were lower than the threshold value (1), suggesting no health hazards for the adult population. In the case of fruits, the value of HI was also lower than the imposed limit, but, for vegetables, the value of this parameter was > 1 (3.727), suggesting non-carcinogenic adverse health effects after vegetable consumption. Regarding the carcinogenic analysis, the obtained results indicated the risk of Pb-induced carcinogenesis [79]. The EDI of Zn, Cu, Pb, and Cd from parsley, kohlrabi, and lettuce indicated a high ingestion rate of toxic metals in rural areas compared with urban areas, most probably due to the cultivation area placed close to non-ferrous

metallurgical plants. Additionally, the THQ of tested metals was higher than the imposed limit, which indicates that those consumers may experience major health risks after consumption of investigated samples [80].

EDI values of As, Cd, Hg, and Ni from tomato and cabbage were below the MTDI [30]. However, the HQ values for As and Hg in tomato, and for As, Hg, and Co in cabbage, exceeded 1. The HI value of target contaminants was higher than the imposed limit, indicating possible adverse health effects for the adult population. The total cancer risk (TCR) analysis revealed potential adverse cancer risks associated with As, Cd, Hg, and Ni from the consumption of both tomato and cabbage. HQ values of As and Pb from vegetables were below 1, indicating insignificant health hazards for consumers. However, the THQ of the tested metals exceeded the imposed limit, which signifies a potential non-carcinogenic health risk for highly-exposed humans. Additionally, the levels of As and Pb from vegetables suggested CR. Contrary, HI values of As, Cd, Cr, Pb, Ni, and Hg in vegetables were reported lower than the imposed limit, indicating a very low health risk associated with the ingestion of the tested samples [41]. The study conducted by Mokarram et al. [81] revealed that the levels of contaminants in vegetables from the southern regions of Nigeria, including Cd, Pb, Zn, Hg, and Ni, exceeded the permissible concentrations. The THQ values for Pb exceeded 1 in all four stages, indicating a significant risk of non-carcinogenic hazards. Additionally, the plant samples exhibited elevated HI values during various growth stages (7.37 during growth, 79.24 during flowering, and 78.85 and 73.1 during fruiting), suggesting unsuitable conditions for cultivating these species in the studied region.

The EDI values of Cd, Pb, and Cr associated with the consumption of various animal edible organs were higher than the MTDI. The HI values of tested metals were higher for children compared with adults, indicating potential non-carcinogenic health issues for children. Also, the cancer risk of Cd in tested samples was higher than the reference value for adults and children, suggesting a potential cancer risk [34]. HQ and HI values of Pb, Cd, As, Ni, Cu, Fe, and Zn in the chicken meat and edible giblets were below the set limit, indicating no risk associated with tested sample consumption [32]. Contrary, the cancer risk analysis demonstrated that 54% of samples exceeded the acceptable level. In the case of milk samples, excepting Hg, the non-carcinogenic analysis of tested metals (Cr, Mn, Ni, Cu, Zn, As, Cd, Hg, Pb, and Fe) was below the safe limit (< 1.0) or close to the safe limit (\leq 1.0). Concerning the metal pollution index (MPI) values, the obtained results indicated elevated levels for powdered milk compared to the other tested samples [59]. A potential non-CR of Pb, As, and Cd especially, for infants associated with honey and egg consumption from 3 polluted areas was demonstrated. The EDI levels exceeded the permissible limits in infants for Pb, As, and Cd in honey, as well as for Cd in eggs. Based on EDI levels, the HI values were higher than the safe limit for children for all tested samples [40].

Most research studies focused on heavy metals detection from food products provided recommendations to prevent and control environmental pollution but did not formulate frameworks for managing health risks. Developing a such framework would be useful for preventing and controlling specific health issues and improving overall health outcomes [82]. Prevention of chemical contaminants in food has been a major challenge for both the food industry and regulatory bodies, given their potential to cause various adverse effects on human health. Monitoring chemical contaminants in food is crucial to ensuring food safety and quality, especially in developing countries where there are significant gaps in the process of monitoring and controlling chemical contaminants. Moreover, further research is needed on the toxicological consequences of food contamination, particularly in developing countries, which involves examining the transmission of chemical toxicants from farm to plate and understanding the impact of environmental factors on food contamination. Risk assessment will be essential in protecting food safety by assessing potential hazards related to chemical contaminants in food products. By conducting these assessments, policymakers and regulatory bodies can make informed choices about food safety standards and develop appropriate control measures to protect public health. Also, gaps in existing regulations on monitoring chemical contaminants in food, especially in developing countries, imply a lack of precise guidelines and legislation on permissible limits for different contaminants. These discrepancies pose

challenges in ensuring food safety and can lead to discrepancies in safety standards between different countries [82, 83].

Conclusions

Over time, growing concern has emerged regarding the presence of chemical contaminants in food due to their potential adverse effects on human health. These contaminants can infiltrate the food supply chain, posing significant risks to consumers upon ingestion.

Literature reviews consistently reveal increasing levels of contamination across various food types and from diverse sources. Particularly concerning are data focusing on both carcinogenic and noncarcinogenic aspects, highlighting the potential health risks associated with prolonged exposure to these contaminants.

The data presented in this study illustrate a range of analytical methods available for the detection and quantification of these chemical contaminants. Moreover, the performance parameters outlined herein underscore the reliability and suitability of the investigated methods for identifying potentially harmful metals in food products. The literature data presented in Table 1 and Table 2 suggest that ICP-MS is a more sensitive and effective technique which can be used for the simultaneous analysis of trace elements compared to other analytical techniques.

As a vital recommendation, it is imperative for governments and national authorities to enhance food testing and control measures. Encouraging compliance, particularly within industries such as agriculture, is essential in mitigating the risks posed by chemical contaminants and ensuring food safety for all.

Abbreviations

AAS: Atomic absorption spectrometry ASV: anodic stripping voltammetry CR: carcinogenic risk CRMs: certified reference materials CV-AAS: cold vapor atomic absorption spectrometry EDI: estimated daily intake F-AAS: flame atomic absorption spectrometry FAO: Food and Agriculture Organization of the United Nations GF-AAS: graphite furnace atomic absorption spectrometry HG: hydride generation HG-AAS: hydride generation atomic absorption spectrometry HI: hazard index HQ: hazard quotient ICP-AES: inductively coupled plasma-atomic emission spectrometry ICP-MS: inductively coupled plasma-mass spectrometry ICP-OES: inductively coupled plasma-optical emission spectrometry LOD: limit of detection LOQ: limit of quantification MAC: maximum allowable concentration MTDI: maximum tolerable daily intake ppb: parts per billion

R²: coefficients of determination SRXRF: synchrotron radiation X-ray fluorescence SV: stripping voltammetry THQ: total hazard quotient TXRF: total reflection X-ray fluorescence WHO: World Health Organization XRF: X-ray fluorescence

Declarations

Author contributions

ELU: Conceptualization, Investigation, Writing—original draft, Writing—review & editing. GM: Conceptualization, Writing—review & editing, Validation, Supervision. Both of the authors read and approved the submitted version.

Conflicts of interest

The authors declare that they have no conflicts of interest.

Ethical approval

Not applicable.

Consent to participate

Not applicable.

Consent to publication

Not applicable.

Availability of data and materials

Not applicable.

Funding

This work was supported by two grants from the Ministry of Research, Innovation and Digitization, CNCS/CCCDI - UEFISCDI [PN-IV-P8-8.1-PRE-HE-ORG-2023-00180165, PN-IV-P8-8.1-PRE-HE-ORG-2023-0168] within PNCDI IV. The funder had no role in study design, data collection and analysis, decision to publish, or preparation of the manuscript.

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