



Recent advances in instrumental techniques for heavy metal quantification

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Abstract Heavy metals (HMs) are ubiquitous; they are found in soil, water, air, and all biological matrices. The toxicity, bioaccumulation potential, and deleterious effects of most of these metals on humans and the environment have been widely documented. Consequently, the detection and quantification of HMs in various environmental samples have become a pressing issue. The analysis of the concentrations of HMs is a vital component of environmental monitoring; hence, the selection of the most suitable analytical technique for their determination has become a topic of great interest in food, environment, and

human health safety. Analytical techniques for the quantification of these metals have evolved. Presently, a broad range of HM analytical techniques are available with each having its outstanding merits as well as limitations. Most analytical scientists, therefore, adopt complementation of more than one method, with the choice influenced by the specific metal of interest, desired limits of detection and quantification, nature of the interference, level of sensitivity, and precision among others. Sequel to the above, this work comprehensively reviews the most recent advances in instrumental techniques for the determination of HMs.

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It gives a general overview of the concept of HMs, their sources, and why their accurate quantification is pertinent. It highlights various conventional and more advanced techniques for HM determination, and as one of its kind, it also gives special attention to the specific merits and demerits of the analytical techniques. Finally, it presents the most recent studies in this regard.

Keywords Advanced techniques · Determination · Concentration · Heavy metals · Interferences · Instrumental technique · Limits of detection

Introduction

The environment is incessantly being exposed to various chemical pollutants of which HMs make up a serious group of interest, which is a result of the skyrocketing trend in industrialization, urbanization, and other anthropogenic activities. Environmental contamination due to HMs has become an ecological catastrophe of alarming concern. HMs are generally seen as the primary and most prominent inorganic contaminants in the environment (Briffa et al., 2020). They are found in high abundance in the environment in varying concentrations. HM pollution has therefore become the topic of focus among various toxicological researchers as a result of their effects on human health and the environment at large. HMs are found naturally within the environment at trace concentrations that are within safe limits; their increasing concentrations are therefore primarily due to anthropogenic activities (Gaur et al., 2021).

HMs are those metallic elements that have high density and are toxic even at trace concentrations. HMs are usually characterized by their unique large atomic mass as well as density. Their densities are usually higher than 5 g cm^{-3} and they have serious deleterious impacts on human health and the ecosystem at large (Masindi & Muedi, 2018). HMs such as selenium, zinc, copper, and iron are essential in biological systems where they are seen as essential trace metals constituting the driving force for various metabolic processes in humans. They are also key components of coenzymes and cofactors in various biological systems. Some other HMs such as mercury, chromium, thallium, cadmium, lead, and arsenic do not have any known function in living systems but are rather toxic even at low contents. HMs are found in all areas of the environment in varying concentrations depending on their geological origin and human

activities going on in such areas. Some of the sources of HMs due to human activities include mining, combustion of fossil fuels, metallurgical processes, and pharmaceutical and electronic processes (Ali et al., 2019; Mathew et al., 2022). A high concentration of HMs in the environment calls for a serious concern due to their toxicity. HMs get into the soil from where they are washed and leached into various water bodies and eventually get into aquatic organisms and are passed along the food chain. They have also been linked to various degenerative diseases such as cancer, cardiovascular malfunctioning, and high toxicity to vital body organs such as the brain, liver, kidney, and lungs (Raimi et al., 2022).

The presence of these metals in concentrations that are greater than the allowed limits based on international standards can affect the activities of living organisms as well as the entire ecosystem. There is, therefore, a need for highly reliable techniques for their determination and quantification in water, air, soil, and biomaterials. These metals usually persist for a long time when present in the environment and are not easily degraded or acted upon by the activities of microorganisms. It has been well established that HMs tend to accumulate within tissues of various organisms in the aquatic and terrestrial environment; hence, the concentrations measured indicate the past exposure of the organisms to these metals (Balali-Mood et al., 2021).

There is a paramount need for highly simplified and precised methodologies for the quantification of the concentrations of HMs in various environmental matrices (Uddin et al., 2016). More recently, novel, highly robust, inexpensive, sensitive, and selective approaches have been developed for the quantification of HMs. The selection of a specific instrumental technique for the determination of HMs is affected by numerous factors such as selectivity, sensitivity, limits of detection, analysis time, preparation of the sample, and the cost-effectiveness of the technique. HM quantification is indispensable in various aspects of environmental and food monitoring such as analysis of wastewater, drinking water, food products, cosmetics, drugs, and composts due to the need to incessantly checkmate the safety levels of such products (Mejías & Garrido, 2016). On this note, various methods have been developed for the detection and quantification of these metals in the environment with some of these methods having their inherent challenges. Though some of the methods provided comprehensive details on the sensitivity and selectivity, they still had their specific setbacks, such as the tediousness in the aspect of the preparation

of samples, the high cost of operation, and the long duration for the analysis of samples (Bulska & Ruszczyńska, 2017). At present, there are novel and highly advanced techniques for the quantification of HMs in various environmental matrices with highly promising and reliable outcomes. This work aims to critically review the most recent advances in the instrumental detection and quantification of HMs in various environmental matrices. It gives a general overview of the concept of HMs, their sources, and why their accurate quantification is pertinent. It highlights various conventional and more advanced techniques for HM determination, and as one of its kind, it also gives special attention to the specific merits and demerits of the analytical techniques. Finally, it presents the future perspectives in this regard.

Concept of HMs

There are various definitions of HMs. They are metals having a specific gravity greater than 4 or 5. They are positioned around the atomic numbers 22–34 and 40–52 in the periodic table. They are generally considered metals that possess a density that is five times higher than the density of water. On the fundamental assumption that toxicity and heaviness are interconnected, HMs are extended to include metalloids such as arsenic. These metals are known to possess specific responses biologically. HMs are generally categorized into two groups: essential and non-essential metals. More than half of the existing HMs are known to be essential biologically due to their roles in the effective functioning of various metabolic processes in biological systems (Raimi et al., 2022). Such trace metals are needed in trace amounts (< 10 parts per million). When these essential trace metals are absent some deficiency symptoms and syndromes occur. Examples of such metals with known physiological roles are iron, manganese, cobalt, zinc, molybdenum, and selenium. There are some HMs that are considered to be non-essential which include arsenic, tin, lead, antimony, aluminum, titanium, and thallium. Some other HMs such as lead, cadmium, mercury, and arsenic have been remarked to be highly toxic even at trace concentrations and are the HMs of greatest concern in terms of their toxicological profiles (Masindi & Muedi, 2018).

Sources of HMs

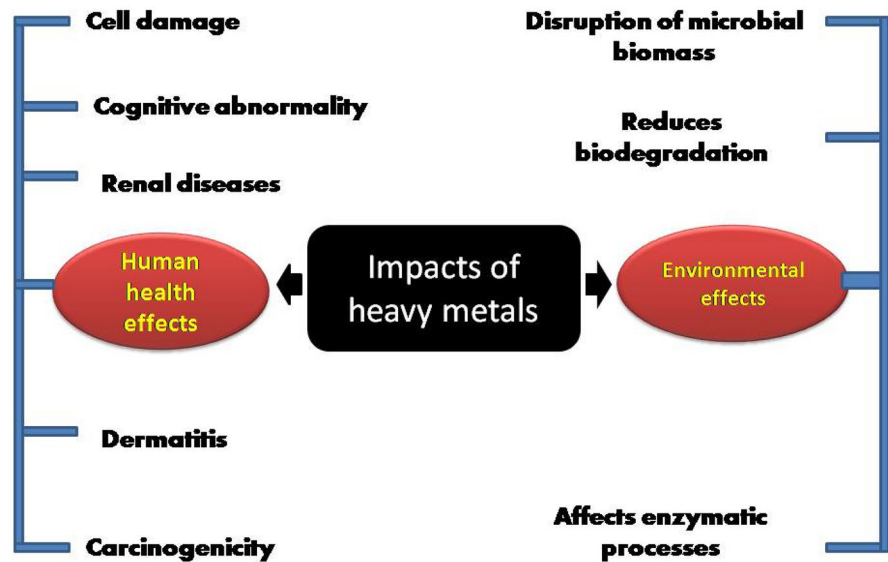
The two primary origins of HMs are geochemical and anthropogenic sources. Although they occur naturally in

low concentrations, they are found all around the earth's crust. Natural processes such as the eruption of volcanoes and weathering result in the discharge of HMs into the environment (Okonkwo et al., 2021). There are several anthropogenic sources of HMs in the environment which include the combustion of fossil fuels, industrial activities, nuclear plant activities, microelectronic plants, and refinery domestic activities, among others. There are also point sources of HMs which include foundries, mining, and smelting as well as activities of metal-based industries. The increasing technological, industrial, agricultural, and domestic activities have increased the concentrations of HMs in recent times (Briffa et al., 2020; Gaur et al., 2021).

Environmental and health effects of HMs

HMs pose serious risks to the environment and humans at large. The toxicological impacts of heavy metals in humans are affected by several factors such as the pathway of exposure, dose exposed to, and chemical speciation or oxidation state of the metal ion, together with the gender, age, genetic composition, and nutritional status of the individual that is exposed to these metals. The HMs that have been identified to be of greatest public health concern include cadmium, chromium, mercury, arsenic, and lead and this is due to their toxicity and potential teratogenicity and carcinogenicity based on recent investigations and documentation by International Agencies for Researches in Cancer (IARC) and the United State Environmental Protection Agency (USEPA). The above-mentioned metals have also been identified as chemical culprits for the induction of multiple damages to various organs such as the brain, lung, kidney, and liver (shown in Fig. 1). There are varying toxicities associated with different HMs. The major sources of exposure to the metals in humans are ingestion, inhalation, and absorption through the skin. The majority of individuals get in contact with the metals through occupational exposure (Inobeme et al., 2022). Exposure to a high concentration of copper for example is linked to Wilson syndrome in humans. Cadmium exposure leads to brain damage and other cognitive-related abnormalities. Metals such as lead and arsenic are connected to various degenerative and respiratory diseases. Experimental studies have also linked cadmium, arsenic, and mercury to cancer in studied animals. Other diseases in humans and other animals linked to prolonged exposure to HMs include

Fig. 1 Environmental and health impacts of HMs



dermatologic, renal, gastrointestinal, and related illnesses. HMs also affect the activities of various micro-organisms in the soil (Inobeme, 2021). This brings about a disruption of the ecosystem due to the interruption of aquatic life and the soil microbial biomass. They interfere with various enzymatic activities in the soil and reduce the biodegradation of various organic materials (Ahmed et al., 2022).

The significance of effective quantification of HMs

Quantification of HMs is a topical issue in various aspects of toxicological studies involving food, drugs, biological samples, and various environmental matrices (soil and water). This is because this is the fundamental step towards quality control and ensuring the safety of humans and the environment from the deleterious effects of these contaminants. The scientific world has therefore been greatly attracted to the need to continually improve devices for the monitoring and quantification of HMs. Methods for HM determinations therefore gradually evolved from wet procedures to instrumental techniques (Kasozi et al., 2021). The instrumental approaches were gradually advanced with the traditional techniques gradually replaced by more advanced instrumentations for HM determination. The determinations of HMs make it possible for the establishment of various international standards for these metals and ease the comparisons of their

concentrations to various reference standards. This also enhances the evaluation of the level of compliance with legal regulations and requirements (Addis & Abebaw, 2017; Agoro et al., 2020).

Analytical procedure for HM quantification

The specific steps for the identification and quantification of HMs vary depending on the metal of interest and some other vital factors such as the nature of the matrix, the chemical nature of the metal, and the analytical technique of interest. Almost all existing analytical technique for HM determination requires first the preparation of standard of different concentrations. Depending on the instrument, there may be a need to convert the sample into a form amenable to the instrumental process (Scaeteanu et al., 2021). Although the analysis of metals can be achieved directly on the sample in solid form through the coupling of ICP-MS or ICP-OES with instruments based on laser ablation, most of the sample analyses are done in the liquid state. For most instrumentation procedures, pretreatment involves the oven drying of solid samples to remove moisture, followed by homogenization through grinding. Techniques such as flame atomic absorption spectroscopy (FAAS), graphite furnace atomic absorption spectroscopy (GFAAS), and UV-Vis require the conversion of solid analyte to solution form. To ensure the metallic elements are all available or free in the solution, the process of digestion is

carried out by various kinds of acids and their combinations are available for the digestion of samples. The choice of digestion acid is dependent on the specific physicochemical properties of the sample matrix as well as the analyte of interest. After the digestion step, filtration is carried out to remove tiny impurities (Fig. 2) (Mejias & Garrido, 2016; Tytla et al., 2022).

Instrumental techniques for HM analysis

Various techniques can be selected for specific HMs depending on varying factors and parameters such as cost, the throughput of a sample, the detection limit, level of sensitivity, regulation standards, ranges of concentrations, and the nature of the environmental matrix and other interfering materials (Kaonga et al., 2021). Instrumental techniques for HM quantification are categorized into two major groups. The first is the spectroscopic technique while the other is the

electrochemical technique (shown in Fig. 3). Each of these techniques has its merits and demerits (provided in Tables 1 and 2).

Spectroscopic techniques for determination of HMs

Atomic absorption spectroscopy

Atomic absorption spectroscopy (AA spectroscopy or AAS) is one of the most prominent and oldest techniques for elemental analysis to be developed for commercial applications. Flame atomic absorption spectroscopy (FAAS or Flame AAS) was first developed in 1952 and then largely commercialized in the 1960s. The technique has gained wide popularity due to its unique simplicity and reliability. It is used for the determination of the concentration of an element in a given sample. It functions on the basis that ions or atoms are capable of absorbing light rays at specific and characteristic wavelengths. On provision of this specific light wavelength, the atom absorbs this

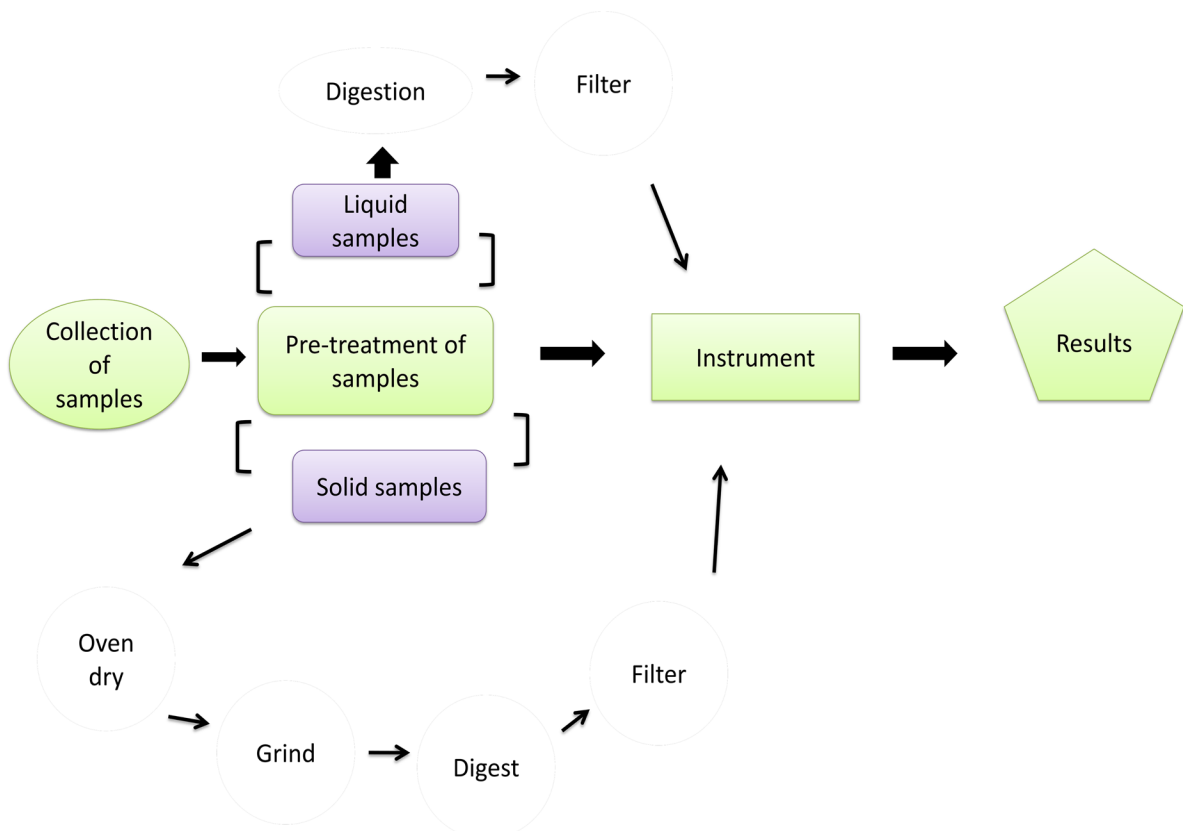
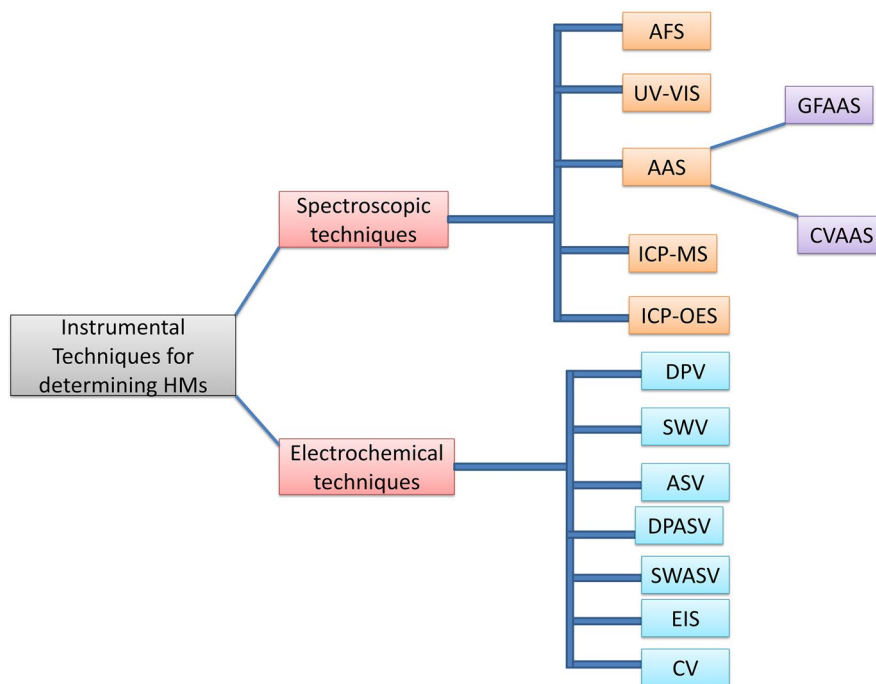


Fig. 2 Procedure for HM determination

Fig. 3 Schematic representation of instrumental techniques for determining HM concentrations



characteristic light energy. This results in the excitation of electrons within the atom (Silva et al., 2017). The quantity of light that is absorbed is then quantified, and the concentration of the specific element in the sample is determined. The relationship existing between concentration and the intensity of absorption is described by the Beer-Lambert

law which states that the amount of absorbed light is directly proportional to the concentration. Measurement using AAS requires initial calibration which involves the use of a solution containing the metals of interest. This is called the blank and is used in determining the baseline absorption (Rhodes, 2019). The absorptions of a series of

Table 1 Spectroscopic techniques for HM determination; merits and limitations

Instrumental technique	Merit	Limitation	Reference
AAS	It is cheap, in terms of cost per analysis. Has high accuracy and sensitivity	It is a destructive technique; hence, samples are not amenable to further analysis and subsequent usage	Oti (2016)
GFAAS	Suitable for varieties of matrices requiring a small amount of the sample. Has a low limit of detection and good sensitivity	It takes time and requires different method optimization for different samples and also has limited dynamic range. It is also a destructive technique	Popovic et al. (2017)
UV-Vis	A non-destructive technique; hence, samples can be re-used. The device is relatively cheaper to acquire	Prone to interferences from the matrices. Measuring errors due to light scattering can occur	Echioda et al. (2021)
ICP-MS	Has a high selectivity and wide linear range and is remarkable for multi-elemental analysis	Readily affected by spectra and chemical interference	Wilschefski and Baxter (2019)
CVAAS	Does not require a sample volatilization step. It is the most reliable for Hg quantification	Expensive to acquire and requires good technical know-how	Onakpa et al. (2018)
ICP-OES	Suitable for multi-elemental analysis	It is an expensive instrument and it is prone to some chemical interferences	Wilschefski and Baxter (2019)
WDXRF	Has remarkable sensitivity and selectivity. Highly robust with high throughput	Poor selectivity for some metals	Hall (2017)
EDXRF	Suitable for various forms of matrices. A non-destructive technique with high accuracy and sensitivity	Expensive to acquire. High technical know-how requirement	Somogyi and Mocuta (2015)

Table 2 Electrochemical technique for HM determination; merit and limitations

Instrumental technique	Merits	Limitations	Reference
Cyclic voltammetry	Highly simplified in operation and permits identification at multiple points	There is difficulty in the control of background noise, challenges in the detection of analyte at very trace concentrations and comparably lower resolution when compared to some other electrochemical techniques	Sandford et al. (2019)
Differential pulse voltammetry	Relatively lesser noise effects on signal, higher detection limits, and good sensitivity	Longer duration of the analysis	Palisoc et al. (2019)
Electrochemical impedance spectroscopy	A simplified system that makes it easy to detect analytes in real-time. High robustness and sensitivity to varying interfacial and bulk parameters of the metallic analyte	Requires the utilization of a Faraday cage for the minimization of noise during analysis. Readily affected by the immediate environment and needs situational approaches in data analysis	Meddings et al. (2020)
Anodic stripping voltammetry	Potential of detecting multiple metallic analytes synchronously even at trace concentration. High cost-effectiveness and sensitivity	Higher time of determination when compared to some other electroanalytical techniques	Vito-Francesco et al. (2022)
Potentiometric technique	High selectivity, speed of detection, cost-effective, with simplified instrumentation	Affected by temperature variation in the environment and also influenced by the activity of the ions and the shift potential	Mei and Ahmad (2021)
Square wave voltammetry	Highly portable, precise, selective, and precise in its measurement	Gives rise to voluminous data that is fairly complex and not easy to understand in comparison to some other techniques	Pingarron et al. (2019)

prepared solutions having varying known concentrations of the HMs are measured. The calibration curve is made from the data which establishes the relationship between concentration and absorbance.

The use of this technique in HM determination has been well documented. Ipeiyeda and Ayoade (2017) used FAAS for the quantification of HMs in surface water after the co-precipitation step using copper (II) hydroxyquinoline. The optimum percentage recovery values for all the metal ions were greater than 85.0%. There was a significant difference in the contents of the HMs among the various samples with the lead having the highest concentration (0.014 mg/L). Rahman et al. (2021) reported their findings on the concentration of HMs in soil samples collected from sediment within the vicinity of a tannery industrial area in Bangladesh using AAS. Spatial distribution analysis showed that the concentration of Cr was highest in the dumping area. Source apportionment studies showed that the HMs emerged from two sources. Idris et al. (2021) investigated the concentrations of HMs in water samples collected around a Gypsum mining site in Daura, Nigeria, using AAS. They reported a remarkably high concentration of Ni (0.98 mg/L), Cd (0.18 mg/L), and As (0.0382 mg/L) which were higher than the maximum limits based on WHO standards. Tibebe et al. (2022), in a similar work, assessed the concentrations of selected HMs in honey samples collected in Ethiopia using AAS. They reported that the contents of Zn (1.97–2.04 µg/g), Cu (1.93–2 µg/g), Mn (0.25–0.45 µg/g), and Cr (0.025–0.031 µg/g) were lower than the maximum limits. Sagagi et al. (2022) studied the accumulation of selected HMs in water, soil, lettuce vegetables, and cabbages cultivated in Wawan Rafi, Nigeria, using AAS for metal quantification. They reported the ecological risk impact to be 225.46 and 86.48 for cabbage and lettuce respectively. The concentrations of the metal in soil and plants were generally lower than the maximum limits. Also, Sisay et al. (2019) analyzed the content of lead and cadmium in soil samples collected along the road in Jimma Town in Ethiopia using AAS. The concentration of Pb ranged from 36.47 to 43.42 mg/kg while Cd ranged from 0.505 to 1.75 mg/kg which were lower than the WHO soil standard for the metals.

Like other techniques, AAS has its merits and weaknesses. However, its advantages outweigh its limitation; hence, it is still widely employed in HM determination. It has high accuracy in measurements; is easily operated, cheap in terms of cost per analysis, free of interference due to different elements; and also has a high sensitivity.

The technique is however more amenable for samples in liquid form and the new equipment is expensive to acquire (Rahman et al., 2021).

Graphite furnace atomic absorption spectroscopy

This technique is also called electrothermal atomic absorption spectrometry (EAAS). It is a well-established analytical technique for the quantification of elements at trace concentrations up to micrograms per liter, and it permits the use of a very small quantity of the sample, mostly lower than 100 µL. This technique involves the injection of a known quantity of the solution of the sample into a pyrolytic graphite tube which is then subjected to heating for the vaporization and atomization of the analyte. This is followed by the absorption of visible light or ultraviolet light by the atoms bringing about electronic transition (Popovic et al., 2017). Samples are introduced into the cuvette made of graphite through injection with volumes usually within the ranges of 10–100 µL. A literature survey documented that samples having benign constituents such as fresh water and rainwater having low contents of minerals are directly injected after some preliminary treatments. For all other samples, there is usually digestion for the removal of various organic matter or extraction carried out for the separation of the arsenic in the matrices. The technique has remarkable similarities to flame atomization but differs in that there is a replacement of the flame with closed graphite that is electrically heated having transparent window ends at a temperature of 10,000 °C thereby increasing the conductivity of the gas which converts the argon molecules from gaseous into plasma state (Infante et al., 2019; Rada-Mendoza et al., 2019).

GFAAS has become widely employed in the quantification of HMs in soil, water, and biological matrices (Popovic et al., 2017). Khalid et al. (2016) developed an alternative method for the determination of arsenic in medicinal products using GFAAS and Hydride generation atomic absorption spectroscopy (HGAAS). They evaluated the efficiency of GFAAS and HGAAS in the quantification of arsenic. The percentage recovery of arsenic for GFAAS and HGAAS were 102 and 98% respectively. The RSD were 2.3–6.7 and 2.5–6.5% for GFAAS and HGAAS respectively. They, therefore, concluded that the two methods evaluated were recommended for the determination of arsenic in local herbal products. Similarly, Gende and Schmelting (2022) developed a method for determining the concentration of Cd and Pb in environmental materials using GFAAS. The

model substance employed was *E. coli* due to its easy availability and ease of preparation. A certified reference material was employed for the validation of the method. The limits of detection and quantification were observed to be very low with a reliable precision based on the RSD. Ulla et al. (2017) formulated and validated a method for the determination of Cr, Pb, and Cd in feed samples for fish in Bangladesh using GFAAS. The limits of detection for Cd, Cr, and Pb were reported to be 0.010, 0.022, and 0.078 $\mu\text{g/g}$ respectively. The percentage recoveries of the analytes were 90–104% while the relative standard deviation was within the range of 4.90 to 9.60%. They concluded from their results of method validation criteria that the method was highly suitable for the determination of the HMs in the feed samples. Furthermore, Forero-Mendieta et al. (2022) in their work validated an analytical technique for the quantification of Pb and Mn in the hairs of humans using GFAAS. The method developed was reported to be linear within concentration ranges of 0.001–0.015 $\mu\text{g}\cdot\text{L}^{-1}$ and 0.002–0.020 $\mu\text{g}\cdot\text{L}^{-1}$ for Mn and Pb respectively. The quantification coefficients obtained were higher than 0.99%. In addition to the standard solutions of the metals, the recoveries obtained varied from 4.80 to 107.98% with a precision value of less than 12.97% RSD. Popovic et al. (2017) carried out HM analysis on tea using GFAAS and advanced multivariate analysis. They reported that the concentration of Cd was higher than the permissible limit (0.3%). The extraction efficiencies of the HMs were quantified and then categorized into highly, moderately, and poorly extractable with Cr having the greatest variations. Rada-Mendoza et al. (2019) determined the concentrations of Cd in biodegradable thermoformed films obtained from cassava. The furnace heating program and analytical instrumental conditions were adjusted through atomization curves and pyrolysis, with a working range of 0.1–1.0 $\mu\text{g/L}$ and quantification and detection limits of 0.07 and 0.02 $\mu\text{g/L}$ respectively. The standard deviations were in the ranges of 1.6 to 4.8%. They concluded that the methods were highly suitable for the determination of the concentration of Cd in the samples.

GFAAS has a higher sensitivity when compared to flame absorption spectrophotometers and also possesses a relatively shorter dynamic range. The limit of detection of this technique is highly remarkable under favorable conditions and could be up to pictogram levels, that is part per billion concentrations. However, this technique takes time and requires different method optimization

for different samples and also has limited dynamic range (Infante et al., 2019).

Cold vapor atomic absorption spectrometry

This is one of the prominent analytical techniques employed for the quantification of mercury. Hg is a unique HM whose quantification poses a serious challenge due to its physicochemical properties. It has a high vapor pressure in comparison to other HMs, and it also exists in different forms. Cold vapor atomic absorption spectrometry (CVAAS) was first introduced by Hatch in the year 1968. The emergence of CVAAS was when Hatch and his co-worker Ott utilized an additional component into AAS which enhanced the reduction of Hg (II) into Hg (0) (Mohammed et al., 2018). The Hg atoms in their ground state were then conveyed into an optical cell component and a detector for quantification (Onakpa et al., 2018). Briefly, after the introduction of this analytical technique to a commercial scale, the USEPA chose CVAAS for the quantification of Hg in fish, soil, and water. The CVAAS detection system had unique detection limits in part per trillion (ng/L), a dynamic range with high linearity of 3–4 orders of magnitude. This method was also considered to be highly sensitive and reliable for the determination of Hg in almost all environment samples. With more recent development, CVAAS are currently more automated, faster, portable, and sensitive and cheaper to afford. The recent models available make a provision for the detection at trace to ultra nano levels and are capable of determining the concentrations within a few seconds. The device system does not need much operator interaction due to its advanced automation. The most commonly available CVAAS possesses a peristaltic pumping component that helps in transporting stannous chloride and the sample into a gas–liquid separator. With this principle, the detector with the integration of the software component is capable of determining the concentration of Hg in various environmental samples (Balali-Mood, 2021). Fernandez et al. (2014) carried out a study on the determination of the concentration of Pb, Hg, and Cd in fish samples using CVAAS and ICP-AES. They analyzed a certified reference material. They reported that the limits of quantification and detection were at least a factor of 5 and 10 lower than the residual maximum limits and concluded that CVAAS is a well-suited technique for the quantification of various elemental impurities in the mercury ore. The linearity regression coefficient was higher than 0.99. Tytla et al. (2022)

carried out an investigative study in which they compared ultrasound-assisted sequential method of extraction and the conventional method for the quantification of HMs present in sewage sludge using CVAAS for Hg. The other metals were quantified using ICP-OES. The findings from their study showed that using ultrasound waves reduced the duration of the extraction step. Sarojam et al. (2011) investigated the concentrations of HM in Chinese herbs and spices using CVAAS and GFAAS. Fernandez et al. (2020) determined the concentrations of HM contaminants in collected rice samples in Cuba using three different instrumental techniques (CVAAS, ICP-AES, and ICP-MS). Tytla et al. (2022) investigated the contents of HMs as well as their ecological risk in municipal sewage treatment plants in Poland, using CVAAS.

CVAAS has remarkable applications in trace levels determinations, and argon gas is not required in its applications. It is preferably used in most laboratories for Hg quantification due to its relative ease of handling when compared to cold vapor atomic fluorescent spectroscopy (CVAAS). It also has less susceptibility to interference. Another advantage is the fact that it does not need any vaporization step since the sample under consideration contains a volatile HM like mercury which remains in vapor at room temperature.

UV-Vis spectroscopy

UV-Vis spectroscopy is an analytical technique that is based on light absorption by an unknown substance. It involves the illumination of the sample with electromagnetic radiation of different wavelengths within the UV-visible and the near infrared region of the electromagnetic spectrum. Depending on the substance being analyzed, there is a partial absorption of the light. The other component of the light is then transmitted and this is recorded about the wavelength using a suitable detector and provides the UV spectrum of the sample. The concentrations of a particular analyte in an aqueous media are determined through the measurement of the absorbance at a particular wavelength; the concentration is calculated from the absorbance. The linearity of the UV-Vis device is affected by various parameters such as signal-to-noise ratio, resolution of the instrument, interferences due to the stray light rays, and interactions between molecules and ions at high concentrations. In UV-Vis spectroscopy, the HMs are reacted with a chemical agent resulting in the formation of a colored intermediate or products. The absorbance of

the resulting colored complex is directly proportional to the content of the analyte which is then measured spectrophotometrically using Beer's law (Ahmed et al., 2022; Echioda et al., 2021). UV-Vis is widely used in the quantification of transition metal ions in solution as well as compounds that are highly conjugated. It is used for determining the molar absorptivity of various kinds of HMs. Through the use of molar absorptivity, the concentrations of the HMs are calculated based on the calibration curve established. The relationship between the concentrations of the metal ions and the absorptivity intensity is considered to be linear.

Various researchers have documented the use of UV-visible for HM determination with reliable results. Echioda et al. (2021) investigated the concentration of As, Cd, Pb, and Cr in biological samples and water with phenyl hydrazone as the chromogenic agent using UV-Vis spectrophotometry. They observed that the reagent glutaraldehydphenyl hydrazone showed a maximum absorption wavelength of 360 nm for Cr and 395 nm for As and Pb within a pH range of 6.5–7.5 at the temperature of 37 °C and wavelength of 2.213×10^4 . The findings from their study helped them to deduce that the reliability, precision, and accuracy were in strong agreement and comparable to results from AAS. It has also been documented that the technique is routinely employed in the determination of the concentrations of HM ions and this is based on the computation of the molar absorptivity of the metal ions from which the concentrations of the HMs are determined using the set calibration curve (Echioda et al., 2021). Ahmed et al. (2022) used the UV-Vis spectrometry technique for the detection of Cr, Cu, Zn, Cd, Ni, and Pb from aqueous media using zinc oxide nanoparticles doped with silver. They reported that the various HMs of interest were detected and successfully degraded using zinc oxide-doped nanoparticles. Goday (2019) carried out a detailed survey and analysis of selected HMs in some medicinal plants using the UV-Vis technique. They reported that the technique was efficient in the detection of the HMs. Ma et al. (2022) evaluated the interaction of water-soluble compounds and HM ions in particulate matter (PM2.5) using fluorescence spectra and UV-Vis spectrometry. They concluded that the combination of the two spectroscopy techniques was a potent tool for revealing the interactions of the HMs and the organic compounds. Simiao et al. (2022) used a validated UV-Vis spectroscopic technique in the quantification of mercury in water samples collected from a river in Brazil. They reported the

concentration of mercury in the water sample to range from 0.13 to 0.35 $\mu\text{g mL}^{-1}$ which was higher than the permissible limits of 0.002 $\mu\text{g mL}^{-1}$ based on Brazilian water standards.

There is no single analytical technique that is perfect; hence, UV–Vis has its strengths and limitations. It is flexible and easy to use and does not require long time training since the data generated are not complex. It is a non-destructive technique; hence, the sample can be used subsequently for other analyses. It is also relatively cheaper to acquire in comparison to other spectroscopy instruments. Some of its setbacks include interferences that may result from other species also within the matrices and absorbing the radiation. There could also be measurement errors resulting from light scattering by some solid particles within the solution of the sample (Cheng et al., 2020).

Inductively coupled plasma/optical emission spectrometry

This is an analytical instrumental technique for the determination of the contents of an element in a particular sample. It is also known as inductively coupled plasma atomic emission spectroscopy (ICP-AES). The plasma refers to a high-temperature source of ionized argon gas. The plasma is generated and maintained through inductive coupling from highly cooled electrical coils usually at megahertz frequencies (Wilschefski & Baxter, 2019). This technique functions on the basis that ions and atoms are capable of absorbing energy resulting in the excitation of their electrons. The energy source for ICP-OES is generated from argon plasma which is at 10,000 K. The excited atoms release light on returning to the ground state. The amount of light that is released for each wavelength is directly proportional to the number of ions or atoms that are making the transition. The relationship is in line with Beer-Lambert law. The concentration of the metal is determined from the calibration graph. This is a very robust approach for analyzing wastewater, groundwater, solid wastes, and soil. It is used in the measurement of pollutants for environmental quality assessment and metals having higher limits of regulations (Sharma, 2010).

Several studies have reported the use of this technique for HM determination with highly promising remarks. Ahmed and Alatawi (2022) carried out a comparative study on the efficiencies of viewing modes of ICP-OES in the quantification of the HM such as Pb and Cd in samples of blood collected. The findings from their work

revealed that radial and axillary views are preferable to dual views during the use of separate axial and radial view ICP. The values for percentage recoveries for Pb and Cd were acceptable though not very sufficient. Shaheen et al. (2022) evaluated the level of contamination of agricultural soils by selected HMs using ICP-OES. Their findings revealed moderate contamination of most of the soil samples with a contamination factor of less than 3 for Zn, Cu, Co, Cr, and V, while that for Mn and Pb was low. Abuseleek et al. (2015) investigated the contents of HMs in cosmetics bought from selected markets in Jordan, using ICP-OES and ICP-MS. They reported a high Pb concentration in two different brands (>10 ppm). Shaheen et al. (2022) assessed the pollution levels by HMs in agricultural soils using ICP-OES. The levels of contamination were established using indices such as enrichment factor, contamination factor, and pollution load indices. V showed the highest contamination with CF less than 3. Cluster analysis results revealed that the metals clustered into three major groups, which points to different sources of anthropogenic origin. Manousi et al. (2022) studied the contents of toxic metals in selected spices using ICP-OES. Digestion was done using nitric acid and hydrogen peroxide. They focused on seventeen different metals. The limit of detection obtained ranged from 0.08 to 5.95 mg/kg.

ICP-OES has some unique merits. It has a wider linear area of the analytical curve and is also possible for making samples with high matrix due to its fewer ionization and chemical interferences. This technique also has the potential of determining various elements such as Zr, P, B, Ta, and rare earth metals which are not easily determined using AAS. It permits synchronous sequential analysis of multiple elements and is very stable. ICP-OES is primarily employed in the case of samples having high total dissolved solids (Wilschefski & Baxter, 2019). While it is possible to carry out multi-elemental analysis quickly and with a high-cost economy through the use of ICP-OES, for some elements such as Pb and As analysis is better achieved through the use of ICP-MS as a result of their extremely low regulatory standards in drinking water (Kaonga et al., 2021).

Inductively coupled plasma mass spectrometry

This is a unique kind of mass spectrometry that utilizes ICP for the ionization of the sample. It creates polyatomic and atomic ions on ionization of the sample which is later detected. This technique is well known for its unique

potential in the detection of metal ions as well as several nonmetals. It also can determine various isotopic forms of these metals, hence very useful in the area of isotopic labeling. It is a multi-elemental analysis with inductively coupled plasma being the source of the ions (Profrock & Prange, 2019). ICP-MS employs a quadrupole mass spectrometer which is able to rapidly and continually determine the mass of various elements. It has the potential of metal detection at extremely trace concentrations as low as one part per quadrillion. Ionization of the sample occurs through the use of the ICP plasma which is generated through the heating of the argon gas. At present, more than seventy different elements can be determined using this instrumental technique (Wilschefski & Baxter, 2019). The limit of detection of the technique for more than 70 different elements is a trillion or less with a linear range reaching a magnitude of ninth order.

ICP-MS has numerous merits in the quantification of HMs, hence has recently become a workhorse in metal quantification (Profrock & Prange, 2019). The first research work reporting the use of ICP-MS was by Ropert which documented the remarkable feasibility of the technique. It has been widely applied in the quantification of various elements in drugs and several food products. Phadke and Gaitonde (2016) used ICP-MS for the quantification of Pb, As, Hg, Cd, and Hg in a capsule shell. They reported the method to be highly sensitive and selective in the determination of the elements. The relative standard deviation was reported to be 25%, with percentage relative standard deviation being 5.34, 3.79, 5.19, and 5.67 for Pb, Hg, Cd, and As respectively. Miedico et al. (2016) in a related study used ICP-MS for the determination of various trace metals present in equine meats. They focused on a total of 22 selected trace elements. The mean values of Ca, Fe, and Zn were observed to be higher than 25 µg/g. The concentrations of As, Cd, Pb, and Hg were found to be lower than 11.3 ng/g. They also reported a strong correlation between Zn and Fe among the metals investigated. Mohammed et al. (2016) employed ICP-MS in the investigation of the HM concentrations in the blood samples collected from smokers in Saudi Arabia. The contents of Cd, Pb, Ar, Hg, and Ni reported were 0.23, 26.42, 19.43, 8.77, and 79.57 mg/kg respectively. They concluded that the contents of the metals investigated were generally higher in the blood samples of the smoker when compared to the non-smokers that were used as control. Voica et al. (2012) in their work investigated the quantification of HMs (As, Cu, Hg, Sn,

and Cd) and essential metals (Zn and Co) present in various kinds of food materials (biscuits, wheat, milk, bread, cheese, rice, coffee, chocolate, and sugar) using the ICP-MS. They reported that the concentrations of the trace elements in some of the food materials studied were greater than the permissible levels of the metals in food based on international standards.

ICP-MS is well known for its high sensitivity, great precision, and speed. However, when compared to other mass spectrometry techniques like glow discharge mass spectrometry (GDMS) and thermal ionization mass spectrometry (TIMS), ICP-MS tends to introduce various interfering chemical species such as argon in the plasma as well as some extent of contamination from cones and the glass wares. The uniqueness of ICP-MS when compared to other kinds of inorganic spectrometric techniques is its capability of taking in the analyte samples continuously without being interrupted. This makes it preferable to TIMS and GDMS which need a two-step process. It is also useful in the aspect of metal speciation which is the determination of the oxidation state of the metal ions such as As and Cr being determined. Unlike AAS which determines only a single element at once, ICP-MS is able to detect and quantify all the elements at once. One of the major issues of concern in the use of ICP-MS is the challenges of interference. ICP-MS though closely related to ICP-OES is more useful in the analysis with low regulatory standard limits. It has a greater tolerance (about 30%) for total dissolved solids. ICP-MS has a relatively lower tolerance (up to 0.2%) for TDS although there are various strategies for the improvement of the tolerance. Though ICP-MS and ICP-OES can be employed in high matrix samples, there is a paramount need for the dilution of the sample in ICP-MS. ICP-MS also possesses a broad dynamic linear range (Phadke & Gaitonde, 2016).

X-ray fluorescence spectrometry

X-ray fluorescence (XRF) technique detects the unique X-rays given by the analyte present in a sample on irradiating a target using highly energetic radiation such as an X-ray beam. This has been employed for a long in a wide scale for the determination of various types of HMs in a broad range of various solid environmental samples. Aside from the broad dynamic working range as well as the potential of multi-elemental analysis, the technique's uniqueness is also connected to its potential of analyzing the HMs in various kinds of samples with minimum

preparation of steps for the sample (Collingwood & Adams, 2017; Pushie et al., 2014). With the XRF technique, a sample in solid form can be prepared in the form of pellets thereby eliminating long time pretreatment and chemicals for the preparation of the sample. Over time, remarkable improvements have been documented in the aspect of XRF for HM determination. This advancement includes aspects of instrumental design as well as detector systems. There are therefore various kinds of XRF designs and configurations that have emerged after the development of the first X-ray spectrometer in the 1940s (Wobrauschek, 2007). The various designs differ in some areas which include the size of the spectrometer, the spatial geometry of the optical route, and the detector modes. At present, the prominent ones are the energy-dispersive systems (EDXRF) and the wavelength detection systems (WDXRF). The non-destructive feature of XRF has made it highly demanded as a promising technique in the quantification of HMs (Pushie et al., 2014).

Energy-dispersive X-ray fluorescence This is a type of X-ray fluorescence technique that involves the excitation of all the elements present in a sample. A dispersive energy detector and a multi-analyzer are employed for the synchronous collection of the radiations emitted from the sample. The resolutions of EDXRF vary depending on the type of detector usually within the ranges of 150 to 600 eV. It uses photons of primary X-ray or other particles at the microscopic level for the excitement of atoms in the material to be tested for the production of the secondary XRF for the analysis of the elemental composition of the sample. The quantitative aspect of X-ray spectroscopy is based on Moseley's law (Somogyi & Mocuta, 2015). The EDXRF spectrometer functions in the following steps of operations: preheating, selection of mode, initialization, starting of measurement, qualitative measurement step, and quantitative analysis.

EDXRF has been employed in various areas of analytical quality control, geological surveying, food inspection, and other aspects of environmental monitoring and assessment. It is vital in measuring the concentrations of HMs in various kinds of products in the evaluation of their compliance with standards (Ribeiro et al., 2017). Numerous studies have been done in this regard documenting the precision, accuracy, and general validation of the technique. Gao et al. (2022) did a study focusing on the quantification of the HMs in Mongolian medicines using EDXRF. They observed that the analytical

method adopted was highly stable and did not need any form of sample pretreatment. The concentration of the metals investigated (Pb, Cd, Ba, Cu, As, Fe, and Cr) was lower than 2.0 mg/kg; the relative standard deviation was 5.49 to 20.0%. The quantification limits for all the samples were lower than 0.1 ppm. Yao et al. (2015) in their work reported that the precision of the EDXRF device in the determination of the elements was lower than 8%, while the repeatability was less than 2%. Similarly, Ma et al. (2022) carried out a rapid quantification of the concentrations of HMs in some Chinese herbs using EDXRF. They reported that each of the tests took a very short duration of 10–30 min with a cost that is 1/5th to 1/10th of the conventional approach. They concluded that the quick screening of the technique would enhance the efficiency of the testing thereby increasing the monitoring of various HMs in herbal samples. Kim et al. (2022) compared the contents of HMs in atmospheric aerosol using EDXRF. They reported that the rate of detection of the HMs within the three different institutions was 90% approximately. They concluded that XRF is vital in ensuring the high reproducibility of results. Koleleni and Haji (2014) evaluated the contents of selected HMs (Zn, Cr, Pb, Cr, Fe, Ni, Cu, As) in various species of fishes collected from the sea port in Zanzibar using EDXRF. They observed that the concentrations of Mn and Cd were below the limit of detections in all the samples investigated. They also observed that the concentrations of As, Fe, and Cr from their work were higher than the values reported in some of the existing works of literature. In related work, Khan et al. (2021) studied the concentrations of selected HMs in rice, paddy soil, and marble powder collected from Malakand in Pakistan using EDXRF. They reported that the highest concentrations of Al, Mn, Cu, and Fe in rice were 6.80, 7.49, 17.60, and 50.70 mg/kg respectively in rice samples with a total hazard index greater than 1. Findings from PCA and cluster analysis for the various metals investigated showed a high level of consistency. Jolly et al. (2017) investigated the concentrations of Fe, Zn, Cr, As, Ni, Pb, Cd, Mn, and Cu in milk samples collected from Bangladesh. They observed that the pollution index of the various metals was higher for the powder milk sample in comparison to the other forms of samples collected. The index of health risk for most of the metals was however reported to be within safe levels. Furthermore, Tholkappian et al. (2018) evaluated the profile of HMs toxicity in sediments collected from the Chennai coast in Nadu Tamil. They reported that the mean concentrations of the

various metals investigated were within the world crustal mean. While their results from pollution index analysis showed that most of the sampling areas were not contaminated by HMs. Multivariate analysis showed that the HMs investigated were of natural origin.

EDXRF has numerous advantages over some other techniques employed for the quantification of HM ions. It has the potential of satisfying various analytical measurement criteria. It can measure various forms of environmental matrices and detect a broad range of metals and nonmetals at the same time. It is highly amenable to various forms of environmental samples such as liquid, powder, bulk, and gaseous samples. It is also capable of measuring particulate matter in the atmosphere. The method is a highly sensitive, accurate, rapid, environmentally friendly, and non-destructive technique in elemental detection and quantification (Ribeiro et al., 2017).

Wavelength detection system X-ray fluorescence

The WDXRF system makes use of diffraction through a dispersing system which is a multilayer or crystal, for the separation of the characteristic wavelengths that are emitted from the sample. It differs from EDXRF, in that EDXRF devices make use of the proportional relationship of a photon detector in the separation of the characteristic photons that emerge from the sample being analyzed with regard to their energies. The two configurations differ in their sensitivities and the mechanisms in which data collection and presentation occur. Various researchers have documented the sensitivity of this technique in the determination of HMs in numerous environmental and biological samples (Hall, 2017). Povarov et al. (2021) utilized WDXRF for the quantification of selected HMs as well as rock-forming elements present in porous materials of carbon origin. They reported that the analytical method provided the same level of accuracy and sensitivity, and a higher reproducibility of the analytical results for different sample densities, mass, and coverage. Huang et al. (2022) developed a fast and novel WDXRF analytical device for the determination of HMs in large areas integrated with unmanned aerial vehicles (UAV). The findings from the testing revealed enhanced regionalized detection efficiency of soil contamination by HMs. The investigation, therefore, made a provision for novel solutions in resolving the current challenges in the rapid determination of HMs present in the soil. Harris et al. (2019) used WDXRF in the quantification of HMs present in cultivated vegetables.

They reported high detection limits of 0.3 $\mu\text{g/g}$ for Pb in the dry vegetables, while for the raw vegetables the detection limit was 1 $\mu\text{g/g}$. They observed that a very robust calibration was obtained for the dried vegetables when WDXRF was used while the little compromise in the accuracy and precision when EDXRF was used was offset by the portability of the technique. Kodom et al. (2012) analyzed the concentrations of HMs in a selected area around Kumasi, Ghana, using WDXRF. They attributed the sources of the HMs to the anthropogenic activities in the area. As had the least concentration (2.3 to 18.6 mg/kg) among the metals, while Zn had the highest (189.2 to 908.6 mg/kg). The concentrations of Hg, Cd, and Cr were higher than the permissible limits. Yuan et al. (2022) determined the contents of Pb, Cr, Cd, Co, Zn, and Cu in sediments in Dongting Lake, China, using WDXRF and also apportioned their sources. The result from the enrichment factor showed very high enrichment in Cd. The result obtained from the geochemical index showed that Cu, Co, Cr, Pb, and Zn were at concentrations considered to be of low pollution. They attributed the high cadmium enrichment to natural and anthropogenic factors.

The WDXRF is about an order magnitude of higher sensitivities in comparison to EDXRF systems. The EDXRF system can measure the various elements that are around its range at once, while WDXRF will only determine the elements it is programmed to detect. WDXRF is mostly employed for high-throughput, routine determinations in which there is a pressing demand for accurate and speedy determination in which flexibility is not of paramount interest. An example is in the determination of minor and major elements in geological samples on an industrial scale (Hall, 2017).

Electrochemical techniques for the detection of HMs

The electrochemical approach in the detection of HM ions has gained remarkable attention as a result of its detection speed, ease of operation, economic efficiency, and on-spot field applications. There are numerous electrochemical technologies for the detection and quantification of HM ions. Some of these methods include differential pulse voltammetry (DPV), potentiometry, square wave voltammetry (SWV), cyclic voltammetry (CV), amperometry, linear sweep voltammetry (LSV), electrochemical impedance spectroscopy (EIS), and the anodic stripping voltammetry (ASV) (Malik et al., 2019; Stortini et al., 2020).

Differential pulse voltammetry This technique obtains information relating to a specific analyte through the measurement of current within an electrochemical cell as a function of the potential applied. The electrochemical cell is made of three electrodes, a counter electrode, a working electrode, and a reference electrode that is immersed within the electrolytes and a potentiostat. The approach has immunity to the residual current which gives a highly rapid measurement with high sensitivity. DPV enhances the increase in the target's selectivity through observance of the various redox reactions when compared to LSV and CV (Khalafi & Rafiee, 2017). DPV therefore ensures a higher limit of detection when compared to the other electrochemical techniques as a result of its higher signal-to-noise as well as the speedy breakdown of the charging current under a greater potential pulse. Numerous HMs like Hg ions, Fe ions, Cr (II), Zn (II), and Cu (II) have been successfully detected using sensors based on derivatives of calixarenes. Various factors affect the detection of HM ions in DPV, which include deposition potential, pH, supporting electrolyte, and deposition potential (Pingarron et al., 2019).

Dinbore et al. (2021) in their study investigated the use of DPV for the determination of the concentration of Cr (VI) in the presence of a chemically modified carbon electrode. They were able to accurately quantify Cr (VI) at very trace content. The limit of quantification (LOQ) and limit of detection (LOD) were 0.2950 and 0.0885 $\mu\text{mol/L}$ respectively. The R^2 value for the linear curve used in calibration was 0.999. Similarly, Kensova et al. (2014) determined the concentration of HMs (Cd, Zn, Pb, and Cu) in the plasma of children having tumor diseases using the same method. They reported that there was a relatively higher concentration of the metals in the plasma of patients that have cancer in comparison to the healthy ones. The method adopted was noted to have high precision and accuracy. Xie et al. (2018) evaluated the concentrations of Cd and Pb using a nanocrystalline carbon black. The LOD for Pb and Cd were found to be 5 nM and 8 nM respectively. Spiking was done to check the accuracy of the method. The method was used successfully for the determination of the actual concentration.

DPASV is one of the most reliable techniques as a result of its unique ability to measure numerous elements at the same time at an ultra-trace concentration as well as its low cost. DPV has another advantage of being able to identify the speciation or the oxidation of the metallic ion in the environmental sample.

Square wave voltammetry. This technique involves the repetition of pulses of square-shaped potentials on a potential sweep and is therefore highly efficient for the differentiation of charging and faradaic current. It is suitable for the determination of metal analytes that are electroactive within a concentration range of nano to picomolar (Pandey et al., 2019).

Various researchers have used this approach for the detection of various metal ions such as Fe (III), Pb (II), and Cd (II). The determination of HM ions using this technique is affected by the pH of the medium and the duration of incubation of the analytes. Liu et al. (2022) carried out a study aimed at validating a method for the determination of Pb (II) and Cd (II) in the presence of Zn (II) and Cu (II) as interfering ions. Their proposed model was adopted for detecting Pb (II) and Cd (II) in soil extracts. Their results were comparable to those obtained using ICP-MS with a percentage recovery of almost 100%. Pandey et al. (2019) detected and quantified the content of Cd using SWV in the presence of ionic graphene oxide in its modified liquid form. They reported that the optimized predicted values for Cd response were observed to be within 95%, while the LOD obtained was lower than the USEPA standards. The sensitivity for the lead was estimated to be 0.0371 $\mu\text{A/ppb}$ with an LOD value of 0.42 ppb within a linear range of 5 to 15 ppb. Similarly, Tesfaye et al. (2021) determined the concentration of Hg (II) using hydroxyl-diphenyl benzamidine that was modified with a paste of carbon electrode. They concluded that the method developed was highly sensitive and selective with a limit of detection within 1.28 nM and an RSD of 3.7%.

DPV has some areas of strengths as well as setbacks. It has a highly improved speed and sensitivity in its analytical detection and measurement. It is one of the most preferred techniques as a result of its outstanding precision, selectivity, accuracy, low cost, and portability. However, as a fairly complex analytical approach, it is difficult to understand voltammetric data from this technique in comparison to CV (Petovar et al., 2017).

Anodic stripping voltammetry This is a technique employed for the detection of metal ions at very trace concentrations. It has been identified as one of the most advanced approaches for analysis involving trace concentrations of HM analytes. It is unique in that it is capable of determining multiple elements synchro-

nously at concentrations ranging up to fractions part per billion using instruments that are portable and relatively less expensive. The functioning of this device is based on a two-step process. The analytes are deposited first on the electrode, after which they are oxidized into the underlying electrolyte. The speed of metal deposition on the surface of the electrode is affected by the concentration, electrode area, and diffusion parameters of the solution (Vito-Francesco et al., 2022). The accompanied stripping step is vital in the detection process which forms the basis for the generation of the signal. The Faradic current is generated after the oxidation and is measured as the oxidation potential of each of the analytes (Finsgar et al., 2019). It has been documented to be highly efficient in the quantification of HM ions.

Durai and Badhulika (2022) used ASV and chemometric techniques for the determination of HMs in blood serum samples. The sensor was observed to possess a low LOD (0.00114 ppb, 0.00261 ppb, 0.00232 ppb, and 0.00154 ppb for Cd, Cu, Hg, and Pb ions respectively). They concluded that the efficiency of the method shows it is promising for bioanalytical and environmental applications. Also, Ma et al. (2022) utilized ASV for a speedy determination of the trace amount of Cd and Pb in wastewater samples. They compared their validated method with standard existing methods and reported the accuracy of their result to be greater than 88%. Similarly, Zhao et al. (2022) investigated the content of HMs in water samples using multiplexed ASV in the presence of nanocomposite screen electrodes integrated with the flow cell. The percentage recovery for the HMs was 95 to 101%. The LOD was 2.4 $\mu\text{g/g}$ and 0.88 $\mu\text{g/g}$ for As and Cd respectively. The accuracy and selectivity of the validated method were reported to be high. Anodic stripping has a major limitation of being able to identify only a limited number of elements due to the possibility of the elements forming an amalgam.

Differential pulse anodic stripping voltammetry This is a novel detection technique for a trace amount of HMs. It aids the pre-concentration and accumulation of the various species of analytes in the solution. There is a surface modification of the electrode in this technique, which could increase the efficiency of the chemically altered electrode. Numerous studies have documented the detection of various kinds of HM ions using this technique in comparison to most other electrochemical instrumental techniques (Palisoc et al., 2021). Numer-

ous HM ions such as Pb (II), Hg (II), Cu (II), and Cd (II) have all been detected in various environmental matrices using this approach. The major factors affecting the detection of HMs using this approach include the reduction potential of the analyte, amplitude of the pulse, accumulation time, nature of supporting electrolyte, and reduction time. The above factors affect the effectiveness of the pre-concentration step as well as the sensitivity of the measurement (Okpara et al., 2022). Saryati (2009) investigated the contents of Zn, Cd, Pb, and Cu in uranium ore using DPASV. The relative standard deviation and percentage recovery of the method were 1.2% and 85.2% respectively. Srogi and Baranowska (2000) investigated the concentrations of Ni, Cd, Zn, Mo, and Pb in moss sample using DPASV. A certified reference standard (oriental tobacco) was used as the benchmark for comparison, and the results were highly promising showing the sensitivity and accuracy of the method. Kumar et al. (2004) determined the concentrations of Cu, Cd, Pb, and Zn in blood samples, diet, and air using DPAS. The observed mean retention times for Zn, Cu, and Cd in the blood were reported as 1.92, 2.12, 7.85, and 17.32 days respectively. The reliability of the method was established using standard reference samples. Maciel et al. (2019) determined the concentration of Cu, Pb, Cd, and Zn in wine samples. They evaluated the accuracy of the method using the standard addition technique obtaining a percentage recovery of ranges 82.5–105.9%. They recommend the method for the quantification of metals in various environmental samples due to its high sensitivity and precision. Xie et al. (2018) investigated the concentrations of Cd and Pb (II). The LOD was established to be 5 nM and 8 nM for Pb and Cd (II) respectively. The sensor linear response ranged from 6 to 1000 nM. This technique has high sensitivity and selectivity. It is however expensive (Palisoc et al., 2021).

Square wave anodic stripping voltammetry. This is a unique type of anodic stripping voltammetry and has numerous applications in sensing detections of various HM ions. It uses a potential waveform that is related to that of DPA. It differs from DPASV in that there are only losses in the sensitivity at marginal levels and also makes provision for a very quick scanning rate hence a rapid experimental process (Pingarron et al., 2019). This analytical process has two steps; the first is the accumulation of the HMs on the surface of the electrode, followed by the electrochemical stripping

of the metal that has been accumulated on the surface of the electrode. Certain factors affect the quantification of HMs using this instrumental technique which includes accumulation potential, pH, the concentration of the modifier, and the concentration of the supporting electrolytic medium (Scandurra & Mirabella, 2021). This technique has been accurately employed for the detection of various metals such as Pb (II), Cu (II), and Tl (II). Liu et al. (2020) detected the contents of Pb in soils in the presence of copper ions as interference using SWASV. The percentage recovery of the method was reported to be 98.70% while the support vector regression coefficient was 0.9942 which shows a very reliable method for quantification. Scandurra and Mirabella (2021) determined Cd (II) and Pb (II) in aqueous solutions using SWASV. They concluded from their results that the method was highly efficient in the quantification of the metals with a very high percentage recovery close to 100%. Tamayo et al. (2014) developed an analytical method for the quantification of HMs in turtle eggs and algae. Two different digested methods were also evaluated. Their best result was obtained from biological samples digested using EPA 3050B method. Bahinting et al. (2021) evaluated Cd (II) and Pb (II) ions using the same method in the presence of gold ultramicroelectrode. The LOD was found to be 7 µg/L and 5 µg/L for Cd and Pb (II) respectively. The findings from the studies showed the potential of the method in quantifying Cd and Pb (II) in aqueous media. The technique has some advantages such as low detection limits, highly cost-effective, and permitting simultaneous detection of multiple metals. It has a high speed of analysis and sensitivity (Munteanu & Apetrei, 2021).

Electrochemical impedance spectroscopy This makes use of alternate electrical signals of varying frequencies for quantifying the electrical signal outputs. It provides details on the electrochemical parameters of the outer surface layers of various electrochemical phenomena and the specific electrode such as the presence of diffusion and kinetic control. It is a system that is highly robust and sensitive to the determination of the resistance of a particular system (Meddings et al., 2020). This technique has the potential of detecting the targeted analyte spontaneously without the need for labeling. This has been employed for the quantification of various metallic ions such as Ni, Eu, Hg, and Al. The efficient detection

of metal ions is affected by various factors such as frequency, pH, and concentrations (Sandford et al., 2019). Knihnicki et al. (2022) determined Cd and Pb (II) ions in aqueous media using EIS in the presence of a carbon nanotube and carbon-modified electrode. A linear response was obtained within a concentration range of 0.1 to 10.0 µmol/L. They concluded that the sensor developed was highly efficient for the determination of the metal ions in honey and natural water samples with percentage recoveries ranging from 96.4 to 101.6%. Similarly, Senila et al. (2022) investigated the simultaneous remediation of Zn, Cd, Cr, Cu, and Ni from an aqueous medium using thermally treated zeolite. Quantification of HMs was done using EIS. This technique permits real-time determination with outstanding robustness and selectivity. It is however prone to noise and this requires the use of a Faraday cage for minimization.

Cyclic voltammetry technique It is a highly versatile electroanalytical technique for the detection and quantification of various metallic species due to its unique ease of usage. It is used for the measurement of the reduction and oxidation process involving various molecular species. The electrical reversibility in this process is connected to the kinetics of electron transfer between the electrode and the analyte of interest (Munteanu et al., 2021). This technique differs from DV due to its sensitivity to residual currents. The detection of metallic ionic species including HMs such as Hg has been documented using various derivatives of calixarene as electrode-modifying agents (Sandford et al., 2019). Paliso et al. (2021) investigated the remediation of HMs from water using *C. microcarpa*. The quantification of the concentration of lead (II) in the remediation studies was determined using a highly sensitive CV technique. The LOD was 267.7 with a strong relationship with the anodic response (R²: 0.99). Similarly, Okpara et al. (2022) reviewed the use of CV in the determination of HMs in various environmental and biological samples. They described the method to be affordable and sensitive for the determination of HMs with appreciable precision and accuracy. Palisoc et al. (2019) utilized CV for the quantification of HM ions in processed food using graphene-modified carbon electrodes. The LOD were 745 ppb, 37 ppb, and 0.74 ppb for Cu (II), Cd (II), and Pb (II) respectively. The simplicity of the use of this technique and its sensitivity are its major merits. It is however affected by the background noise effect during operation (Elgrishi et al., 2018).

Table 3 Spectroscopic techniques for the quantification of HMs and remarks

HMs	Sample matrix	Instrumental technique	Remark	References
1 Pb and Mn	Human hairs	GFAAS	The method showed remarkable linearity within concentration ranges of 0.001–0.015 $\mu\text{g}\cdot\text{L}^{-1}$. The RSD was 12.97% showing high precision	Forero-Mendieta et al. (2022)
2 Cr, Pb, and Cd	Fish feeds	GFAAS	The LOD for Cd, Cr, and Pb were 0.010, 0.022, and 0.078 $\mu\text{g}/\text{g}$ respectively. The %R of the analytes was 90–104% while the RSD was within the range of 4.90 to 9.60%	Ullia et al. (2017)
3 Pb, As, Hg, Cd, and Hg	Capsule shell	ICP-MS	The RSD was 25%, with RSD being 5.34, 3.79, 5.19, and 5.67% for Pb, Hg, Cd, and As respectively. The method was highly sensitive and precise	Phadke and Gaitonde (2016)
4 Pb	Cultivated vegetables	WDXRF and EDXRF	A very robust calibration was obtained for the samples when WDXRF was used while a little compromise in the accuracy and precision when EDXRF was used	Harris et al. (2019)
5 Cr, Cu, and Pb	Cosmetics	ICP-OES and ICP-MS	A high concentration of Pb, in two different brands (> 10 ppm). Methods were accurate based on % recovery studies	Abuseleek et al. (2015)
6 As, Cu, Pb, and Ni	Surface water	FAAS	The optimum %R of the metal ions was greater than 85.0%	Ipeaiyeda and Ayo (2017)
7 Zn, Fe, Cd, Pb, and As	Agricultural soil	ICP-OES	Cluster analysis results revealed that the metals clustered into three major groups, which points to different sources of anthropogenic origin	Shaheen et al. (2022)
8 Co, Zn, Cu, As, Pb, and Cd	Particulate matter in the air (PM2.5)	UV-Vis	The combination of the two spectroscopy technique was a potent tool for revealing the interactions of the HM and the organic compounds	Ma et al. (2022)

Table 3 (continued)

HMs	Sample matrix	Instrumental technique	Remark	References
9 Cd and Cr	Water sample	GFAAS	Cd was higher than the permissible limit (0.3 mg/L). Extraction efficiencies are categorized into high, moderate and poorly extractable with Cr having the greatest variations	Popovic et al. (2017)
10 Cu, Zn, Pb, Co, Cd	River water, soil, lettuce and cabbages	AAS	The ecological risk impacts were 225.46 and 86.48 for cabbage and lettuce respectively	Sagagi et al. (2022)
11 Pb and Cd	Soil sample	AAS	Pb ranged from 36.47 to 43.42 mg/kg while Cd ranged from 0.505 to 1.75 mg/kg which were lower than WHO standard	Sisay et al. (2019)
12 Cr	Tannery soil samples	AAS	Spatial distribution analysis showed the concentration of Cr was highest at the dumping area. Source apportionment studies showed that the HMs emerged from two sources	Rahman et al. (2021)
13 Zn, Cr, Pb, Cr, Fe, Ni, Cu and As	Fish samples	EDXRF	Mn and Cd were below the limit of detections	Koleleni and Haji (2014)
14 As and Cd	Rice	CVAAS, ICP-AES, and ICP-MS	Concentrations of As and Cd were lower than the maximum limits	Fernandez et al. (2020)
15 Pb, Zn, and Cr	Atmospheric aerosol	EDXRF	The rate of detection of the HMs within the three different samples was 90% accurate approximately	Kim et al. (2022)
16 Cd and Pb	Soil and water	GFAAS	The LOD and LOQ were observed to be very low with reliable precision based on the RSD	Gende and Schmelting (2022)
17 Zn, Pb, Co, Cd, and As	Chinese herbs	CVAAS and GFAAS	The RSD and percentage recoveries show that CVAAS was more precise and sensitive	Sarojram and Chen (2011)
18 Cd, Pb, Cu, and Zn	Medicinal plants	UV-Vis	The technique was very efficient and precise in the quantification of the HMs	Goday (2019)

Table 3 (continued)

HMs	Sample matrix	Instrumental technique	Remark	References
19 Pb, Hg, and Cd	Fish samples	CVAAS and ICP-AES	The LOD and LOQ were at least a factor of 5 and 10 lower than the residual maximum limits. The linearity regression coefficient for CVAAS was higher than 0.99	Fernandez et al. (2014)
20 Pb and Cd	Blood samples	ICP-OES	The values for percentage recoveries for Pb and Cd were acceptable though not very sufficient	Ahmed and Alatawi (2022)
21 As	Medicinal plants	GFAAS and HGAAS	The percentage recovery of arsenic for GFAAS and HGAAS were 102 and 98% respectively. The RSD was 2.3–6.7 and 2.5–6.5% for GFAAS and HGAAS respectively	Khalid et al. (2016)
22 Hg, Cd, Cr, As, and Zn	Surface soil	WDXRF	As had the least concentration (2.3 to 18.6 mg/kg) while Zn had the highest (189.2 to 908.6 mg/kg)	Kodomo et al. (2012)
23 Co, Zn, Cd, Pb, As	Rice, paddy soil, and marble powder	EDXRF	Rice samples with a cumulative index of hazard greater than 1. PCA and cluster analysis showed a high level of consistency	Khan et al. (2021)
24 Cd, Pb, Ar, Hg, and Ni	Blood samples from smokers	ICP-MS	Cd, Pb, Ar, Hg, and Ni reported were 0.23, 26.42, 19.43, 8.77, and 79.57 respectively. The contents of the metals were higher in the blood samples of the smoker than non-smokers	Mohammed et al. (2016)
25 Zn, Pb, Cd, and AS	Water sample	EDXRF	Precision was less than 2%	Yao et al. (2015)
26 Pb, Zn, Hg, Pb	Sediments	EDXRF	The method was precise. Multivariate analysis showed that the HMs were of natural origin	Tholkappian et al. (2018)
27 Cd, Zn, Pb, and Co	Chinese herbs	EDXRF	The analysis took a very short duration of 10–30 min with a cost that is 1/5th to 1/10th of the conventional approach	Ma et al. (2022)

Table 3 (continued)

HMs	Sample matrix	Instrumental technique	Remark	References
28 Cd, Zn, Hg, Pb, and Cu	Sewage samples	CVAAS	Samples were moderately to highly polluted with Cd, Zn, Hg, Pb, and Cu	Tytila et al. (2022)
29 Hg	River water sample	UV-Vis	Concentration ranged from 0.13 to 0.35 µg mL ⁻¹ which was higher than the permissible limits of 0.002 µg mL ⁻¹ based on Brazillian water standards	Simiao et al. (2022)
30 Cr, Cu, Zn, Cd, Ni, and Pb	Water sample	UV-Vis	The lowest concentration detected was 100 µM. The method had a very low detection limit	Ahmed et al. (2022)
31 Ni, Cd, and As	Water sample	AAS	The concentration of metals was higher than WHO/FAO standards	Tibebe et al. (2022)
32 Cd	Films from cassava	GFAAS	LOD and LOQ were 0.07 and 0.02 µg/L respectively. The RSD was in the range of 1.6 to 4.8%. The method was highly suitable for the determination of the concentration of Cd in the samples	Rada-Mendoza et al. (2019)
33 Fe, Zn, Cr, As, Ni, Pb, Cd, Mn, and Cu	Milk samples	EDXRF	The index of health risk for the metals was within safe levels	Jolly et al. (2017)
34 As, Sn, Cd, Cu, and Hg	Wheat, milk, bread, cheese, rice, coffee, chocolate, and sugar	ICP-MS	The concentration of metals studied was greater than the permissible levels	Voica et al. (2012)
35 Pb, Cr, Cd, Co, Zn, and Cu	Surface soil	WDXRF and EDXRF	WDXRF is about an order magnitude of higher sensitivities in comparison to EDXRF	Yuan et al. (2022)
36 Hg, Cu, and Zn	Sewage sludge	CVAAS and ICP-OES	The ultrasound wave reduced the duration of the extraction step. The CVAAS had higher precision	Tytila et al. (2022)
37 Pb, Cd, Ba, Cu, As, Fe, and Cr	Mongolian medicines	EDXRF	The technique was highly stable and precise. RSD was 5.49 to 20.0%. The LOD for all the samples was lower than 0.1 ppm	Gao et al. (2022)

Table 4 Studies on HM determination using electroanalytical techniques

	HMs	Sample matrices	Technique	Remark	Reference
1	Pb and Cd	Surface soil	SWV	The result was comparable to that obtained using ICP-MS with a percentage recovery of almost 100%	Liu et al. (2022)
2	Cu, Zn, Pb, and Cd	Water sample	ASV	The percentage recovery for the HMs was 95 to 101%. The LOD was 2.4 µg/L in As and 0.88 µg/g for Cd	Zhao et al. (2022)
3	Cu, Pb, Cd, and Zn	Wine	DPASV	Obtained a % recovery of ranges 82.5–105.9%. The method has high sensitivity and precision	Maciel et al. (2019)
4	Cd (II) and Pb (II)	Water	SWASV	The method was highly efficient in the quantification of the metals with very high percentage recovery of close to 100%	Scandurra and Mirabella (2021)
5	Cd and Pb (II)	Water and soil	DPASV	The LODs were established to be 5 nM and 8 nM for Pb and Cd (II) respectively. The sensor linear response ranged from 6 to 1000 nM	Xie et al. (2018)
6	Cd (II) and Pb (II)	Water	SWASV	LODs were found to be 7 µg/L and 5 µg/L for Cd and Pb (II) respectively	Bahinting et al. (2021)
7	Cu, Cd, Pb, and Zn	Blood samples, diet, and air	DPASV	The observed mean retention times for Zn, Cu, and Cd in the blood were reported as 1.92, 2.12, 7.85, and 17.32 days respectively	Kumar et al. (2004)
8	Cd	Wastewater	SWV	The sensitivity for the lead was estimated to be 0.0371 µA/ppb with an LOD value of 0.42 ppb within a linear range of 5 to 15 ppb	Pandey et al. (2019)
9	Zn, Cd, Pb, and Cu	Uranium ore	DPASV	The RSD and percentage recovery of the method were 36.8 to 1.2% and 174 to 85.2% respectively	Saryati (2009)
10	Cd and Pb (II)	Honey and water samples	EIS	Highly efficient for the determination of the metal ions in honey and natural water samples with percentage recoveries ranging from 96.4 to 101.6%	Knihnicki et al. (2022)
11	Cd and Pb	Water sample	ASV	Reported the accuracy of their result to be greater than 88%	Ma et al. (2022)

Table 4 (continued)

	HMs	Sample matrices	Technique	Remark	Reference
12	Ni, Cd, Zn, Mo, and Pb	Moss sample	DPASV	Results were highly promising showing the sensitivity and accuracy of the method	Srogi and Baranowska (2000)
13	Zn, Cd, Cr, Cu, and Ni	Water samples	EIS	The technique permits real-time determination with outstanding robustness and selectivity	Senila et al. (2022)
14	Hg (II)	Soil	SWV	The method developed was highly sensitive and selective with a limit of detection within 1.28 nM and RSD of 3.7%	Tesfaye et al. (2021)
15	Cd, Zn, and Pb	Blood sample	ASV	The sensor was observed to possess a low LOD (0.00114 ppb, 0.00261 ppb, 0.00232 ppb, and 0.00154 ppb for Cd, Cu, Hg, and Pb ions respectively)	Durai and Badhulika (2022)
16	Pb	Wastewater	CV	The LOD was 267.7 with strong relationship with the anodic response (R ² : 0.99)	Palisoc et al. (2021)
17	Cu, Pb, Mn, and Zn	Milk sample	SWV	The linear range of the detection was 3.0–30 µg/L with an LOD of 0.15 µg/L for Pb and 0.21 µg/L for Cd	Fang et al. (2019)
18	Pb, Cd, and Zn	Turtle eggs and algae	SWASV	Best result was obtained from biological samples digested using EPA 3050B method	Tamayo et al. (2014)
19	Zn, Co, Pb, and Cd	Processed food	CV	The LOD were 745 ppb, 37 ppb, and 0.74 ppb for Cu (II), Cd (II), and Pb (II) respectively	Palisoc et al. (2019)
20	Pb	Soil	SWASV	The percentage recovery of the method was 98.70% while the support vector regression coefficient was 0.9942 which shows a very reliable method for quantification	Liu et al. (2020)

Summary of studies in HM determination using various instrumental techniques

Numerous studies have documented the applications of various spectroscopic and electrochemical instrumental

techniques in the determination of the concentrations of heavy metals in numerous environmental samples (soil, water, and air) as well as food products, drugs, and cosmetics among others. Tables 3 and 4 summarize the findings from various studies in this regard.

Conclusion

There is a pressing need for continual improvement and development of novel and advanced strategies for the quantification of HMs. The quantification of HMs in various environmental and human samples is paramount for effective monitoring and assessments. This also aids in ensuring that concentrations are kept within safe limits. This work has reviewed novel published studies on advanced instrumental techniques and other recent advances in the quantification of heavy metals. Studies based on advanced techniques in heavy metals detection have shown that researchers have explored numerous spectroscopic-, optical-, electrochemical-, and nanotechnology-driven methods. More recently, various SPE techniques integrated with spectrophotometric methods such as atomic absorption spectrometry (AAS) using numerous adsorbents such as graphene, graphene oxides, and quantum dots for the determination of heavy metal concentration at ultra-trace levels have been developed. The integration of electrochemical methods has also contributed to the advancement of portable and miniaturized potentiostats, having tailorable electrodes that do not require calibration. Presently, numerous analytical techniques are available for the determination of HMs at trace concentrations in various environmental matrices. It is paramount to also ensure that the analytical results are of the utmost desired quality. For proper selection of the best analytical method for particular metal analysis, various parameters such as the limits of detection and quantification as well as the potential for a multi-elemental determination and cost-effectiveness are taken into consideration. There is no single method that is perfect for the determination of various metals. Each method has its strengths and areas of limitations. There are highly specialized techniques suitable for the determination of selected metals for example mercury and arsenic. The specific oxidation state of the metal in the matrices is also vital as in the case of Cr (III) and Cr (VI) where each of the oxidation states poses varying toxicity; this should also be considered in the choice for instrumentation. One of the prominent setbacks of the atomic spectroscopic analytical technique (FAAS, ICP-OES, and ICP-MS) in the analysis of samples in solid form is such instrumentation is most amenable for liquid samples and therefore requires that samples in solid forms must first be brought in solution state before their analysis through chemical treatments such as digestion. More recent advancements in the fabrication of high-resolution continuum sources

have enhanced the commercialization of some of these devices such as AAS systems thereby making it possible for rapid synchronous and sequential multi-elemental determination. There is also a need for further studies focusing on the development of in situ advanced techniques for heavy metal determination with the potential of meeting international requirements.

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Data availability The work was based on review of various literatures. Therefore there is no data availability.

Declarations

Competing interests The authors declare no competing interests.

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