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Evaluation of Some Spectroscopic Techniques for Trace Elements Assessment in Human Biological Samples During 2000-2022: (A-Review)

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ABSTRACT

Trace elements (TEs) are the chemical components that naturally occur in very minute quantities. They are very important and vital for good development and optimal metabolic functioning of human organisms. According to WHO classification there are about twenty known TEs. These elements are categorized in three main groups, essential, non-essential and toxic TEs. This review provides some detailed information's and important criteria needed to assess TEs levels in different human biological samples (HBSs) using the most used spectroscopic techniques (STs). Also, this review covers some of the fundamental and basic principles underlying the most important STs that have been used for TEs assessment in HBSs over the last 22 years. Furthermore, this review also focuses on the instrumentations and operating conditions of STs that based on electromagnetic radiation (ER) in UV/Visible region for the transition of bounding electrons. These techniques include absorption, emission, and luminescence (photoluminescence and chemiluminescence).

Keywords: TEs, HBSs, STs, AAS, AES, AFS.

INTRODUCTION

An overview of publications focused on the period since 2000-2022 and outlining modern STs for determination of TEs in various HBSs is presented in this review. Spectroscopy is a general term (field of study) used for the science that deals with all the interactions that occur between different types of ER and matter (molecules and/or atoms and/or ions)[1]. Therefore, these types of scales are only possible if the interaction between matter and photons causes one or more changes in the properties of the samples. According to the region of the electromagnetic spectrum (ES) and the transition type of bounding electrons, different types of STs can be utilized[2]. Based on the spectral regions and types of electronic transitions, STs are divided into absorption, emission, and fluorescence in the ultraviolet (UV) and visible radiation in the UV/Visible region (10-780nm). These STs are classified into atomic absorption techniques like UV/Visible spectrometry, flame, and flame less

(graphite furnace) atomic absorption spectrometry (FAAS and GFAAS). In addition to, atomic emission techniques like inductively coupled plasma-atomic emission or mass spectrometry (ICP-AES or ICP-MS). Also, STs includes photoluminescence techniques like AFS and APS and chemiluminescence techniques like ACLS[3-7]. This review is focused on the modern publications focused on STs for direct or indirect determination of TEs (viz. Fe, Mn and Zn) in various HBSs like blood, urine, and milk during the period between 2000-2022.

Spectroscopic techniques

STs: This technique uses light to interact with a matter and thus exploring certain features of a sample to learn about its composition and/or structure. The basic principles of these techniques are the interaction of an ER with a matter. An understanding of the interaction properties leads to the measurement and estimation of a variety types of spectra. Therefore, different types of STs and their applications in solving analytical problems. According to this phenomenon which depends on the type of energy transfer required for the interaction between energy and target materials, there are three types of STs. These techniques includes absorption, emission and luminescence. Luminescence consist of two main forms at play: photoluminescence and/or chemiluminescence. The term fluorescence and phosphorescence are usually referred as photoluminescence because both are similar in excitation caused by photon absorption. The differences between them are that the electronic energy transition responsible for fluorescence does not change in electron spin, which results in short live-electrons (10–5 s) in the excited state of fluorescence. In phosphorescence, there is a change in electron spin, which leads to a longer lifetime of the excited state (about second to min). The two phenomena were occurred at longer wavelength than the excitation radiation[3–5]. These STs were summarized in Table 1.

Table 1: STs Based on ER at Ultraviolet/Visible Region a for Transition of Bounding Electrons[b]

Type of energy transfer	STs		
Absorption			UV/Visible spectroscopy[c]
			Atomic absorption spectroscopy (AAS)
Emission (thermal excitation)			Atomic emission spectroscopy (AES)
Luminescence	Photoluminescence	Fluorescence	Atomic fluorescence spectroscopy (AFS)
		Phosphorescence	Atomic phosphorescence spectroscopy (APS)
	Chemiluminescence		Atomic chemiluminescence spectroscopy (ACLS)

[a]Region of ES, [b]Quantic transition type, [c]UV/Vis: ultraviolet and visible ranges

Spectroscopy based on absorption

Absorption spectroscopy: In absorption techniques samples are vaporized into free, neutral atoms and illuminated by a light source that emits the atomic spectrum of the element under analysis. It occurs when the target material absorbs energy from the radioactive source. It is often determined by measuring the portion of the energy transmitted through the target material, with absorption reducing the transmitted portion. The ER absorption in the ultraviolet/visible region results from the excitation of bounding electrons and their transition from the ground state to the excited state. The UV/Visible radiation has sufficient energy to enhance electronic transitions, and this is the fundamental principle investigated by UV/Visible spectroscopy. The absorbance gives a quantitative measure of the concentration of the element. This technique remains very useful for identifying most inorganic compounds that normally absorb light in the visible region of the spectrum. The specific wavelength of the maximum absorption band depends mainly on the number of d-electrons, the geometry and shapes of the compounds, and the number of atoms (ligands) that were coordinated with the central transition metal ion or atom[3,4].

In flame spectroscopy technique (FAAS) the atomization process is done by flame, where molecules are broken down and vaporized into atoms. In this technique the samples were transformed into a fine mist consisting of very small droplets of solution. A significant improvement in the sensitivity is achieved by using resistive heating in place of a flame. This technique is very sensitive and can be used to measure the total element (multi-element) content within a sample. However, the accuracy and precision of these techniques can be affected by sample matrix[1].

Another common method of atomization technique is to use a graphite furnace (GFAAS or ETAAS). In which the energy that used for volatilization

and atomization is supplied by an electric current that applied to the graphite furnace. In this case, a small sample cloud arises inside the tube of pizolithic graphite which is placed in the center of a specially designed furnace through which the analyzed light stream passes. The tube is heated to a high temperature caused by a high electric current. As a result, the sample is first dried, then decomposed, burned and finally atomized. The temperature in the tube can reach a value of more than 3000 K, and such a high temperature, more than the flame temperature results in significantly lower detection limits (DLs) compared to FAAS technique[6].

The choice of the atomization method (FAAS or GFAAS) is mainly determined by the content of the analyte in the samples being analyzed. Because of its high sensitivity and low DLs, most of the analyzes used GFAAS extensively. The better precision when using FAAS makes it the preferred method when the analyte concentration is much greater than the DLs for flame atomization. In addition, FAAS is less subject to interferences, allows for greater throughput of samples, and requires less operator expertise. GFAAS becomes the method of choice when the analyte's concentration is less than the DLs for FAAS[6].

Spectroscopy based on emission

Emission spectroscopy: The phenomenon of releasing a photon after thermal excitation is called emission, and the phenomenon after absorption of a photon is called photoluminescence. In the phenomenon of chemiluminescence, excitation is caused by a chemical reaction. AES is ideally suited for multi-elemental analysis technique because almost all analytes in the sample are excited simultaneously. A scanning monochromator can be programmed to move very quickly to the desired wavelength of analysis, pausing to record the intensity of its emission before moving on to the next wavelength for analysis and so the analysis continues. In this way, it is possible to analyze three, four to five analytes per minute[7].

In AES technique they use a highly-energy plasma consisting of electrically neutral gas (usually Ar-gas) which is converted into positive ions and electrons. This plasma contains enough energy (very high temperature) to ionize, almost all the elements and nearly excite them into more energetic electronic exited states. These species tend to return quickly to the low ground state, releasing energy at distinct wavelengths depending on the target elements present in the analyzed sample. The emitted light is directed to a detector, and the optical signals are processed to values for the concentrations of the elements. The intensity of the ER in this case is directly proportional to the concentration(s) of the analyte(s) in the sample[1]. In ICP-MS a mass spectrometer separates and detects ions produced by the ICP, according to their mass/to/charge ratio.

Spectroscopy based on luminescence

Luminescence: Luminescence is the most conveniently defined as the phenomenon of ER that emitted by an atom or a molecule when these species return back to the ground state from the exited state. According to the source of excitation, this phenomenon could be classified into photoluminescence spectrometry and chemiluminescence spectrometry.

Photoluminescence spectrometry: It is like emission spectroscopy; uses quantitative measurements of optical emission from excited photons to determine concentration of an analyte. In this phenomenon, the glow of a substance is triggered by light, unlike the phenomenon of chemiluminescence, where the glow is caused by a chemical reaction. According to the direction of photon spin, it divided into two types, fluorescence and phosphorescence. Both phenomena are based on the ability of the material to absorb and emit light with a longer wavelength and therefore lower energy. The main difference between the two phenomena is the time it takes to do this. In fluorescence, the emission is basically instantaneous and therefore generally visible only, if the light source is constantly on (viz. UV lights). While the phosphorescent material can store the absorbed light energy for some time and release it later on, resulting a subsequent glow that persists after the light is turned off. Depending on the material, this afterglow can last anywhere from a few seconds or minute to about an hour. So, if the phenomenon disappears immediately, it is fluorescence, but if it persists for a period of time, it is phosphorescence, and if it needs activation, it is chemiluminescence. In fluorescent emission, photons return to the lower energy level with the same spin that occurs in the higher energy level. Whereas in phosphorescence the emission of photon take place when the analyte returns back to a lower energy level with the opposite spin as a higher energy level[6].

Chemiluminescence spectrometry: It's like emission spectroscopy, it uses quantitative measurements of the atomic or optical emission

from an excited chemical species such as an atom or molecule to measure analyte concentrations[6].

Trace elements

TEs: TEs are dietary minerals in very fine concentrations (<0.01%) of an organism's mass. They play an important role in many biochemical and physiological processes in human body, as it mainly components of various vitamins and enzymes. Other TEs may cause cellular damage that results in a variety of syndromes caused by abnormal proteins[8,9]. Also, TEs are very important for proper growth and maintaining and restoring the health of the human being. Some of them are very important components of enzymes that attract substrate molecules and facilitate their conversion into other specific components. Others accept or donate electrons in redox reactions that lead to the generation and use of the metabolic energy. Moreover, some of them alter the structural stability of many important biological molecules. Others control certain biological processes through specific actions such as facilitating the binding of the molecules to receptor sites on the outer cell membranes.

Some of them change the ionic nature or the structure of membranes to allow or prevent specific molecules from leaving or entering the cell. Others, stimulates gene expression that results in the formation of proteins that participate in life processes of elements within a specific range. In addition, despite the different intakes, they involve the processes of absorption, storage, and excretion. The relative roles and importance of these processes differ between TEs. In addition, some of them are important for proper development of the brain because they provide protection from diseases. The homeostatic regulation of TEs existing positive ions primarily occurs during absorption from the gastrointestinal tract. While others negative ions are absorbed freely in the form of negative ions, they are usually freely and completely absorbed from the digestive system. Thus, it is primarily regulated by its excretion through sweat, urine, bile and breath. Many TEs occur in different matrices at very low levels of content, with an average concentration of 100ppm. In the second half of the twentieth century, a new term appeared for Ultra-TEs with an average concentration of 1.0ppm. Knowledge of TEs and ultra-TEs is very important in various fields of science and technology. Therefore, the need for accurate measurements in very low quantities is very important[10-12].

According to the classification of the WHO, there are about twenty TEs that are based on the nutritional importance have been divided into three main categories. Essential TEs (viz. Fe, Zn and Cu), probably essential TEs (viz. Al, Ni and Mn) and potentially toxic TEs (viz. Pb, Cd and Hg)12. Essential TEs are needed by adult individual in amounts ranging between 50 ug/day–20 mg/day. These elements are catalytic and/or structural components of larger molecules. Severe marginal or primary imbalance in essential TEs can be considered as a risk factor for many diseases of public health importance[13].

The common use of highly sensitive instrumentations needs to adequately control the level of contamination and check the accuracy and precision of the determination. Gaining analytical sensitivity doubled contamination as well as other measurement problems. Therefore, proper precautions must be taken seriously to determine TEs at a concentration of ppb or less. Errors can occur during analysis of TEs by sampling and/or storage and/or during improper sample preparation and analysis. Therefore, the accuracy and precision of analytical processing and determination of TEs must always be well-established[13].

Human biological samples

HBSs: It refer to any substance derived from a human body such as tissues, organs, blood and urine. In addition to, any other cells or fluids whether collected for research purposes or as residual samples from diagnostic and/or therapeutic and/or surgical procedures[14].

Samples preparation

Determination of TEs in complex very matrices often require extensive sample preparation and/or extraction prior to instrumental analysis. A large and diverse number of samples that need to determine the concentration of essential and toxic TEs belong to food samples[15,16], environmental samples[17,18], clinical and biological samples[17–21]. Routinely, nearly almost all TEs are identified by AAS and/or AES in addition to, AFS and/or APLS and/or ACS. However, the matrix of many samples like BSs are very complex and consists of high amounts of soluble solids. In addition to large quantities of inorganic compounds like phosphates, chlorides, sulfates, …etc. Direct analysis of these types of samples with complex components presents many difficulties in the introduction of the sample, in addition to the spectral and non-spectral interferences in the measurements by STs. Therefore, samples should

be mineralized with solutions like mineral acids and/or oxidants prior to analysis to destroy the organic matter or at least diluted it to reduce the contents of associated substances in the samples[12].

Several different analytical procedures have been developed for the pre–concentration and separation of TEs required prior to instrumental determination to lower DLs. This will be performed in order to improve the accuracy and precision of analytical results, and to bring analytes concentrations into the dynamic range of the detector. Pre-concentration methods such as solvent extraction, ion exchange, adsorption, and co-precipitation have been used to analyze TEs in different works[7,10,14,22–29]. The results obtained from the followed analyses shall be based on an appropriate sample preparation procedure and on analysis using at least one or more validated methods to ensure traceability of the test sample results.

STs for TEs Assessment in HBSs

Almost all STs to analyses TEs with different types of sample preparation methods depending on their sensitivity and selectivity. The choice and selection of the appropriate analytical method should be based on the objectives and purpose of the analysis and the DLs of a particular method of analysis. If the analysis is to determine the quantitative and/or qualitative component of the elements, it is necessary to choose spectroscopic methods. FAAS and GFAAS, are highly sensitive and selective spectrophotometers suitable for the determination of TEs. Thus, it has become a powerful method of analysis that have been used for TEs determinations in most analytical labs for a wide variety of applications. The detailed descriptions of the instrumentation were mentioned in many references. The operating conditions and parameters of FAAS and GFAAS include an appropriate wavelength (nm) selection, a good atomizer (Graphite furnace or Spell flame), and pure gas (Ar or air acetylene), and a good background correction method (Zeeman effect or Deuterium lamp), ... etc[3,4].

ICP-AES or ICP-OES provides a good range for the identifying TEs with high sensitivity and selectivity. This is due to the very high atomization temperatures (up to 3000 K or more) of plasma used to break up and to atomize the analytes present in a sample. ICP is generated by Ar-gas, which is ionizes in the intense electromagnetic field and flows in a specific rotationally symmetrical pattern toward the magnetic field of the RF coil. Stable plasma is created because of the collisions between neutral Ar-atoms and charged particles (usually ions). During the introduction of the sample into the plasma, it immediately collides with electrons and positive ions and splits into positive ions. The different molecules will disintegrate into their respective atoms, which then lose electrons and combine repeatedly in the plasma. Excited ER atoms emit at wavelengths characteristic of a particular element. The intensity of this emission is indicating the concentration of the element(s) within the sample and is measured by the detector (photomultiplier detector or semiconductor detector)[3,4].

Even ICP-AES has LODs like FAAS; it can detect many analytes simultaneously (multi-element determination) and has a much larger dynamic range. On the other hand, ICP-AES suffers from spectral interference and is much more expensive than FAAS and ETAAS. Since the state of the ICP is changed by matrix element in the sample solution, the intensity of the emission or absorption signal derived from analytes might be affected. In the analysis of high-density solutions such as slurries, the injection volume of sample might not be constant, which may lead to non-reproducible results or higher LODs levels. Therefore, investigation of the effect of sample matrix for elements and the high-density sample should be indispensable for accurate and reproducible determination by ICP-AES. One of the practical solutions used to overcome the effect of some matrix elements may be to evaporate some of the ions, reduce the viscosity of the sample, lower the pH of samples, or decompose the organic matter in the sample[30].

Before detection with ICP-AES, an effective pre-concentrations steps were required, similarly like in FAAS and GFAAS analysis[31,32]. Various variables and factors affecting these steps such as sample volume, eluent concentration, sample and eluent flow rates must be adjusted. In addition to the precision and accuracy of the method should be improved. The approximate operating conditions for ICP-AES are described in Table 2[14].

Table 2: Approximate Operating Conditions and Descriptions of ICP-AES

Parameters	Conditions
Instrument	ICP-AES
RF power-(KW)	1.0-1.6
Nebulizer pressure-(KPa)	230-270
Viewing high-(mm)	8.0-12.0
Plasma gas flow rate-(L/min)	13.0-17.0
Auxiliary gas flow rate-(L/min)	1.0-2.0
Sample uptake rate-(mL/min)	0.6-1.0
Sample uptake delay-(s)	28-32
Instrument stabilization delay-(s)	13-17
Pump rate-(rpm)	18-22
Rinse time-(s)	18-22
Replicates-(times)	2-4
Replicate read time-(s)	6-8

At the last three decades, ICP-MS became one of the best tools that used in trace elemental determination. It differs from ICP-OES by the type of detector used. The DLs for ICP-MS are at/or below (10-12ppt) and the isotopic ratios can be easily achieved. Therefore, the most abundant natural isotope of each element can easily be identified. It is widely used in routine multi-elemental at trace and ultra-trace level determination in liquid samples with different matrix components. This method is based on the generation of single-positive ions from selected analytes in plasma with stringent parameters. In this method the number of double-charged ions is very strictly limited and should usually not exceed 2-3% of all charged particles. These ions, after passing through a properly designed ionic optics based on the mass/charge (m/z) ratio, are determined using a mass separator and detector.

Different types of separators are usually used, depending on the assumed degree of ion separation. The most used quadrupole separator is existing in many different configurations. Photomultipliers are usually used as detectors, which are adapted to detect ions by placing scintillation crystals in the optical path that convert the flow of ions into photons. The generation of single-charged ions requires fine tuning for different plasma conditions and parameters. The most important conditions and parameters are the temperature, plasma flow, gas flow of the nebulizer and the electrostatic potential. In addition, sample depth and sampling time are also important factors[33].

Due to the low background signal and the large number of ions produced in plasma, it is possible to obtain a very low DL for almost all analytes (in the ppb range). The main advantages of the ICP-MS method include high sensitivity, good accuracy and precision and low limits of detection and quantification (at µg/L-ng/L levels). In addition, exceptionally high linearity of the calibration curve including up to ~9 orders of magnitude, relatively short analysis time, multi-element analysis of most elements of the periodic table and a small amount of samples are required for decision-making[34,35].

In ICP-MS technique, samples are ionized in the same way of Ar-plasma as in ICP-AES technique. In the first stage, the liquid sample is nebulized using an active nebulizer that turns the liquid into a fine mist (aerosol), which is then transferred along with Ar-gas to an ICP torch. In plasma, the nebulized liquid matrix and chemical compounds are vaporized, and molecules are dissociated into atomic components, which ionize into positively charged ions. Ions are extracted from Ar-plasma into dual-focus field (SF-MS), quadrupole (Q-MS) and time-of-flight (TOF-MS) mass analyzers. In mass analyzer, the ions are separated according to the m/z or energy/charge (e/z) ratio in double focus SF instruments. The separate ion beams are detected by a photomultiplier detector or by Faraday cups. Approximate operating conditions and description of ICP-MS are described in Table 3[36].

Table 3: The Approximate Operating Conditions and Description of ICP–MS

Parameters	Conditions
Instrument	ICP-MS
Forward RF power-(KW)	1.3-1.5
Reflected RF power-(W)	1–2 W
Nebulizer pressure-(L/min)	0.60-0.90
Plasma gas flow rate-(L/min)	9.0-14.0 L/min
Auxiliary gas flow rate-(L/min)	0.6-0.9 L/min
Sample uptake rate-(mL/min)	1.0-2.0 mL/min
Spray chamber	Water-cooled at 5-10^{o}C
Expansion chamber-(mbar)	1-2
Intermediate-(mbar)	$1.0\text{-}10^{-4}$
Analyzer-(mbar)	$2.0\text{-}10^{-6}$
Dwell time-(ms)	20-25
Points/peak	2-3
DAC step	3-5
Acquisition time-(s)	40-60
Resolution-(amu)	0.7-0.8

Advantages of ICP-MS over other elemental analysis techniques such as atomic absorption spectroscopy (FAAS and GFAAS) and atomic emission spectrometry such as ICP-AES. This includes ICP-MS DLs for most elements equal to or approximately better than those obtained by GFAAS technique. Also, it has very fast analysis times for all elements at once and handling both simple and complex matrices with minimum matrix interferences due to the very high temperature of the ICP source. Moreover, ICP-MS is more superior in detection ability to ICP-AES with the same sample throughput. Also, ICP-MS has the advantage of getting isotopic information easily. Moreover, ICP-MS technique can be combined with a high-temperature ICP source with a mass spectrometer. Farther more, specialized sample introduction systems can be coupled to ICP-MS, including spark or laser ablation systems, hydride generators and various chromatography systems like HPLC and GC[3,4].

The analytes and the overview of analytical performance including the LOD and the relative standard deviations (RSD%) of selected techniques used for TEs assessment in HBSs during the period 2000–2022 were given in Table 4.

Table 4: The Representative Examples of the Application of Selected Techniques Used for TEs Assessment in HBSs During 2000-2022

Analytes and Samples	Decomposition Conditions	Analytical Technique	Metrological Characteristics LOD	RSD [%]	Ref.
Cu, Fe, Ag, Al, Co, Cr, As, Cs, Mn, Ni, Pb, Se, Sr, U, Tl, V, Be, Cd, Zn, Ba in Whole Blood, Urine	Microwave digestion with conc. HNO_3 used for blood samples, Urine samples were analyzed after 1 to 50 (v/v) dilution with 5% HNO_3	ICP-MS	Ag=0.7, Al=16, As=3.4, Ba=0.02, Be=1.5, Cd=7.7, Co=1.0, Cr=2.8, Cs=9.8, Cu=27, Fe=1.1, Mn=1.8, Ni=17, Pb=13, Se=0.07, Sr=5.7, U=0.1, Tl=0.2, V=0.7, Zn=1.2 (ng/L for all analytes)	5-10	36
Zn in Hair, Nail, Liver	Dilution factor (DF)=40 fold for 12.6 mL	Fl- FAAS	2.2 µg/L	1.2	37
Al, Cd, Cr, Be, Hg, Mn, Pb, Ni, Tl in Blood	Blood samples diluted with de-ionized H_2O or 0.1% Triton X-100 (TX-100) for Tl, DF=1-5 per volume for Be, Tl, 1-20 per volume for Cd, Pb	GFAAS	2.0 for Al, 0.08 for Be, 0.10 for Cd, 2.3 for Ni, 2.2 for Cr, 7 for Hg, 0.4 for Mn, 3.4 for Pb, 0.5 for Tl (µg/L for all analytes)		38
Th in Blood	Sample treatment: 5-fold per volume dilution of blood with 0.1% TX-100	GFAAS	0.2 µg/L	>12	39
Mn, Serum	Samples were diluted 1:4 with 1% HNO_3 +0.1% TX-100	GFAAS	0.2 µg/L	4.7-7.0	40
Th in Serum	3.5% HNO_3 was employed as a protein precipitant for treatments of serum	GFAAS	0.01 µmol/L	4.74	41
Cd, Cr, Cu, Pb, Zn in Scalp Hair, Fingernails	Microwave digestion of samples: 0.5 g+3 mL of conc. HNO_3:H_2O_2 (2:1) at ~37°C for ~4 min, then	ICP-OES	0.6 for Cd, 1 for Cu, 5 for Pb, 0.9 for Cr, 0.5 for Zn (µg/L for all analytes)	3-7	14
Cd, As, Pb, Se in Whole Blood, Serum	Digestion: 0.1-0.2 g samples +3 mL conc. HNO_3+ 1 mL of conc. H_2O_2 ~30 min	ETAAS	Cd=0.021, Se=1.1, As=0.62, Pb=1.2 (µg/L for all analytes)	~5	42
Cd, Pb in Whole Blood	Decomposition of protein samples with $C_2HCl_3O_2$	ETAAS	0.026 for Cd, 0.65 for Pb (µg/L for all 2-7 for Cd, 1.7-2 for Pb analytes)		43
Mn, Fe, Cu, Ni in Urine	Ultrasonic decomposition and concentration of urine samples on column with acid groups sorbent	FAAS	Mn, Ni=0.8, Fe=1.1, Cu=0.5 (µg/L for all analytes)	Mn=0.6–3.7, Cu=0. 5–3.0, Fe=0.5–0.9, Ni=2.5–7.5	44
Hg in Whole Blood	Decomposition with BrO3, microwave irradiation followed by flow injection analysis	AAS	0.14 µg/L	05-10	45
Mo in Whole Blood	Direct dilution with 0.1% TX-100	ETAAS	0.6 µg/L	0.8-1.5	46
Cu, Co, Cd, Ni, Pb in Urine	Digestion of urine samples with conc. HNO_3 ~22 min, absorption on nitrocellulose membrane filter complexes with $C_5H_9NS_2$·NH_3 then filter dissolution in HNO_3	FAAS	Cd=1.1, Ni=55, Co=10, Cu=33, Pb=31 (µg/L for all analytes)	5-7	47
Al, Sr, As, Sb, Ba, Cd, Sn, Zr, Mo, Ni, Pb, Co, Cr, Li, Mn, Se, V in Whole Blood	Digestion of blood samples with conc. HNO_3, DF=10	ICP-MS	Al=4.73, V=0.71, Cd=0.2, Cr=0.15, Sr=5.63, Li=1.5, Se=37.7, Mo=0.15, Ni=0.72, Ba=11.2, Co=0.8, Pb=5.74, Sb=0.44, As=2.03, Sn=0.2, Mn=5.3, Zr=0.08 (µg/L for all analytes)	Al=4.5, As=3.8, Ba=4.9, Cd=6.5, Co=5.7, Cr=3.4, Li=6.8, Mn=2.9, Mo=3.2, Ni=5.5, Pb=4.1, Sb=5.8, Se=6.9, Sn=2.5, Sr=3.6, V=2.5, Zr=4.1	34

Pb, Mn, Al, Cd, Cr, Co, Hg, Ni, Be, V in Whole Blood, Serum, Urine, CSF	Microwave digestion of samples with conc. HNO_3, DF=5	ICP-MS	Al=0.05, Be=0.004, Cd=0.001, Co=0.002, Cr=0.002, Ni=0.002, Hg=0.005, Mn=0.004, Pb=0.006, V=0.002 (µg/L for all analytes)	2.5-5	48
B in Blood plasma, Urine	Protein denaturation with HNO_3	ICP-MS	0.6 µg/L	>2	49
Cd in Urine	Decomposition of urine samples with HNO_3 at ~60°C ~90 min)+$C_6H_{12}O$ extraction of Cd chelate with $C_5H_9NS_2{\cdot}NH_3$	ICP-AES	0.04 µg/L	6.2	50
Pb in Whole Blood	Dilution of blood samples with 0.2% HNO_3+0.5% TX–100, DF=10	ETAAS	15 µg/L	6–14	51
Se in Whole Blood	Dilution with 0.2% HNO_3+0.5% TX-100, DF=5	ETAAS	50 pg	3	52
Cd in Whole Blood	Dilution of blood samples with 0.1% solution of TX-100, DF=5	ETAAS	0.02 µg/L	~10	53
Cd, Pb in Whole Blood, Urine	Dilution of urine samples with 4% HNO_3, dilution of blood samples with 0.25% TX-100, DF=2	ETAAS	Cd 0.01, Pb 0.03 (µg/L for both analytes)	01-14	54
Al in Blood Serum, Urine	Dilution of samples with 1% HNO_3+0.1% TX-100, DF=2	ETAAS	0.40 µg/L	>5	55
Cd in Urine	Dilution of urine samples with 4% HNO_3, DF=2	ETAAS	0.2 ug/L	9	56
As, Mn, Co, Ni in Urine	Direct determination (without dilution) of analytes in urine samples	ETAA	S0.78 for As, 0.054 for Mn, 0.22 for Co, 0.35 for Ni (µg/L for all analytes)	02-08	57
Cd, Pb, Hg in Whole Blood	Dilution of blood samples with 0.05% TX-100 + 0.01 $C_5H_9NS_2{\cdot}NH_3$, 1% C>H>O + 100 µg/L, Ir, DF=50	ICP-M	S0.40 µg/L (Hg), 0.33 µg/L (Cd), 4.82 µg/L (Pb)	02-05	58
As. Cd, Pb, Hg in Urine	Dilution of 500 µL urine samples+500 mL (1% HNO_3+1% H>NSO> +9000 µL 2% HNO_3+10 µg/L Y, Rh, Ga, Ir+0.005% TX-100), DF=50	ICP-MS	0.003 µg/L (Cd), 0.1 µg/L (As), 9-Mar5 0.006 µg/L (Pb), 0.2 µg/L (Hg)	3-9	59
As, Ba, Cd, Co, Cu, Sr, Zn, Fe, Ga, Mn, U, Mo, Ni, Pb, Rb, Se, Tl, V in Biological Samples	Samples+with CH_2O, kept at 90°C ~1 h, diluted with HNO_3 to 50% CH_2O, 1% HNO_3 final concentrations	ICP-MS	Between 0.0005 mg/kg (Tl)-0.22 (Fe) mg/kg Between 0.2 (Sr)–3.5 (Ga)		60
Ag, Cu, As, Au, B, In, Ba, Pd, Be, Cs, W, Bi, Cd, Ce, Rb, Ga, Hg, La, Mn, Ni, Mo, Se, Tl, U, Co, Pb, Rh, Ru, Sb, Sn, Sr, Te, Th, V, Y, Zr, Hf in Whole Blood	Dilution of blood samples with 0.1% TX-100+0.5% NH_3, DF=10	ICP-MS	Between 0.003-0.1 µg/L for all analytes	1–6	61
Sr, I, Mn, As, Mo, Ba, Se, Cd, Pb, Co, Sb, Cr, V, Cu, Fe, Mg, Zn in Biological samples	Digestion of 75 mg samples+1 mL of 50% TMAH ($C_4H_{13}NO$)+ incubated at room temp. ~12 h, volume made up to 10 mL with 0.5% HNO_3+0.01% TX-100+10 gm/L of Rh	ICP-MS	0.0027, 0.0020, 0.0189, 0.0051, 0.02, 0.5, 0.1, 0.0030, 0.0043, 0.0066, 0.0009, 0.020, 0.0017, 0.0043, 0.1794, 0.1, 0.2145 µg/g for Co, As, Cr, Ba, Cu, Fe, Mg, Mn, Mo, Pb, Sb, Se, Cd, Sr, V, Zn, I respectively	–	62
Cd, Cu, Mn, Ni, Pb, Zn in Nails	Dilution of 10-20 mg nail samples + 1 mL 25% TMAH ($C_4H_{13}NO$) solution+incubated at room temp. overnight, diluted to 10 mL with 1% HNO_3, Rh used as internal standard for ICP-MS	ICP-MS, ETAAS	3.0, 5.0, 1.0, 0.1, 4.5, 1.5ng/g for Cu, Zn, Mn, Cd, Ni, Pb respectively for ICP-MS 26, 1000, 30, 24, 143, 130ng/g (respectively for ETAAS)	–	63
As, Cd, Cu, Mn, Ni, Pb, Se in Blood	Dilution of 200 µL blood samples with 500 µL 10% TMAH solution, incubated ~10 min, subsequently diluted to 10 mL 0.05% EDTA+ 0.005% TX-100. Rh was used as internal standard for ICP-MS	ICP-MS	0.04, 0.08, 0.5, 0.12, 0.09, 0.1, 0.04 µg/L for Cd, As, Cu, Ni, Mn, Se, Pb (respectively)	–	64
Al, As, Ba, Be, Cd, Co,	25 mg of hair samples+2 mL 20% HNO_3+sonicated ~2 min	ICP-MS	0.1, 0.2, 0.4, 0.09, 0.08, 2.9, 1.0, 0.1, 0.9,	–	65

Pb, Mn, Al, Cd, Cr, Co, Hg, Ni, Be, V in Whole Blood, Serum, Urine, CSF	Microwave digestion of samples with conc. HNO_3, DF=5	ICP-MS	Al=0.05, Be=0.004, Cd=0.001, Co=0.002, Cr=0.002, Ni=0.002, Hg=0.005, Mn=0.004, Pb=0.006, V=0.002 (µg/L for all analytes)	2.5-5	48
B in Blood plasma, Urine	Protein denaturation with HNO_3	ICP-MS	0.6 µg/L	≥2	49
Cd in Urine	Decomposition of urine samples with HNO_3 at ~60°C ~90 min)+$C_6H_{12}O$ extraction of Cd chelate with $C_5H_9NS_2{\cdot}NH_3$	ICP-AES	0.04 µg/L	6.2	50
Pb in Whole Blood	Dilution of blood samples with 0.2% HNO_3+0.5% TX–100, DF=10	ETAAS	15 µg/L	6–14	51
Se in Whole Blood	Dilution with 0.2% HNO_3+0.5% TX-100, DF=5	ETAAS	50 pg	3	52
Cd in Whole Blood	Dilution of blood samples with 0.1% solution of TX-100, DF=5	ETAAS	0.02 µg/L	~10	53
Cd, Pb in Whole Blood, Urine	Dilution of urine samples with 4% HNO_3, dilution of blood samples with 0.25% TX-100, DF=2	ETAAS	Cd 0.01, Pb 0.03 (µg/L for both analytes)	01-14	54
Al in Blood Serum, Urine	Dilution of samples with 1% HNO_3+0.1% TX-100, DF=2	ETAAS	0.40 µg/L	≥5	55
Cd in Urine	Dilution of urine samples with 4% HNO_3, DF=2	ETAAS	0.2 ug/L	9	56
As, Mn, Co, Ni in Urine	Direct determination (without dilution) of analytes in urine samples	ETAA	S0.78 for As, 0.054 for Mn, 0.22 for Co, 0.35 for Ni (µg/L for all analytes)	02-08	57
Cd, Pb, Hg in Whole Blood	Dilution of blood samples with 0.05% TX-100 + 0.01 $C_5H_9NS_2{\cdot}NH_3$, 1% C>H>O + 100 µg/L, Ir, DF=50	ICP-M	S0.40 µg/L (Hg), 0.33 µg/L (Cd), 4.82 µg/L (Pb)	02-05	58
As. Cd, Pb, Hg in Urine	Dilution of 500 µL urine samples+500 mL (1% HNO_3+1% H>NSO> +9000 µL 2% HNO_3+10 µg/L Y, Rh, Ga, Ir+0.005% TX-100), DF=50	ICP-MS	0.003 µg/L (Cd), 0.1 µg/L (As), 9-Mar5 0.006 µg/L (Pb), 0.2 µg/L (Hg)	3-9	59
As, Ba, Cd, Co, Cu, Sr, Zn, Fe, Ga, Mn, U, Mo, Ni, Pb, Rb, Se, Tl, V in Biological Samples	Samples+with CH_2O, kept at 90°C ~1 h, diluted with HNO_3 to 50% CH_2O, 1% HNO_3 final concentrations	ICP-MS	Between 0.0005 mg/kg (Tl)-0.22 (Fe) mg/kg Between 0.2 (Sr)–3.5 (Ga)		60
Ag, Cu, As, Au, B, In, Ba, Pd, Be, Cs, W, Bi, Cd, Ce, Rb, Ga, Hg, La, Mn, Ni, Mo, Se, Tl, U, Co, Pb, Rh, Ru, Sb, Sn, Sr, Te, Th, V, Y, Zr, Hf in Whole Blood	Dilution of blood samples with 0.1% TX-100+0.5% NH_3, DF=10	ICP-MS	Between 0.003-0.1 µg/L for all analytes	1–6	61
Sr, I, Mn, As, Mo, Ba, Se, Cd, Pb, Co, Sb, Cr, V, Cu, Fe, Mg, Zn in Biological samples	Digestion of 75 mg samples+1 mL of 50% TMAH ($C_4H_{13}NO$)+ incubated at room temp. ~12 h, volume made up to 10 mL with 0.5% HNO_3+0.01% TX-100+10 gm/L of Rh	ICP-MS	0.0027, 0.0020, 0.0189, 0.0051, 0.02, 0.5, 0.1, 0.0030, 0.0043, 0.0066, 0.0009, 0.020, 0.0017, 0.0043, 0.1794, 0.1, 0.2145 µg/g for Co, As, Cr, Ba, Cu, Fe, Mg, Mn, Mo, Pb, Sb, Se, Cd, Sr, V, Zn, I respectively	–	62
Cd, Cu, Mn, Ni, Pb, Zn in Nails	Dilution of 10-20 mg nail samples + 1 mL 25% TMAH ($C_4H_{13}NO$) solution+incubated at room temp. overnight, diluted to 10 mL with 1% HNO_3, Rh used as internal standard for ICP-MS	ICP-MS, ETAAS	3.0, 5.0, 1.0, 0.1, 4.5, 1.5ng/g for Cu, Zn, Mn, Cd, Ni, Pb respectively for ICP-MS 26, 1000, 30, 24, 143, 130ng/g (respectively for ETAAS)	–	63
As, Cd, Cu, Mn, Ni, Pb, Se in Blood	Dilution of 200 µL blood samples with 500 µL 10% TMAH solution, incubated ~10 min, subsequently diluted to 10 mL 0.05% EDTA+ 0.005% TX-100. Rh was used as internal standard for ICP-MS	ICP-MS	0.04, 0.08, 0.5, 0.12, 0.09, 0.1, 0.04 µg/L for Cd, As, Cu, Ni, Mn, Se, Pb (respectively)	–	64

CONCLUSION

This review was focused on the STs, absorption, emission, and luminescence of ultraviolet (UV) and visible radiation by bounded electrons of TEs in BSs. For ER to cause electronic excitation, it must be in the visible and/or UV region of the ES. In conclusion, as we consider the importance of TEs in BSs, all the detailed studies indicate that a careful balance in the concentration of TEs must be obtained in order to secure health and sustain the life of the organisms. However, there is a great danger of overdose, most elements above certain concentration limits have many toxic effects. TEs may also work against each other, and in a few cases, one may or may not assist the other. However, it is more extraordinary that one element can replace another.

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Conflict of interest

The author states that this review was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of personal or public interest.

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