A REVIEW ON MULTI-ELEMENT ANALYSIS OF DIFFERENT SAMPLES BY ICP-OES

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Abstract

Heavy metals over acceptable limits established by the world health organization can source complications to human beings and animal life in the environment. Several analytical approaches have been established to screen the air, water, food quality by tracing different heavy metal ions in samples. The review work begins with the introduction of pharmaceutical analysis, including metal's effect on the body and various instruments used in the heavy metal determination. The potential of ICP-OES to sense heavy metal ions was discussed. This review article provides an impression of the metals present in the environment and their detection through ICP-OES. In addition, recapitulates the body of work on heavy metal determination in the previous years using ICP-OES. The strengths and limitations of ICP-OES have also been conversed. The review illustrates that ICP-OES has great prospective in heavy metal ion determination.

Keywords*: ICP-OES, Heavy elements, Multi-element determination, Plasma, Metals*

Introduction

Pharmaceutical analysis is a wide phrase that has a variety of definitions. It is a set of procedures for identifying, determining, separating, purifying, and elucidating the structure of a molecule used in the manufacture of pharmaceutical goods. Impurities and degradation products in pharmaceutical raw materials and finished products must be evaluated as part of medication development and manufacture. Furthermore, any drug-related contaminants with a concentration of more than 0.1 percent of the active pharmaceutical ingredient must have toxicity data[1]. APIs, pharmaceutical excipients, impurities contained in pharmaceutical goods, and drug breakdown products are typically the components for which pharmaceutical analysis is performed. Finished pharmaceutical goods, biological samples, contaminants, toxins, and pharmaceutical raw constituents are common samples in pharmaceutical analysis. Various analytical techniques can be used to do pharmaceutical analysis[2]. Based on the goal of the analysis (identification and/or determination), pharmaceutical analysis can be separated into the resulting types. Qualitative analysis is a non-quantifiable way of determining what component or chemical is present in an unfamiliar sample in pharmaceutical analysis. Identification of a certain component, element, or functional group in the sample, for instance. As a result, identification is also known as qualitative analysis[2]. Quantitative analysis is a sort of pharmaceutical analysis that aims to determine the precise quantity of a material of notice in a sample. Because we want to quantify the exact amount of the material of notice in quantitative analysis, it's also called determination[2].

Metals

“A substance that conducts electricity, has a metallic sheen, is malleable and ductile, produces cations, and has basic oxides”, accords to chemistry[3]. When compared to water, heavy metals are metallic substances with a relatively more density. Heavy metals also include metalloids, such as arsenic, which can bring toxicity at a small level of contact. In recent years, environmental poisoning by these metals has been a growing source of ecological and worldwide public health concern. Likewise, human contact has risen dramatically due to an exponential growth of their use in some manufacturing, farming, domestic and technical applications. Industrial, agricultural, pharmaceutical, home effluents, and atmospheric sources are all common sources of heavy metals. Point sources of pollution, such as mines and smelters, as well as other metal-based industrial processes, are notorious for polluting the environment[4].

Analysis of metals

Due to the metals toxicity some heavy metals are fundamental to keep up with ordinary human body roles at trace quantities. In some cases, they might stay hazardous or poisonous if present in higher concentrations. Heavy metals like Pb, Hg, Cd, and As are considerably poisonous components identified for their capacity to bioaccumulate in the body of a human, causing impairment of many organs. Heavy metal poisoning has a variety of mechanisms disclosed by their capacity on the way towards collaborating with atomic proteins and DNA, triggering oxidative decay of organic macromolecules. Because of The toxicity of metals and their negative repercussions for the general wellbeing and the climate, it is fundamental to surely gauge their positions in various samples[5]. The concentration level of heavy metals in various samples was calculated using a variety of instrumental analytical methods[6]. The utmost principal methods are atomic absorption spectrometry[7]; atomic emission spectrometry[8]; inductive coupled plasma-mass spectrometry[9]; inductive coupled plasma-optical emission spectrometry[10]; neutron activation analysis[11], X-ray fluorescence[12]; and anodic striping voltammetry[6].

Metals effect on body

Metallic ions are essential to humans as its existence is required for biological activities in humans, and their scarcity can result in illnesses. Due to their poisonous properties, a few metal ions, such as Hg and Pb, could be harmful. Vital metal ions can also be harmful if existing in surplus, but they are key for endurance. The primary group of elements includes potassium, magnesium, calcium, and sodium, whereas the transition metal group includes copper, zinc, molybdenum, cadmium, vanadium, chromium, manganese, iron, cobalt, and nickel. These metals are currently thought to be necessary for human biological function. The deficit of Fe and Co primes to anaemia, whereas deficit of Cu primes to diseases related to brain and heart, anaemia. Growth retardation and skin alterations are caused by deficiency of Zn, while bone degeneration is caused by Ca. Deficiency of Cr lessens the glucose tolerance[13]. Heavy metal poisoning can have a variety of negative health consequences. Organs like brain, kidney, lungs, liver, and blood could be damaged and altered by heavy metals. The effects of heavy metal poisonousness might be severe or persistent. Long-term contact to heavy metal elements can cause degenerative muscular, physical, and nervous progressions that are akin to Parkinson's disease, multiple sclerosis, muscular dystrophy, and Alzheimer's disease. Long-term contact to several heavy metals has been linked to the development of cancer[14].

Metal analysis by inductive coupled plasma-optical emission spectrometry (ICP-OES)

ICP-OES (inductive coupled plasma-optical emission spectrometry) is a spectroscopic method that can be used to analyse trace elements in a variability of samples. Solid samples should be acid-digested before injection, while gas and liquid samples can be injected directly to the device. Aerosol is moulded from the sample solution and then transported to the plasma's centre, which is held at a high atomization temperature of about 10,000 K. As plasma creates free flowing atoms in the gas state, adequate energy is frequently obtainable to alter the atoms to ions, which could then be accelerated to excited levels. The ionic excited state species then emit energy to return to the ground level. The elements could be characterized using a specified wavelength of photons, and the quantity of photons is related to the quantity of the element in the sample. This methodology employs a diversity of sample introduction methods, involving nebulization, hydride generation (HG) intended for some metals such arsenic, selenium, and antimony, along with electrothermal vaporisation (ETV) and laser ablation for other elements[6].

Importance of ICP-OES

Multi-element investigation: A distinguishing characteristic of ICP-OES is indeed the simultaneous, sequential assessment of different components using a mixture of charge coupling device chip detector and echelle cross disperser. The instrument's speed produces 72 pieces of data in the shortest period of time. ICP-OES can easily study zirconium, tantalum, rare earth minerals P, and B that are hard to assess through traditional spectrometry approaches. Analytical range is extensive, with extraordinary sensitivity: The ICP-OES technique's major benefit is its small detection parameters that extend from ppm to ppb. High sample throughput: Due to the automation of experiments, it can handle a high amount of data in a short amount of time. Preparing an essay sample: Solid samples are liquified or processed in solvents like HNO_3, HCl acid, definite organic solvents to form a solution. Higher TDS tolerance instrument is well adapted for ecotoxicological research. ICP-OES is used to examine compounds with high dissolved solids or suspended things like water, industrial run-offs, soil, groundwater, and metal-enriched water from mines[15].

Limitations of ICP-OES

Inter-element interference, high detection limit. Some restrictions include the charge of equipment and lab arrangements with specialised technical employees. Still, in biological research, ICP-OES is the greatest auspicious method for metal discovery[15].

Different metals present in food

The analysis was done using ICP-OES for concurrent multielement assessment of food samples. The table no 1 show different metals present in the food samples.

Table 1. Data of food samples analysis by ICP-OES

S. No	Sample	Metals Determined	Parameters	References
1	Fruit Juices, Fruits Canned	Cd, Hg, Sn, Al, Pb, As	Concentration	[16]
2	Infant Formulas, Milk Powders and Liquid Milk	Ca, Cu, Fe, K, Mg, Mn, Na, P, Zn	Recovery, Precision, R^2, Instrument detection limit, Method detection limit	[17]
3	Cheese Samples	Cd, Co, Cr, Cu, Mn, Ni, Pb, Se, Zn	R^2, Detection limits, Concentration	[18]
4	Sugarcane Juice	Ca, Cu, Fe, K, Mg	Accuracy, Precision, LOD, Concentration	[10]
5	Chinese Rice Wine	Co, Cr, Cu, Fe, Mg, Mn, Se, Zn	Range, Accuracy, Precision, R^2	[19]
6	Mushroom Species	Fe, Co, Ni, Sn	Concentration	[20]
7	Banana tree	Al, As, Ca, Cd, Co, Cr, Cu, Fe, K, Mg, Mn, Mo, Na, Ni, P, S, Se, V, Zn	Recovery, LOD, LOQ, R^2	[21]
8	Indian Spices	As, Hg, Se, Zn, P, Pb, Cd, Fe, Mn, Cr, Mg, Cu, Ca, Na, K	Range	[22]
9	Rice Grain	As, Ba, Ca, Cd, Co, Cr, Cu, Fe, K, Mg, Mn, Mo, Na, Ni, Pb, Sb, Se, Sn, Sr, V, Tl, Zn	R^2, LOD, LOQ, Accuracy	[23]
10	Chinese Liquor Samples	Al, Ca, Fe, K, Mg, Na	R^2, Concentration	[24]
11	Tomato Samples	Al, Ba, Cu, Fe, Mn, Sn, Sr, Zn	LOD, Accuracy	[25]
12	Yogurt	Na, K, Ca, Mg, Al, B, Ba, Cd, Co, Cr, Cu, Fe, Mn, Mo, Li, Pb, Zn, Ni, Sr, V	LOD, LOQ, Concentration, Standard Deviation	[26]
13	White and red wines	Al, Cd, Ca, Cu, Fe, Pb, Zn, Cr	Concentration	[27]

14	Ground water	B, Mg, Na	Concentration	[28]
15	Dark Chocolate	K, P, Mg, Ca, Na, Fe, Si, Al, Zn, Cu, Mn, B, Sr, Sb, V, Ba, Ni, Li, Cr, Sn, Pb, Mo, Co, Se, Cd	Precision, accuracy, linearity of the calibration curve, detection and quantification limit	[29]
16	Sea Water	Cd, Co, Cu, Mo, Ni, Pb, V, Zn	Accuracy, Precision, R^2,	[30]

Fathabad et al.[16] assessed the amount of tin, aluminium, lead, cadmium, mercury, and arsenic of seventy-two samples of three diverse products comprising of orange, cherry, peach, and pineapple bought in Tehran, Iran, using ICP-OES technique. Aluminium, tin, arsenic, cadmium, mercury, and lead concentrations in fruit juices varied from 340.62 (65.17-1039.2) to 72.33 (49.76-119.4), 3.76 (1.137-18.36), 2.12 (0.89-3.44), 0.351, and 40.86 (27.87-66.1) g/kg, respectively.

Mckinstry et al.[17] indicated a method for analysing some heavy elements in infant formulas, milk powders, and liquid milk by means of ICP-OES. Products were produced as slurries and evaluated to aqueous standards using the Lu internal standard compensation method to account for just any matrix effects. The apparatus employed was outwardly organized and also had a charge-transfer device detector that permitted multi-element and multi-line measurements to be recorded simultaneously. Precision, linearity, concentrations, LODs, and accuracy were estimated for instrument and technique performance characteristics.

Bakircioglu et al.[18] analysed the amount of chromium, copper, manganese, nickel, cobalt, cadmium, lead, selenium, and zinc in cheese samples packed in plastic and tin vessels by means of ICP-OES after microwave, wet, and dry digestion procedures. Cd <Co< Mn< Cr< Se< Pb< Cu <Ni <Zn was found to be the order of elements in white cheese samples packed in tin containers, and Cd <Mn< Co< Cr <Se< Pb <Cu <Ni <Zn was found to be the order of elements in samples of cream cheese in plastic boxes. There were major changes in the trace metal content of samples of cheese packed in tin and plastic boxes, illustrating that type of cheese and materials used for packaging are important factors in trace metal content.

Souza et al.[10] established this process for the assessment of elements in sugarcane juices samples. He found calcium, copper, iron, potassium, and magnesium with LOD of 2.0, 0.04, 0.2, 1.0 and 1.5 mg L−1, correspondingly. The precision was calculated as a percent RSD,

which was more than 1.4 percent (n = 3). The accuracy of the methodology was validated by correlating it to the sample digestion process. The average levels of the nutrient's calcium, copper, iron, potassium and magnesium in fourteen samples of sugarcane juice were 108, 0.506, 6.40, 470, and 114 mg L1, respectively, according to the outcomes of the study. The proposed analytical approach for concurrent assessment of elements in sugarcane juice engaging slurries and confirmation by ICP OES is a good option.

Pan et al.[19] evaluated a straight sampling technique by ICP-OES for assessing trace elements in Chinese rice wine. The trace metal concentrations in Chinese rice wine were assessed and the results such as cobalt (0.088– 0.106 mg/L), chromium (0.097–0.164 mg/L), copper (0.085–0.126 mg/L), iron (0.181–0.308 mg/L), magnesium (0.179–0.311 mg/L), manganese (0.102–0.184 mg/L), selenium (0.219–0.349) mg/L), and zinc (0.090–0.139 mg/L).

Durkan et al.[20] determined heavy metal levels in 34 edible plants *(Mushroom species)* that thrive in the wild, Turkey by ICP-OES. The quantity of heavy elements in the samples of mushroom was in the range of 53.96 – 3308, 0.229 – 46.93, 0.005 – 2.224, and 2.809 – 4.711 mg/kg for Al, B, Co, and Sn, respectively. Boron was uppermost in *Coprinus micaceus* (46.93 mg/ kg), the lowermost in *Oudemansiella radicata* (0.229 mg/kg). The amount of aluminium was the maximum in *Pleurotus ostreatus* (3308 mg/kg), and the lowermost in *Laetiporus sulphureus* (53.96 mg/kg). It was found that Cobalt content was found to be high in *Clavulina cristata* (2.224 mg/kg) and low in *Agaricus bitorquis* (0.005 mg/kg). Tin content was the highest in *Agaricus campestris* (4.711 mg/kg) and the lowest in *Suillus bellinii* (2.809 mg/kg).

Rosa et al.[21] used microwave-assisted equipment to digest the samples, and elemental amount was evaluated using ICP OES. The occurrence of metals along with non-metals (S and P) was confirmed. The inflorescences, conferring to RDA, might be good resources of Mg, P, Cr, Cu, Zn, and Fe for females, males, pregnant women, and children aged 4–8 years. Bracts are a terrific provider of zinc for males and pregnant women, and also a decent source of iron for kids. All of the samples had great amounts of Mg, Ca, P, Ni, Cu, Zn, and Fe, but still not enough to cause adverse consequences.

Kumaravel and Alagusundaram[22] determined 15 heavy metals in 5 Indian spices. Fe (5.402.0 mg/kg), Mg (270.107.0 mg/kg), Ca (602.84.0 mg/kg), Na (365.103.3 mg/kg), and K

(887.8011.0 mg/kg) were found in the spice aniseed. P (3980.013.5 mg/kg), Fe (5.4752.5 mg/kg), Mg (287.2014.0 mg/kg), Ca (690.504.0 mg/kg), Na (81.165.0 mg/kg), and K (746.706.0 mg/kg) were all found in the spice poppy seeds. P (6355.020.0 mg/kg), Fe (1.6990.2 mg/kg), and K (318.015.0 mg/kg) were found in spice cloves. P (1764.016.0 mg/kg), Fe (17.878.0 mg/kg), Mn (5.7292.6 mg/kg), and Ca (1353.0100.0 mg/kg) were found in the spice ajwain seeds. Fenugreek seeds contain P (2950.017.5 mg/kg) and K (124.822.0 mg/kg), according to the spice. All five spices are devoid of the heavy metals As and Hg. Chromium, Cadmium, and Lead are not present in fenugreek, cloves, or ajwain plants. The spice powder is a good source of Ca, K, Mg, Fe, and P, according to the studies.

Runge et al.[23] evaluated five countrywide rice products originate in resident market, so as to confirm amount of heavy elements giving the variances and relocation forms amid brown, poached and cultured rice for each product. Statistics were assessed by means of ANOVA, post-hoc Tukey, and PCA. The two significant components showed 94.33% variance, demonstrating strong diversity in samples by their handing out types from their mineral configuration. K is extensively disseminated over the grain, Mg, Fe and Ba are mostly spread in the external layers, being more vulnerable to loss, and calcium, strontium, and zinc are more subtle to the parboiling hydrothermal procedure.

Xiong et al.[24] constructed all the calibration curves from a wide range of concentrations 0, 100, 200, 500, 1000, 2500, 5000, 10000 mg/L for ICP-OES. The linear correlation coefficients were fine than 0.999. Bressy et al.[25] accomplished the determination of diverse elements like aluminium, barium, copper, iron, manganese, tin, strontium, and zinc by ICP OES. Because ICP OES parameters can impact the signal strengths and the method's sensitivity. The LODs for aluminium, barium, copper, iron, manganese, tin, strontium and zinc determinations were 0.022, 0.025, 0.098, 0.043, 0.006, 0.073, 0.010 and 0.028 μg- g−1, correspondingly. Analyses of tomato leaf certified reference material had been used to assess the accuracy of the determinations.

Luis et al.[26] quantified the concentrations of 20 elements by ICP-OES in 72 yogurt samples, bought from the stores in the island of Tenerife (Canary Islands, Spain). Mean concentrations in mg/kg wet weight were found to be: 455 (Sodium), 1101 (Potassium), 1018 (Calcium), 115.1 (Magnesium), 0.59 (Aluminium), 0.07 (Boron), 0.40 (Barium), and (Cadmium), 0.002 (Cobalt), 0.02 (Chromium), 0.27 (Copper), 0.33 (Iron), 0.52 (Lithium), 0.02 (Manganese),

0.04 (Molybdenum), 0.01 (Nickel), 0.002 (Lead), 0.02 (Vanadium), and (Strontium), and 2.79 (Zinc). The amount of metals spotted did not disclose any poisonous hazard for customers.

Lara et al.[27] developed a way to assess the metal concentration in wine samples. Ten samples of white wine along with red wine were obtainable in the store. They were analysed for the heavy metals by ultrasonic nebulization which was coupled to ICP-OES. The aluminium, cadmium, calcium, copper, iron, lead, zinc, chromium concentrations were in the range of 17.0–18.0μg/l, 1.0– 4.7 μg/l, 10.0–15.0mg/l, 23.0–28.0 μg/l, 480–790 μg/l, 50–90 μg/l, 24–130 μg/l, and <0.2–6.25 μg/l.

An evaluation of groundwater value and its agreement with Brazilian environmental protection values was carried out by Espinoza Quinones et al.[28]. ICP-OES had been used to assess ground water samples from ten wells. Three elements (Barium, Magnesium and Sodium) were measured by ICP-OES. Metal ion concentration levels were then related with Brazilian environmental legislation (BEL).

Mrmosanin et al.[29] devised the ICP-OES technique for detecting macro and micro components in dark chocolate. The proposed technique was used to measure the occurrence of 25 various components in dark chocolate samples. The corresponding macro and micro elements exhibited mean concentrations in mg/kg: 9380 (potassium), 2360 (phosphorus), 1390 (magnesium), 1120 (sodium),660 (calcium), 106 (iron), 58.2 (silicon), 46.5 (aluminium), 23.3 (zinc), 14.2 (copper), 13.3 (manganese), 7.0 (boron), 6.5 (strontium), 6.2 (antimony), 6.1 (vanadium), 5.4 (barium), 3.2 (nickel). Dark chocolate ingestion on a regular basis lead to dietary trace element intake, particularly Cr, Cu, and Fe.

Sajid et al.[30] have suggested an easy but distinctive impression that proposes the wrapping of the fluid samples inside a permeable membrane sack. After the extraction process, the last extract was exposed to ICP-OES examination. The projected way was used for extraction of eight metals from salt-water samples and decent extraction recoveries (75–94%) were gained.

Different metals present in oils and graphite samples

The analysis was done using ICP-OES for concurrent multielement assessment of oil and metal samples. Table no 2 illustrates different metals present in the oils and metals samples.

Table 2. Data of oils and graphite samples analysis by ICP-OES

S. No	Sample	Metals Determined	Parameters	References
1	Crude Oil	Ni, V	Concentration, LOD, LOQ, Accuracy, Precision	[31]
2	Fish Oil Capsules	Hg	Concentration, Linearity, LOD, LOQ, Accuracy, Precision	[32]
3	Edible Oil Samples	Cd, Cr, Cu, Fe, Mn, Ni, Pb, Zn	R^2, Recovery	[33]
4	Light Crude Petroleum	Ca, Fe, V, Ni	Concentration, data accuracy, standard deviation	[34]
5	Graphite Samples	Cd, Co, Cr, Cu, Mn, Mo, Ni, V, Zn,	Concentration	[35]

This method confers the enhancement of a technique in preparing the sample using microwave-assisted digestion to determine nickel and vanadium in crude oil by ICP-OES developed by Dos Anjos et al.[31]. For a processed sample mass of 0.1 g, nickel and vanadium were tested with LOQs of 0.79 and 0.20 g g-1, respectively. Five duplicates of two oil samples were also used to determine precision, obtaining readings of 1.63 and 3.67 % for nickel and 0.42 and 4.64 % for vanadium. Internal standards for Bi and Yt were also studied, and the outcomes indicate that Y allows for more precision in the approach. Examination of the authorized reference material trace element in fuel oil confirmed the accuracy.

Shabestari et al.[32] devised a technique development and validation approach for assessing mercury in capsules of fish oil as an impurity employing ICP-OES. The validation test was carried out by using the assessment of several performance criteria. The coefficient of linear range regression (R2) was 0.999. Its detection limits were 0.0016 g/l, and recovery was measured by spiking fish oil samples with varied Hg amounts, producing repeatability of 94-108 percent with intermediate precision RSDs of 1.86 and 3.24. Validation outcomes specify that this process based on environmental examination might be useful in the research laboratory for the routine assessment with satisfactory analytical performance.

The concentration of elements in oils that are edible from Turkey was assessed deploying inductive coupled plasma-optical emission spectrometry by Bakircioglu et al.[33]. After ultrasonic extraction, wet digestion, and extraction caused by emulsion breaking techniques, the outcomes were determined. The results (in mg kg1) were: 0.022–0.058, chromium 0.126–7.106, copper 0.570–4.504, iron 8.004–12.588, manganese 0.035– 0.054, nickel 0.908–2.182, lead 0.099–0.134 and zinc 2.206–8.982. The recovery test was performed. The recoveries were in the range of 96–109%.

Direct injection of diluted crude oil samples in organic solvents for elemental analysis employing ICP-OES is an appealing approach, especially for facilities with a high sample volume and a quick turnaround time is important. Poirier et al.[34] presented the results attained by carrying out direct injection of a wide-range of petroleum crude oils diluted in o-xylene and analysed by ICP-OES. They set out to evaluate data like accuracy, standard deviation, and recovery, predominantly in the mg kg1 to g kg1 range, employing appropriate sample preparation and instrument tuning settings.

Sandra et al.[35] proposed a microwave-induced combustion for graphite digestion, using ICP-OES to assess heavy elements. Employing 20 bar O_2 and HNO_3 (1 to 14.4 mol L-1) as an absorbing solution, a huge graphite mass (400 mg) was totally burned. With a solution as diluted as 4 mol L-1 HNO_3, a high digestion efficiency (>99%) was gained, with recoveries better than 95 percent for all analytes.

Different metals present in herbals

The analysis was completed by ICP-OES for concurrent multielement assessment of herbal samples. Table no 3 shows different metals present in samples of herbals. Okem et al.[36] conducted a study in which metal amounts in commercial herbal mixtures were assessed. 14 herbal formulations were acquired from traditional herbal (muthi) shops and their total and bioavailable metal amounts were assessed. Of all the mixtures evaluated only Vusa umzimba and sejeso herbal formulation confined peak quantities of cadmium (2.2 and 0.6 mg/kg) respectively, surpassing the threshold of 0.3 mg/kg (WHO, 1998). Vusa umzimba also displayed high quantities of bioavailable cadmium (1.2 mg/kg) thereby making it more dangerous for human intake. Astonishingly, both the ingwe muthi mixture and the sejeso herbal mixture revealed elevated levels of mercury (14.9 and 12.3 mg/kg, respectively). Sejeso herbal blend included rather significant levels of lead. The high amounts of

bioavailable metals found in this study rise worries not only about consumer safety, but also the quality of herbal formulations being used traditional South African medicine.

Table 3. Data of herbal samples analysis by ICP-OES

S. No	Sample	Metals Determined	Parameters	References
1	African Commercial Herbal Concoctions	Zn, Cr, Mn, Ni, Pb, Cu, Cd, Hg, Al	Concentration	[36]
2	Argentinian Herbal Medicines	Al, Cr, V	Concentration, Recovery	[37]
3	Medicinal plants	As, Cd, Cr, Cu, Ni, Pb	LOD, Accuracy, Precision	[38]
4	*Hypericum perforatum* (St John's Wort)	Al, As, B, Ba, Be, Ca, Cd, Co, Cr, Cu, Fe, Hg, In, Mg, Mn, Mo, Ni, Pb, Pt, Sb, Se, Sr, V, Y and Zn	Concentration, Accuracy	[39]
5	*Celocia argentea* leaves	Ag, As, B, Ba, Ca, Cd, Co, Cr, Cu, Fe, K, Mg, Mn, Na, Ni, P, Pb, S, Zn	Concentration, LOQ	[40]
6	Cat's Claw Teas	Ba, Ca, Cu, Fe, Mg, Mn, P, Pb, Zn	Concentration, LOD, LOQ, Accuracy	[41]
7	*Cynara scolymus* L., *Harpagophytum procumbens* D.C., and *Maytenus ilifolia* (Mart.)	Al, As, Ba, Cd, Co, Cr, Cu, Fe, Mn, Mo, Ni, Pb, Sb, Se, Si, Sn, Sr, V, Zn, Ca, K, Mg, Na, P	Concentration, Accuracy, Precision, Stability	[42]
8	Vegetable seeds	Ca, K, Mg, Na	LOD, LOQ, R^2, Accuracy, Slope	[43]
9	Nuts and Seeds	Al, Ba, Ca, Cu, Fe, K, Mg, Mn, Sr Zn, B, Si, Cl, P and S	LOD, LOQ, Wavelength, Linearity	[44]

Hypericum perforatum leaves and flowers, and also their teas, tinctures, and tablets, were assessed for trace elements by Gomez et al.[37] using Ultrasonic Nebulization System attached to ICP-OES. The analytical data attained for all metals show that they exist at concentration under the adequate daily intake suggested by the WHO. Based on the outcomes attained, it is concluded that the methods were acceptable for the assessment of heavy metals concentration in phytopharmaceuticals.

The recoveries obtained by Gonçalves et.al[38] remained between 96.90–99.90 percent and RSD of 1.40%. The quantification of standard reference materials (SRM) demonstrates outstanding process accuracy. The levels of elements existing in therapeutic plants had contents above than permitted for arsenic, chromium, copper, nickel and lead when related to the maximum parameters acceptable by the Brazilian Pharmaceutical, WHO, National Sanitation Foundation International and European Medicines Agency. The results confirmed that the multi-wavelength calibration (MWC) was an substitute to the procedures employed by the major regulatory authorities to evaluate elemental contaminants in pharmaceutical products and phototherapeutic plants that is fast, accurate, and very sensitive.

Owen et al.[39] evaluated elemental profiles of 54 herbal samples by monitoring 25 elements using ICP-OES. The main basic constituents in the St. John's wort (SJW) models were calcium (300-199,000 µg/g), magnesium (410-3,530 µg/g), aluminium (4.4-900 µg/g), iron (1.154-760 µg/g), manganese (2.4-261 µg/g), strontium (0.88-83.6 µg/g), and zinc (7-64 µg/g). Principal component analysis replicas acknowledged 7 crucial elements (i.e., barium, calcium, cadmium, magnesium, molybdenum, nickel and yttrium). In the first three main components, this explained 85 percent of the variance in the dataset.

Celocia argentea has respectable number of macronutrients like Mg, Ca S, P, K and Fe. Markandeya et al.[40] found the ashing and microwave digesting processes had shown to be more trustworthy than the wet digestion method, and were so suggested for better recovery. In comparison to wet digestion, ash and microwave digestion processes provide enhanced recovery of the elements Ca, Cu, and Fe. Toxic elements have concentrations even below the allowable limit.

The assessment of heavy elements by inductively coupled plasma-optical emission spectrometry has been done by Pereira & Dantas[41]. 11 cat's claw plant specimens were

examined in dry matter and teas. The precision and accuracy metrics were compared to GBW 07604 (Poplar leaves) reference material that has been certified. Outcomes displayed a high content of calcium in the herbal plant considered, followed by magnesium and phosphorus. The peak stages were detected in calcium and magnesium, and the lowermost for lead, via infusion as well as decoction. Teas prepared from this plant were identified as having safe amounts of these substances for human consumption, implying that they could be used as sources of these nutrients in the diet.

De Arago Tannus et al.[42] investigated macro- and microelements in therapeutic plants and herbal medicines: "globe artichoke" - *Cynara scolymus L*., "After acid digestion and microwave radiation, total concentrations of 24 (essential and possibly damaging) elements in herbal samples from Brazil were assessed using a sequential optical emission spectrometer with ICP OES. An exploratory study of material was carried out employing principal component analysis (PCA) and hierarchical cluster analysis (HCA). The following elements were assessed (in g/g): aluminium (20.24–1261.64), barium (18.90–63.18), calcium (2877.6–19,957.40), chromium (0.28–1.38), copper (4.16–21.99), iron (8.54–627.49), potassium (1786.12–32,297.19), magnesium (505.82–6174.52), manganese (0.40–205.64), sodium (1717.23–18,59). All of the investigated samples had amounts of As, Cd, Co, Mo, Pb, and Sb which were below the ICP OES's limit of detection and quantification. Al was found in large amounts in all of the samples.

Method for the assessment of 5 major in vegetable seeds by ICP-OES was projected by Chaves et al.[43]. For the majority of elements, the detection limits remained in the range of 0.01 (Mg) to 0.3 μg g−1 (Na and K). The LODs were sufficient for the seed analysis. The accuracy was confirmed by analysing a botanical certified reference material (Pine Needles). The RSDs were below 10 percent representing a satisfactory precision. Amongst the four chief studied elements, K was more concentrated, assisted by phosphorus, magnesium and calcium for most of the seeds.

Naozuka et al.[44] confirmed accuracy of the complete presented process by standard reference material analysis. At a 95 percent confidence level (Student's t-test), the certified standards showed good agreement. The average RSD for calibrating solutions repeatability observations were 1.1–6.7%. Quantification limits varied from 0.00072 to 0.0532 mg/l. The

macro and micronutrient ranges in the different nuts and seeds did not surpass the dietary reference consumption, with the exception of Mn in the babassu nut (DRI).

Different metals present in biological samples

The analysis was done by ICP-OES for concurrent multielement assessment of biological samples. Table no 4 shows different metals present in the biological samples.

Table 4. Data of biological samples analysis by ICP-OES

S. No	Sample	Metals Determined	Parameters	References
1	Serum and Whole Blood	Na, Ca, Mg, K, Fe, Zn, Cu, Se	Concentration, Interday and Intraday Precision	[45]
2	Hair	As	Concentration, Accuracy, Precision	[46]

Harrington et al.[45] measured intraday and interday precision for the elemental content of the serum and blood samples for 8 essential elements —sodium, calcium, magnesium, selenium, potassium, iron, zinc and copper by plasma spectrometric methods. The results extended from 0.635 to 10.1 percent relative standard deviation for serum and 0.348–5.98 percent for whole blood. An evaluation of the determined ranges for 10 serum models and 6 whole blood models showed decent accordance with literature reference ranges. The outcomes establish that the analysis and digestion procedures can be used to quantity the content of these elements and potentially of other elements.

Baker et al.[46] used ICP-OES to determine the level of As. The methodology's validity, precision, and accuracy were assessed using a "pooled" sample and verified reference materials, respectively. With a decreased range of RSD (1.1 percent) and an appropriate range of elemental recovery (97.72 percent), the validation procedures achieved acceptable precision and accuracy.

Different metals present in cosmetic products

The analysis was done using ICP-OES for concurrent multielement assessment of cosmetic samples. Table no 5 illustrates different metals present in the cosmetic products.

Table 5. Data of cosmetic samples analysis by ICP-OES

S. No	Sample	Metals Determined	Parameters	References
1	Lipstick, Eyeshades, Kohl, Hair Dye, Face Cream, Deodorant, Soap, Rose Powder and Talcum Powder	As, Cd, Cr, Hg, Ni, Pb, Co, Zn	Concentration	[47]

Mayildurai et al.[47] investigated the levels of heavy metals such as As, Cd, Cr, Hg, Ni, Pb, Co, Cu, and Zn in 20 different cosmetic samples. All of the samples were processed following suitable procedures, and the heavy metal composition was analysed and determined using an ICP-OES. The findings suggest that the test samples contained a substantial amount of such elements. Arsenic amounts as high as 0.523 ppm were found in hair dye. Nickel extends from 0.015 ppm to 0.139 ppm, whilst chromium goes from 0.011 ppm to 0.421 ppm. The maximum levels of lead found in hair dye was 1.458 ppm, while the least amount was 0.05 ppm in eye shade.

Different metals present in active pharmaceutical ingredients & formulations

The analysis was done using ICP-OES for concurrent multielement assessment of active pharmaceutical ingredients (API) and formulation samples. Table no 6 shows different metals present in active pharmaceutical ingredients & formulations samples. Raghuram et al.[48] tested API levetiracetam for 23 metals, 10 metals listed in USP and 15 metals listed in Ph. Eur and 13 metals in the EMEA Guidance document. The 23 metals tested were not detected in the active pharmaceutical levetiracetam tested. The LOQ levels were checked by spiking with sample (acceptance criterion 80–120%, Table 4) and with an acceptable precision (acceptance criterion ≤15% [n = 3]). The LOQ of all the metals was 0.4 ppm except for lead and ruthenium for which the LOQ was 0.1 ppm.

ICP-OES and heavy metals limit test were used to measure the elemental impurities in samples by Bouaffad & Hayyani[49]. Except the fluconazole 5th sample, all samples were conformers. This was shown by the results of limit tests. The ICP-OES study displayed that the amount of individual elements is usual in all samples except Co amount is superior than the limit essential in ciprofloxacin 4th sample.

Table 6. Data of active pharmaceutical ingredients (API) and formulation samples analysis by ICP-OES

S. No	Sample	Metals Determined	Parameters	References
1	Levetiracetam	Pb, Hg, Bi, As, Sn, Sb, Ca, Ag, Cu, Mo, V, Pd, Pt, Au, Ru, Ir, Rh, Os, Ni, Cr, Mn, Fe, Zn	LOQ	[48]
2	Ciprofloxacin Hydrochloride, Fluconazole	Cd, Pb, As, Hg, Co, Ni, Ag, Cu, Sn, Cr	Concentration	[49]
3	Methadone Hydrochloride	As, Pb, Cd, Hg, Co, V, Ni	Accuracy, Precision, Linearity, LOD, LOQ	[50]
4	Captopril, Enalapril, Benazepril, Lisinopril, Ramipril, Quinapril, Valsartan, Losartan, Olmesartan, Candesartan, Hydrochlorothiazide, Carbamazepine, Diclofenac, Paracetamol, Tilidine, Naloxone	Fe, Cu, Zn	Concentration, Recovery, LOQ	[51]

Janchevska et al.[50] proposed an ICP-OES technique for determining heavy metals, which has been effectively confirmed in terms of linearity, system precision, accuracy, LOD, and LOQ as per Pharmacopoeia standards. With the exception of As and Pb, the results indicate that the ICP-OES technique is an effective tool for analysing the possible presence of the selected elements with high accuracy and precision.

Wollein et al.[51] conducted a market surveillance study, utilizing different atomic spectrometric methods developed for the analysis of specific elemental impurities of particular interest, in order to gain a better understanding of the quality of commercially available drug products and their bulk drug substances. The limit tests were done in compliance with the prevailing EMA guideline for residuals of metal catalysts or metal reagents specification limits. The possible adoption of two new chapters of the United States pharmacopoeia (USP) defining limit concentrations of elemental contaminants was also discussed. ICP-OES was used to determine the metal residues (ICP-OES). The development

and validation of criteria for determining 21 chosen metals in 113 samples from medicinal products and their active pharmaceutical components are presented in this paper. The ICP-OES validation recovery ranged from 100.7 to 104.6 percent, with the greatest RSD of 2.1 percent for Fe.

Conclusion

The detection of trace elements and heavy metals has piqued people's curiosity. Many technologies have been successfully employed, including atomic absorption spectrometry, inductively coupled plasma optical emission spectrometry, and inductively coupled plasma mass spectrometry. ICP OES is the most widely used of these techniques, and it has a number of advantages, including ease of use, quick analysis time, good detection limits, and a large analytical dynamic range. This review presents the various samples analysed to detect heavy metal ions by using ICP-OES. This review briefly discussed the effect of heavy metal ions on the body and also listed other instruments through which heavy metal determination can be done. Moreover, the advantages and limitations of ICP-OES in heavy metal determination are also discussed.

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