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Science of the Total Environment

journal homepage: www.elsevier.com/locate/scitotenv



How ICP-OES changed the face of trace element analysis: Review of the global application landscape

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<https://doi.org/10.1016/j.scitotenv.2023.167242>

Available online 22 September 2023

0048-9697/© 2023 Published by Elsevier B.V.

HIGHLIGHTS

- ICP-OES has revolutionized trace elemental analysis in various fields.
- Valuable insights into the current state of the art in trace element analysis.
- Overview of the global application landscape of ICP-OES.
- Key advantages and promising applications of ICP-OES.
- Current advancements, limitations and future developments of ICP-OES are proposed.

GRAPHICAL ABSTRACT

MICROPLASTICS

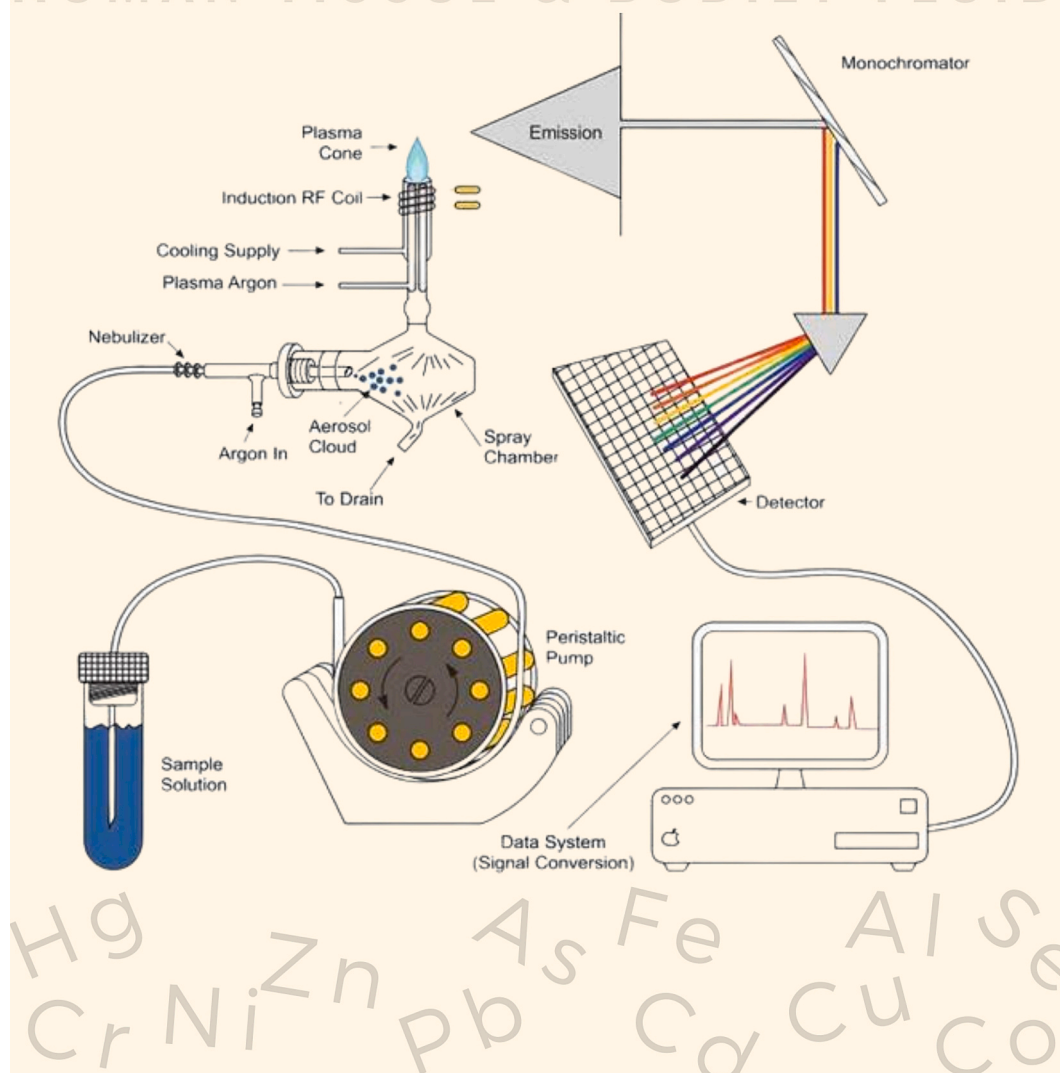
HUMAN TISSUE

HEMP AND CANNABIS

FOOD ANALYSIS

DIETARY SUPPLEMENTS & HUMAN SCALP HAIR

HUMAN TISSUE & BODILY FLUID



ARTICLE INFO

Editor: Damia Barcelo

Keywords:
Inductively coupled plasma optical emission spectroscopy

ABSTRACT

The 50th anniversary of Inductively Coupled Plasma-Optical Emission Spectrometry (ICP-OES) will be observed in 2024. ICP-OES was first commercially available in 1974, and since then, it has become one of the most widely used analytical techniques in the world. ICP-OES is a powerful tool for the determination of trace and ultratrace elemental concentrations in a wide variety of samples specifically for multielement analysis. It is used in a wide range of applications, including environmental monitoring, food analysis, and medical diagnostics.

Food analysis
Microplastics
Materials and biologicals materials

This review aims to explore recent applications of ICP-OES in areas such as food analysis, microplastics, materials, dietary supplements, human tissue, and bodily fluids. The utilization of ICP-OES in these fields has ignited the interest of prospective ICP-OES users and inspired current practitioners, as the 50th anniversary approaches, it is of value of providing an updated review. It is important to note that this work does not seek to encompass a comprehensive review of ICP-OES, given the vast number of published results in this field. Undertaking such a comprehensive task would be a daunting challenge. Consequently, an overview of the ICP-OES instrumental technique is provided, followed by a highlighting of recent significant applications in the aforementioned fields.

1. Introduction

The detection and quantification of chemical elements, particularly those with high toxicity, are crucial aspects of chemical analysis. (Pastorino et al., 2021; da Silva et al., 2011) Traditional methods for determining element concentrations include gravimetric, volumetric, colorimetric, and spectroscopic methods. Among these, inductively coupled plasma (ICP) methods, such as inductively coupled plasma-mass spectrometry (ICP-MS) and inductively coupled plasma-optical emission spectroscopy (ICP-OES), are known for their exceptional accuracy, precision, and low detection limits. (Ward and Carpenter, 2010)

ICP-OES, in particular, has emerged as the preferred method for elemental analysis due to its capability of simultaneously measuring multiple elements. (Bulska and Wagner, 2016) This technique utilizes inductively coupled plasma to generate excited atoms and ions that emit characteristic electromagnetic radiation. (Charles and Fredeen, 1997) The plasma, a key component of any ICP instrument, is an ionized gas containing free electrons and cations at high temperatures and low pressures, and powered usually by a free running radio frequency (RF) generator. (Thomas, 2013) Plasma is recognized as one of the primary states of matter. (Burm, 2012) Induction plasma, or “inductively coupled plasma,” refers to the utilization of a flowing gas under specific pressure and temperature conditions as a plasma source. (Thomas, 2013)

The spectral excitation properties of induction plasma have attracted considerable interest from spectroscopists and analytical chemists, leading to its application in sample analysis. (Fassel, 1978) The benefits of ICP-OES have made it extensively utilized in both academic and

industrial laboratories for various applications. (Fassel and Kniseley, 1974) Fig. 1 illustrates a typical example of an ICP-OES plasma under operation.

Following the 1950s, significant advancements were made in the development of plasma excitation sources, including induction torches and other forms of inductively coupled plasma. (Fassel, 1978; Hieftje, 2000) These technological breakthroughs played a crucial role in establishing ICP-OES as a practical method for trace metal analysis. (Clases, 2022) The utilization of more advanced torch designs enabled ICP-OES to achieve lower detection limits, reduced interferences, and expanded linear working ranges. (Charles and Fredeen, 1997) These improvements demonstrated the superiority of ICP-OES over previous emission sources. (Charles and Fredeen, 1997) While recent advancements in ICP-based methodologies have predominantly focused on ICP-MS, it is worth noting that many of the fundamental principles regarding sample introduction and plasma generation exhibit remarkable similarities, if not identical techniques, to ICP-OES. (Wilschefski and Baxter, 2019)

Both ICP-MS and ICP-OES rely on analogous principles for sample introduction and plasma generation. (Thomas, 2013; Thomas, 2023) The crucial aspects of delivering the sample into the plasma, such as nebulizers and spray chambers, remain consistent between the two techniques. Additionally, the generation and stabilization of the plasma itself, achieved through radio frequency induction, are shared components. (Thomas, 2013)

Although the recent advances in ICP methodologies have predominantly favored ICP-MS due to its superior sensitivity and mass-based

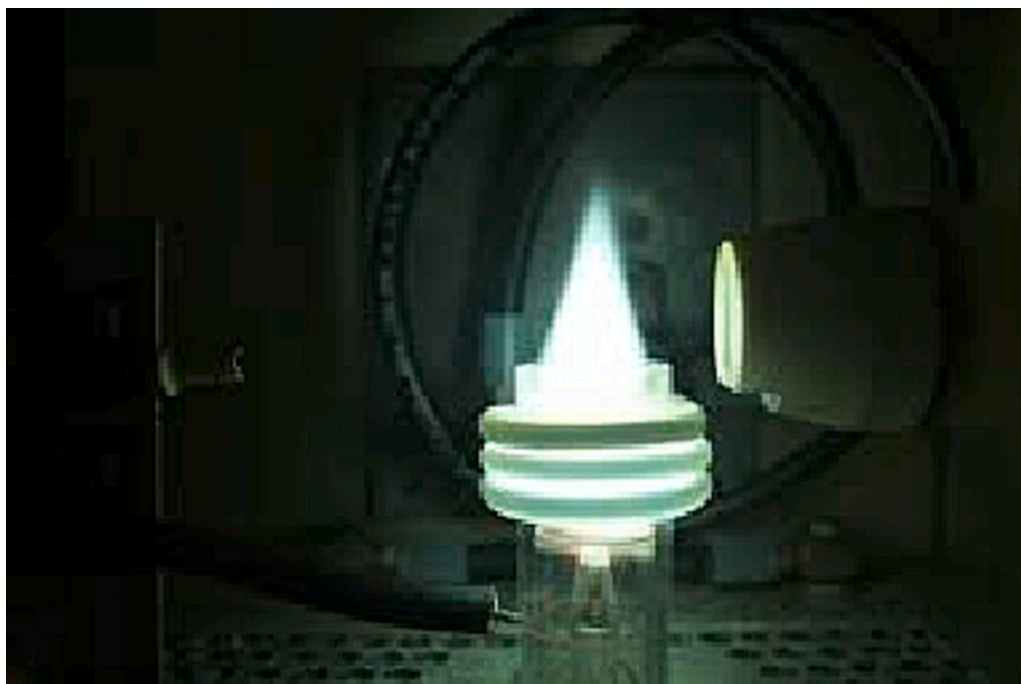


Fig. 1. ICP-OES plasma under operation (Blanchard, n.d.).

detection capabilities, it is important to recognize that the core principles and techniques involved in sample introduction and plasma generation exhibit substantial similarities between ICP-MS and ICP-OES. (Wilschefski and Baxter, 2019)

Within an ICP, each element emits photons with distinct wavelengths that can be attributed to specific elements. (Yeung et al., 2017) The intensity of light emitted is directly correlated to the concentration of the element. (Wright and Stuczynski, 1996) In its ground state, an electron occupies the lowest energy orbital available. (Pyle et al., 1995) However, when supplied with sufficient energy, typically from an excitation source like a plasma, an electron can transition to a higher energy level, referred to as an excited state. (Boffard et al., 1999) Subsequently, as the electron returns from the higher energy level to a lower one, it emits photons with a wavelength corresponding to the energy difference between the two levels. (Lajunen and Perämäki, 2004) A schematic of the typical components of ICP-OES system are shown in Fig. 2.

In many instances, sample preparation is necessary to transform the sample into a suitable form for the sample introduction system. The majority of sample introduction systems utilized in ICP-OES are designed for liquid solutions. Fig. 3 provides an overview of the general procedures involved in preparing solid samples for ICP-OES analysis. For example, to ensure accuracy and prevent contamination, it is crucial to employ trace metal grade acids and solvents, as well as vessels that have been acid soaked and rinsed with deionized water. A typical example is the use of using trace metal grade acid to clean glassware, that ensures

that the container is free of any possible contaminate that contains metal ions in a way so that inaccurate results are prevented. In addition, vessels that have been rinsed with deionized water are also important for ensuring accuracy and preventing contamination in ICP-OES analysis. This is because deionized water is free of impurities, including metal ions. Soaking and rinsing vessels in deionized water helps to remove any residual contaminants that could interfere with the results of the analysis.

Sample preparation commonly encompasses various steps, including drying, grinding, sieving, dissolution, filtration, and occasionally pre-concentration techniques. These processes aid in achieving a homogeneous and representative sample that can be effectively introduced into the ICP-OES system for analysis. (Mitra, 2003)

Solid samples are typically dried to assure the sample analyzed is not influenced by varying water content percentages. (Sneddon et al., 2006) If drying is necessary, it must take place for a consistent amount of time for all samples, usually at temperatures below 105 °C to reduce analyte losses due to volatilization. (Hoening, 2001) Drying of the sample in a temperature-controlled oven is one of the most common methods of drying. (Mitra, 2003) Alternative techniques for drying samples include employing a gentle stream of inert gas for an extended duration, which effectively prevents analyte losses due to volatilization. (Beaty and Kerber, 1978) Once the sample has undergone the drying process, it is essential to perform grinding, sieving, and mixing to ensure proper sample homogenization. (Kurfürst, 2013) This homogenization step

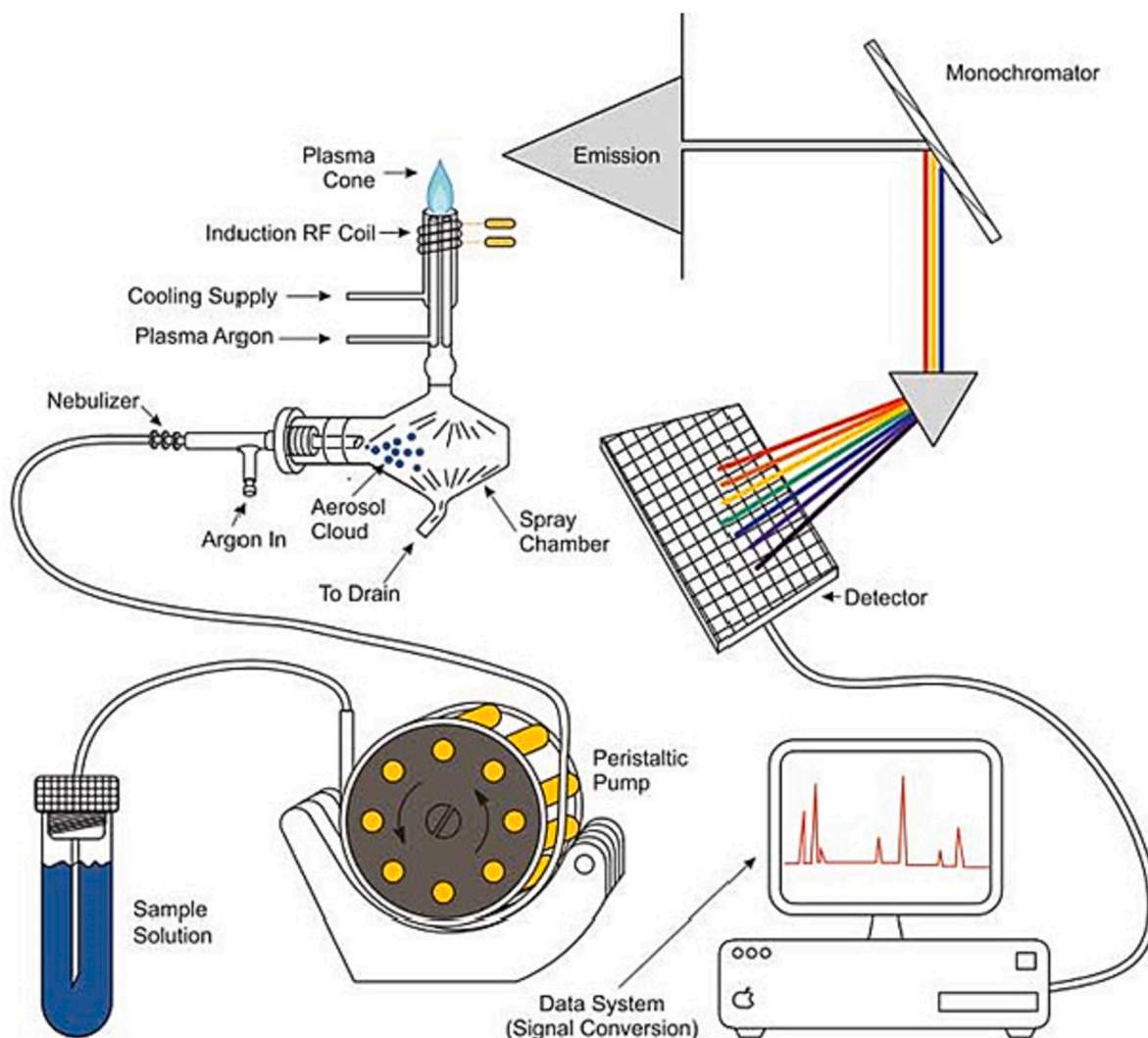


Fig. 2. Typical components of an ICP-OES system.

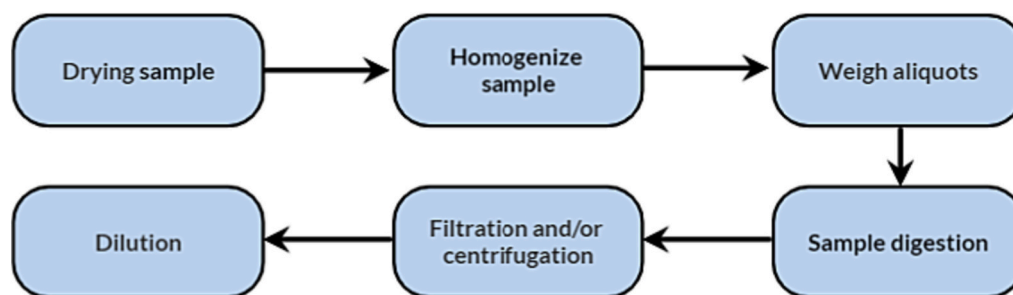


Fig. 3. Generalized solid sample preparation process.

guarantees a consistent distribution of the analyte of interest throughout the sample, enhancing the accuracy and representativeness of subsequent analyses. (Kurfürst, 2013)

To dissolve samples, the common approach involves acid digestion, wherein the sample is heated in the presence of acid(s) to facilitate metal solubilization. (Thomas, 2013) The application of heat, along with the addition of oxidizing agents, aids in breaking down the sample matrix. (Thomas, 2013) As the resulting nitrate salts are highly soluble in water, nitric acid is often the acid of choice due to its oxidizing properties and ability to minimize the formation of insoluble salts. (Hoenig, 2001) In cases where a complete digestion is not achieved with nitric acid alone, perchloric acid, hydrochloric acid, and/or sulfuric acid can be added to enhance sample digestion. (Thomas, 2013) For samples containing silicates, such as plant materials, hydrofluoric acid (HF) can be used to dissolve these silicates. (Krachler et al., 2002) If there is an excess of HF, boric acid can be used to neutralize it. (Chen and Ma, 2001) Additionally, hydrogen peroxide can be introduced to aid in the oxidation of organic components. (Mitra, 2003) Hydrochloric acid introduces spectral interferences near chlorine's wavelengths, while nitric acid induces spectral and matrix-related interferences. Effective mitigation involves optimizing instrumental conditions and utilizing matrix-matching calibration standards for both acids in ICP-OES analysis of solid samples. Internal standards further enhance accuracy by accounting for these interferences.

In situations where the signal of the analyte(s) falls below the detection limit of the instrument, preconcentration becomes necessary. (Olesik, 1991) This is particularly relevant when analyzing water samples for certain trace elements like As. (Gil et al., 2007) Various methods can be employed for preconcentration. (Özdemir et al., 2013; Fisher and Kara, 2016) An example involves evaporating some or all of the sample solution, followed by digesting the resulting residue in an acidic solution. (Hastiawan et al., 2015)

To circumvent the issue of volatilization, preconcentration techniques utilizing columns can be utilized. One such method involves employing high-performance liquid chromatography (HPLC) with an octadecylsilane packed column. The aqueous sample is passed through the column, where the metal(s) of interest are adsorbed, aiding in their concentration. This technique helps enhance the analyte signal and improves detection sensitivity, enabling the accurate determination of trace elements. (Okano et al., 2015; Ali and Aboul-Enein, 2006) The desorption of the metals from the column and their subsequent collection can be achieved by eluting an acidic solution through it.

Filtration may be necessary when undissolved materials are present following digestion to prevent tubing blockage and ensure consistent sample flow to the instrument. In this regard, it is imperative to underscore the significance of selecting varying filter sizes (0.45, 0.22, or 0.1 μm) to accurately discern the fraction that is authentically dissolved. An extensively employed filtration methodology encompasses the utilization of a 0.45 μm glass or polypropylene filter. Polypropylene filters are preferred over glass fiber filters as they do not adsorb or introduce metals, offering an advantage in maintaining sample integrity. (Fuhrmann and Fitts, 2004)

After filtration, the final step in sample preparation is dilution, which must match the matrix of the calibration standards. Matrix matching is crucial for accurate analysis. If there is a suspicion of suspended solids in the solution, centrifugation can be performed before analysis. It should be noted that the presence of metals in suspended solids can lead to poor recovery for certain metals. (Radis Steinmetz et al., 2009)

As the 50th anniversary of ICP-OES approaches, it is highly beneficial for the scientific community to be presented with an updated review on recent applications of ICP-OES. Although this work does not seek to encompass a comprehensive review of ICP-OES, given the numerous published results, it aims to inspire and attract scientists and students to the highly interesting and useful ICP-OES field. (Canepari et al., 2009)

2. Applications

2.1. Hemp and cannabis

The projected value of the global legal cannabis market is estimated to reach USD 97.35 billion by 2026, while the global hemp market is expected to reach USD 27.72 billion by 2028. (Insights, n.d.; Research, n.d.) Cannabis can be consumed in various ways, including inhalation, oral ingestion, sublingual administration, and topical application, similar to tobacco products. On the other hand, hemp is commonly consumed as food through its seeds, seed oil, and seed protein. Additionally, hemp shows great potential for industrial applications, particularly in the textile industry.

As the legalization of cannabis and hemp expands globally, it becomes crucial to test these materials for trace elements, considering the increasing consumption and demand for these products. Both cannabis and hemp have a remarkable ability to accumulate significant amounts of trace elements from the environment. These plants absorb trace elements due to nutritional requirements, enzyme activation, metabolic processes, and for maintaining optimal plant health. (Hooda, 2010; Douvris et al., 2022) Due to the lower startup costs compared to ICP-MS instruments, many laboratories seek to use for ICP-OES instruments. However, it is important for global laboratories that do not have regulations for toxic elements, which often employ personnel without a background in this type of instrumentation, to educate users about the instrumentation used for testing products intended for human consumption. (Thomas, 2013; Thomas, n.d.-a; Bussan et al., 2022a; Bussan et al., 2022b)

Rezić et al. (Rezić et al., 2011) investigated the determination of twenty-eight selected elements in four different types of textiles i.e. cotton, flax, hemp, and wool by axially viewed inductively coupled plasma optical emission spectrometry. Method development, specifically sample preparation, is extremely important for getting accurate measurements. A common way to dissolve samples into solution is via microwave digestion, incomplete sample digestion can lead to inaccurate results. To check for accuracy of the microwave digestion, Rezić et al. (Rezić et al., 2011) used a certified reference material IAEA-V-9 (for trace elements in cotton cellulose). This reference material was specifically chosen as its matrix matched one of the samples in the study

(cotton) and closely matched the matrices of the other samples. At the time of analysis there were no certified hemp reference materials for trace elements. For sample preparation the textile samples were dried for 48 h at 60 °C before analysis. Then 0.5 g of each dried sample was transferred into microwave digestion tubes and completely digested with 8 mL of 7 M nitric acid. The following temperature program was used on an MLS 1200 Mega (Milestone): 5 min at 150 °C (power 250 W), 15 min 180 °C (300 W) and 20 min at the maximum temperature of 200 °C (350 W). After digestion the solutions were allowed to cool and then the volume made up to 10 mL with 7 mol L⁻¹ nitric acid. They were then analyzed using Perkin Elmer Optima 3000 XL ICP-OES. Two different nebulizers, Low-Flow and Meinard, were compared, and the authors opted for a Gem Cone Low-Flow nebulizer due to several advantages it offered. One of these advantages was its ability to process small nondigested particles effectively, thus minimizing the risk of clogs. Interfering elements or compounds were determined through the analysis of data using ICP WinLab software and referring to literature data.

The relative standard deviation (RSD) of the elements ranged from 1.8 % to 30.9 % for most elements, except for lead which was 60.0 %. While the digestion and analysis techniques employed were sufficient for most elements in this study, the presence of lead in textile materials posed challenges and required further consideration. (Rezić et al., 2011)

As cannabis and hemp plants can uptake trace elements from the soil, a geographical profile based on elemental analysis can be used to determine the origin of the plants with multivariate analysis techniques. (Douvris et al., 2022; Kuras and Wachowicz, 2011) A study by Kuras et al. (Kuras and Wachowicz, 2011) set out to determine if cannabis profiling based on its elemental composition would be possible. The researchers analyzed eighty-five cannabis samples, for the analysis of Pb they used a graphite furnace atomic absorption spectrometer (Avanta Ultra Z made by GBC), and for the analysis of B, Ba, Cu, Sr, Zn, Mn, Fe, Mg, and Ca an ICP-OES (Optima 3100XL by Perkin Elmer). For the sample preparation, samples were homogenized with a Fritsch planetary ball mill. Next, 250 mg of the sample was weighed and transferred to a Teflon microwave digestion vessel. Then 3 mL of 65 % nitric acid and 1 mL of 30 % hydrogen peroxide was added. The samples were then placed in a high pressure MULTIWAVE sample preparation system made by Anton Paar. For quality control, standard reference materials INCT TL1 (tea leaves), INCT MPH2 (mixed Polish herbs), CTA VTL2 (Virginia tobacco leaves), and CTA OTL1 (Oriental tobacco leaves) were analyzed in addition to the samples. The measured values were within 90–108 % of the certified values. Table 1 shows the operating ICP-OES parameters used in the experiment by Kuras et al. (Kuras and Wachowicz, 2011)

In addition, 20 samples of hemp were also analyzed for the same trace elements. The regions of Poland where the hemp samples came from included Batorz (south-eastern Poland), Strzelin (north-eastern region), Nowy Korczyn (south), and Mleczewo (north). By applying discriminant analysis to the obtained results, a plot was generated as depicted in Fig. 4 which clearly illustrates the distinct separation of locations. The data obtained from this study provides evidence that ICP-OES, when combined with mathematical modeling, can be utilized to confirm the origin of the product.

Table 1
Operating parameters of ICP OES.

Parameter	Unit	Value
Plasma gas flow	L min ⁻¹	15
Auxiliary gas flow	L min ⁻¹	0.5
Gas flow through atomizer	L min ⁻¹	0.5
Plasma power	W	1450
Plasma observation height	mm	15
Sample flow	mL min ⁻¹	0.65
Delay time	sec	90

2.2. Food analysis

Quality control and quality assurance measures are essential to maintain consumer confidence in food products. No more is this ever so important than to maintain quality in infant food products as these consumers can be the most vulnerable, and their bodily and mental health depends on the food eaten. Many trace elements can enter natural foods through human activities such as storage, processing, soil uptake, and water. Ensuring public safety necessitates the critical examination of trace elements through testing. (Bussan et al., 2019; Snaychuk et al., 2022; Khan et al., 2013; Hardaway et al., 2016; Topalidis et al., 2017; Benipal et al., 2017; Harris et al., 2018) Khan et al. (Khan et al., 2013) validated a method for the simultaneous determination of Cr, Mo and Se in infant formulas and compared the measurements of ICP-OES with ICP-MS analyses. The researchers measured a total of 24 commercially available infant formulas from local supermarkets all over South Korea. The limits of detection values of the ICP-OES were 0.909, 5.890 and 4.443 µg kg⁻¹ for Mo, Se, and Cr, respectively, with the recovery (%) of NIST-1549 reaching 109.4 % for Mo, 40.8 % for Se and 0 % for Cr. Although Khan et al. concluded that their method was not appropriate for Se and Cr, but it was highly appropriate for Mo determination.

Kiani et al. (Kiani et al., 2021) used ICP-OES to assess the health risk of baby food and milk powder for the following elements; As, Cd, Cr, Al, Pb, Hg, Co, Ni, Cu, Fe, Mn, Zn, and Se. Risk was assessed by estimating the daily intake (EDI, mg kg⁻¹) of the foods studied. The toxicity ranking of elements for babies was determined by conducting a Monte Carlo simulation, resulting in the following Hazard Quotient (HQ) order; Hg > Ni > As > Cd > Al. A total of 120 samples (60 powdered milk and 60 baby food) from five distinct brands were collected from Iranian pharmacies during 2019. The concentration of toxic elements in both milk powder and baby food was found to be below the recommended standard limits by the European Commission. Additionally, consumption of the examined milk powder and baby food was not a notable carcinogenic risk for the consumer. It may be concluded that the toxic elements content in the tested products was sufficiently low, and all of the milk powder and baby food sold in Iran could be considered safe for infants and children.

As eggs are one of the most economical foods, they also are an important food due to the high protein and nutrient content. Eggs provide folic acid, riboflavin, vitamins and have a low caloric content as well as important concentrations of cholesterol. (Exler et al., 2013; Naviglio et al., 2012) The variety of laying hen and their feeding habits have a significant impact on the characteristics of the eggs they produce. Homegrown hen eggs have gained popularity in the market due to the perception of being healthier, as the hens are believed to have a better quality of life with more freedom. However, several studies have indicated that homegrown hen eggs may contain higher levels of toxic elements. This is attributed to factors such as contaminated soils, the consumption of homegrown plants, and exposure to pollution. (Van Overmeire et al., 2009; Waegeneers et al., 2009) Rubio et al. conducted an exposure assessment of trace elements in fresh eggs from free-range and home-grown hens analyzed by ICP-OES. In this study, a total of 21 metals and metalloids (Na, K, Ca, Mg, V, Mn, Fe, Cu, Zn, Cr, Mo, Co, B, Ba, Li, Sr, Ni, Si, Al, Pb and Cd) were analyzed. (Rubio et al., 2018) The eggs were prepared by separating the yolk and egg white using a plastic egg yolk separator and homogenized with a plastic fork. The certified reference materials used in the Rubio et al. study consisted of apple leaves (NIST SRM 1515), typical diet (NIST SRM 1548a) and wheat flour (NIST SRM 1567a). Percent recoveries ranged from 97.7 to 103 %. Na was found in the highest concentration in egg whites (1210 mg kg⁻¹), in the yolks the most abundant element was Ca (87.9 mg kg⁻¹). The most abundant toxic metal found in the egg whites was Al (8.92 mg kg⁻¹) followed by Pb (0.04 mg kg⁻¹). Aluminum was found at (15.6 mg kg⁻¹) in yolks and Pb was found to be (0.06 mg kg⁻¹) in yolks. The results from this study are shown in Fig. 5.

The study revealed that the home-grown hens exhibited the highest

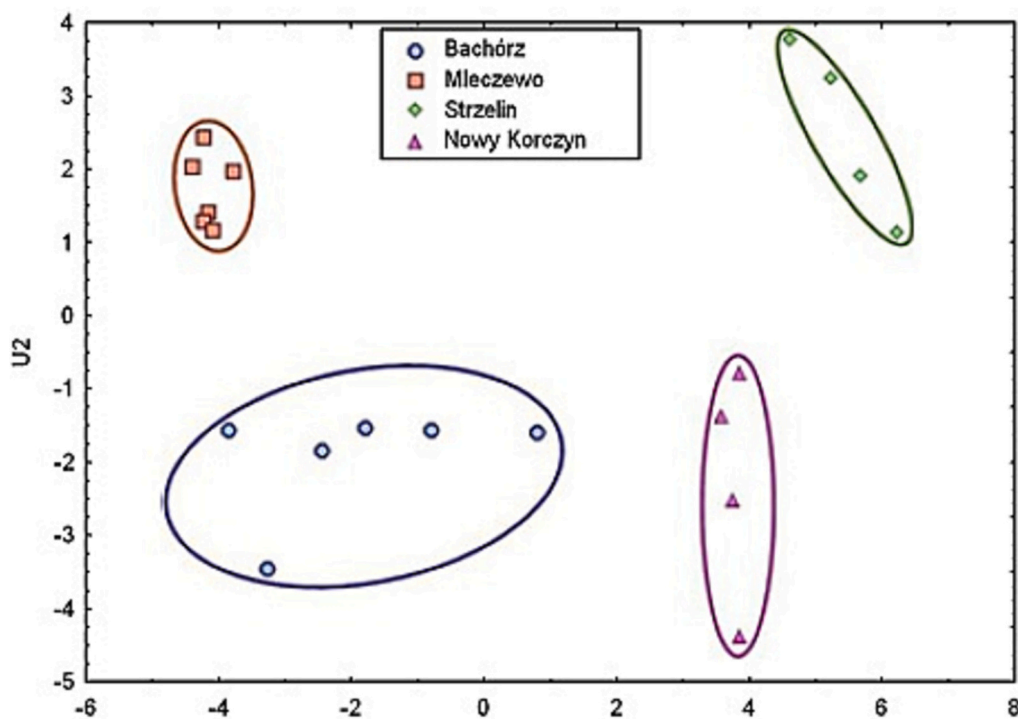


Fig. 4. Scatter diagram of function 1 versus 2.(Kuras and Wachowicz, 2011)

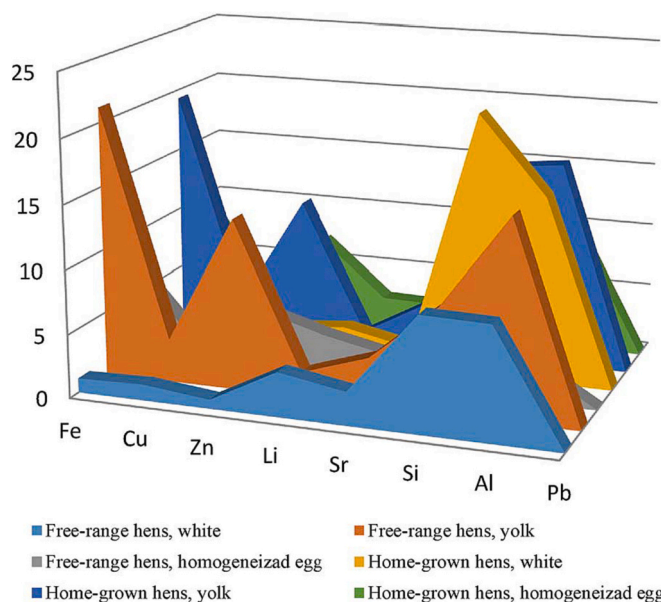


Fig. 5. Comparison of the metal content (mg kg^{-1}) of some studied metals depending on the type of sample and breeding system.(Rubio et al., 2018)

concentrations of toxic elements. The authors attributed this observation to potential contamination originating from the soils or the home-grown vegetables used as feed for the animals.(Rubio et al., 2018)

Honey, a natural sweetener produced by honeybees, comprises water, sugar, and various components derived from flower nectar or bee secretions. The composition of honey, including its mineral content and concentrations of toxic metals, varies significantly depending on the geographical origin. Honey can be classified into two main categories: blossom honeys and honeydew. In this study, researchers employed inductively coupled plasma optical emission spectrometry to analyze the mineral content and detect toxic metals in honey.(Louppis et al., 2019)

Louppis et al.(Louppis et al., 2019) collected 19 honey samples of distinct origin directly from beekeepers. To prepare the samples for inductively coupled plasma optical emission spectrometry, 10 g of all the samples were digested and subsequently mineralized with 10 mL of 65 % Nitric Acid. The samples were then heated in a water bath with the temperature set to 60 °C for 30 min. The mixture was then diluted, sonicated and brought up to a final volume of 100 mL. The analysis was performed using the Thermo Scientific IRIS Intrepid II XDL inductively coupled plasma-atomic emission spectrometer.

Louppis et al.(Louppis et al., 2019) found that there was a significant difference in mineral contents of the honey based on the botanical origin of the honey in several regions in Greece. The order from highest to lowest mineral concentration is as follows: Fir honey from Aitolokarnania, forest flower honey from Zagorochoria, cotton honey from Larissa, flower honey from Samos Island, flower honey and asfaka honey from Aitolokarnania, Greece. Consistently, Ca, Mg, Si, and B were the most abundant metals and metalloids followed by Mn, Fe, and Zn.

When examining individual elements, it was observed that forest flower honey from Zagorochoria exhibited the highest concentration of Ca at $58.30 \pm 2.24 \text{ mg kg}^{-1}$. On the other hand, the fir honey samples from Aitolokarnania contained the highest Mg content at $81.71 \pm 1.43 \text{ mg kg}^{-1}$. In terms of Si, the flower honeys from Samos Island displayed the highest concentration at $16.08 \pm 2.94 \text{ mg kg}^{-1}$. The concentration of Cu, Al, As, Ni, Pb, and Sb were lower across the board for all the samples analyzed, and for Pb, As, Cu, and Ni, it fell below 1 mg kg^{-1} , except for the flower honey sample from Samos Island, which was above 1 mg kg^{-1} for Cu.

Spanish Asfaka honey was found to have significantly lower Cu and Mg content compared to other domestic honeys, such as Spanish rosemary, heather, orange blossom and eucalyptus honeys, as well as Greek blossoms honeys, Moroccan thyme honey, Egyptian clover honey, and Polish Honeydew honeys. Uruguayan and Brazilian honeys were found to have higher Ca contents (64.45 ± 25.50 – 77.60 ± 28.81 and $338.7 \pm 14.61 \text{ mg kg}^{-1}$, respectively). The Ni content in the study was found to be significantly higher in fir honeys compared to the other samples. Specifically, Swiss fir honey showed a high Ni content (1.57

mg kg⁻¹).

Trace amounts of Ba, Cd, Cr, Co, Mo, Se, Be, Ti, Tl and Va were detected. All values except Co and Al were in agreement with previous reports dealing with honey analysis from the regions indicated. (Louppis et al., 2019) The majority of samples had a higher lead content than the regulated upper limit, which is 0.10 mg kg⁻¹. (Louppis et al., 2019)

Rice (*Oryza Sativa*) is a vital source of food and nutrition worldwide and is commonly found in various cereal-based products. (Sneddon et al., 2017; Oliveira et al., 2012; Pasiás et al., 2013) Being a nutrient-rich food and a significant source of complex carbohydrates, it serves as a staple food for more than half of the global population. Given its widespread consumption, Sneddon et al. (Sneddon et al., 2017) conducted a study to assess and report the concentrations of toxic chemicals present in various rice and cereal products, which could potentially pose health risks. In this study, samples were collected and stored in plastic bags. Prior to preparation, the samples were placed on watch glasses and dried in a drying oven at 115 °C until a constant mass was achieved. Sample preparation involved weighing 0.5 g of each sample and adding 10 mL of ultrapure nitric acid to a digestion vessel. The mixture was then subjected to microwave digestion, followed by dilution with 50 mL of deionized water to facilitate analysis using ICP-OES. The lower limit of detection for all metals in the analysis was approximately 0.1 mg kg⁻¹.

Sneddon et al. (Sneddon et al., 2017) tested for a variety of metals and a metalloid including Ni, Pb, Sb, Se and V but did not find detectable concentrations of these metals in most of the samples, aside from Al, Cr, Cu, Fe, Mg, and Zn, which were detected in all samples. Each of the 26 rice and cereal products were divided into 3 separate samples and tested to ensure accuracy. Five of the products showed concentrations in the mg kg⁻¹ range for Ni, Pb, Sb, Se, and V, and were as follows: Red gram, green gram, and black gram were found to contain nickel, with red gram having 6.8 mg kg⁻¹, green gram having 8.0 mg kg⁻¹, and black gram having 8.8 mg kg⁻¹ for Ni. Additionally, Black gram, cow peas, and black sesame seeds had detectable levels of vanadium, with black gram having 4.8 mg kg⁻¹, cow peas having 8.8 mg kg⁻¹, and black sesame seeds having 3.4 mg kg⁻¹.

The US Food and Drug Administration (FDA) currently has no established limits for the concentrations of Al, Cr, Cu, Fe, Mg, and Zn in foods. Al, Cr, and Cu are trace elements which are toxic at high doses, while Fe, Mg, and Zn are key nutrients in which many individuals globally are deficient. The concentrations of all the aforementioned elements were found to be at normal levels relative to previous studies on the subject. The concentration of Al ranged anywhere between 3.9 mg kg⁻¹ to 207 mg kg⁻¹, aside from Black gram, which was significantly higher at 4400 ppm. Cu concentration was between 1.7 and 13.6 mg kg⁻¹, Mg was between 243 and 1526 mg kg⁻¹ (aside from Black Sesame Seeds, which was an outlier at 3230 mg kg⁻¹). Mn was between 4.3 and 118 mg kg⁻¹, and Zn concentrations were between 4.3 and 118 mg kg⁻¹. Fe was between 8.9 and 99.5 mg kg⁻¹, with Flattened Rice being the outlier at 210 mg kg⁻¹.

Finally, there were no significant differences in concentrations of metal(loid)s based on which geographic region the products were derived from, although some differences were noted, such as Black Gram rice from India containing high concentrations of Al compared to the other samples, and Black Sesame Seeds from India containing higher levels of Cu. It is worth noting that Mg was the metal found at the highest concentrations across the board, and Mn and Zn had the lowest concentrations. (Sneddon et al., 2017)

Areas that are in the vicinity of industrial complexes are often prone to potential pollution that can contaminate plants and potential sources of food in said vicinity. Southern Louisiana (USA) can be taken as one of those locations, as there are petrochemical industries and oil refinery facilities in the area that may have hazardous implications on the seafood industry. (Bussan et al., 2019)

American oysters are found in the waters of the region surrounding Southern Louisiana. As filter feeders, they help improve the water quality, which facilitates the survival of aquatic vegetation, promoting a

steady food supply for the aquatic animals in the region. (Sneddon et al., 2013) In a study conducted by Thibodeaux et al. elevated metal concentrations were determined in oysters sampled from Southwest Louisiana. (Thibodeaux et al., 2010) Subsequently, a follow-up investigation by Sneddon et al. was carried out in the same laboratory to implement these findings. (Sneddon et al., 2013) In particular 15 oysters were picked randomly from a sack of 150 oysters which were obtained from a local Louisiana merchant. The oysters were shucked to obtain the oyster meat, dried at 110 °C for 24 h, and ground to a fine powder. Approximately 250 mg of oyster meat was placed in a teflon digestion bomb, wherein a solution of 6 mL of 70 % HNO₃ was added to each teflon bomb for the digestion. The bombs were placed in a conventional microwave oven at 60 s at 30 % power. After cooling to room temperature 4 mL of H₂O₂ was added to add in breaking up organic material. The bomb was subsequently placed in the microwave for another 30 s at 30 % power. The samples were then filtered and diluted up to 10 or 50 mL using a volumetric flask and finally analyzed by ICP-OES analysis. (Thibodeaux et al., 2010) To ensure accurate results, each metal was determined a total of five times. Standard reference material SRM 1566b which is an oyster standard from the National Institute of Standards and Technology (NIST) was used as a measure for accuracy. It is important to note that SRM 1566b does not include Cr, however, the concentrations of Cd, Cu, Fe, and Zn were found to be comparable to the NIST results, with the concentration of Pb under the limit of detection for the ICP-OES used in this study.

The study revealed varying concentrations of metals in the rice samples, ranging from 24.7 to 107.8 µg g⁻¹ for Cd, 22.2 to 57.4 µg g⁻¹ for Co, and 131.0 to 355.0 µg g⁻¹ for Pb. According to the authors, these metal concentrations may have accumulated gradually over time. Alternatively, the occurrence of Hurricane Rita in 2007, a category 5 hurricane could have disturbed the environment and released dormant metals into the water, leading to their presence in the rice samples. The authors emphasized the importance of conducting ongoing studies to determine metal concentrations in oysters and other seafood, particularly considering the common practice of consuming oysters raw. They highlighted the fact that certain metals, such as Cd, can be retained in uncooked oysters, as they tend to volatilize upon heating. However, the study did not include information about organic pollutants resulting from oil spills and industrial products, focusing solely on the metal concentrations found in oysters. (Sneddon et al., 2013; Thibodeaux et al., 2010)

2.3. Microplastics

Microplastics, which are commonly defined as any plastic particles measuring <5 mm in diameter, are documented to assimilate contaminants from seawater. (Andrady, 2011; Kershaw and Rochman, 2015) This assimilation is partly due to the interaction with the environment in which breakdown of the plastics produce anionic surfaces upon which metal cations may adsorb. (Holmes et al., 2012; Holmes et al., 2014) Marine organisms in turn assimilate the microplastics, and if toxins are leached from the microplastics they may be introduced into the food chain. A study by Vedolin et al. (Vedolin et al., 2018) examined the relationship between accumulation of microplastics and heavy metal absorption at 19 beaches along the coast of São Paulo State in south-eastern Brazil. From each site three hundred sample pellets were collected. The microplastics collected were compared against those of virgin pellets by using ICP-OES to test for metal presence of the following: Al, Cr, Cu, Fe, Mn, Sn, Ti and Zn. This investigation found wide variability in metal concentrations both within a beach (among the three hundred samples tested from each beach in three pools of 100) and among the 19 total beaches investigated. Part of the explanation for this phenomenon is due to the frequency of beaches constant reburial and unearthing of the samples. Interestingly metal concentrations in microplastic pellets were high with some of them reaching levels twice or greater than the virgin pellets. Despite this measurable difference, the

microplastic pellets' importance as reservoirs for metals is still minor compared to that of organic pollutants.(Vedolin et al., 2018)

When equipped with an inverted type-torch, temporally and spatially resolved ICP-OES is shown to be a powerful technique for estimating the size distribution of microplastics in water.(Teramoto and Kim, 2021) Teramoto & Kim(Teramoto and Kim, 2021) purchased uniform non-functionalized polystyrene microspheres with known nominal diameters of 1.5 and 3 μm . The quantity of 1.5 and 3 μm microspheres per mL was calculated and from that the probability of particle presence in one droplet was determined for each size, respectively. Microplastics in the environment, however, occur in various forms and it was found that this research could not accurately predict their sizes without first assuming that their form is spherical. In ICP-OES, a plasma event is followed by local plasma cooling and then reheating again to steady-state conditions. When emission intensity was recorded in brief time intervals (temporally), it was found to be related to particle mass. The serial photographs of the emission process showed that the temporal characteristics of particle atomization were dependent on the particle size. This suggested that the particle size can be estimated from the temporal characteristics of particle atomization depending on the particle size and emission intensity.

Particle size plays a significant role in the emission signal obtained in ICP-OES analysis. The size of particles affects the efficiency of sample transport, aerosol formation, and vaporization processes within the ICP-OES instrument, ultimately influencing the intensity of the emission signal.(Bussan et al., 2019; Teramoto and Kim, 2021; Olesik, 1996) These results imply that the temporally and spatially resolved ICP-OES, when used with an inverted type-torch, could accurately and precisely analyze microplastics in water.(Teramoto and Kim, 2021)

2.4. Materials

To properly characterize semiconductors, it is important to determine the stoichiometries. Morrison et al.(Morrison et al., 2020) analyzed six different specimens for their M/E ratio via ICP-OES. M was Cd and Zn, and E was S, Se, Te, Te + Se, or Te + S. The results from the ICP-OES analysis were as follows: CdSe[n-octylamine]_{0.53} Quantum Belts "QBs" M/E ratio was 1.00 ± 0.02 , {CdSe[Cd(oleate)₂]_{0.19}} QBs M/E ratio was 1.27 ± 0.02 , CdTe_{0.50}Se_{0.50}[oleylamine]_x QPs M/E ratio was 0.98 ± 0.01 , CdTe_{0.73}S_{0.27}[oleylamine]_z Quantum Platelets QPs M/E ratio was 1.05 ± 0.02 , (CdSe)₁₃(n-PrNH₂)₁₃ cluster M/E ratio was 1.00 ± 0.01 , and Zn(S₂CNEt₂)₂ M/E ratio was 0.26 ± 0.02 .(Morrison et al., 2020)

Morrison et al.(Morrison et al., 2020) identified several important pitfalls associated with conventional ICP-OES analysis and offered suggestions for improving reproducibility and accuracy in methods for sample digestion, calibration-curve construction, and emission-line and calibration-standard selection as it relates to semiconductor materials.

When using multi-element calibration standards which contain either Cd and Pt or Cd and As, spectral overlap of emission lines at 214.438 nm and at 228.802 nm, respectively may occur and therefore these multi-element combinations should be avoided. Additionally, emission data for Cd over the 0–100 mg L⁻¹ concentrations were found to be nonlinear while concentrations over 0–10 mg L⁻¹ were linear. It is recommended that concentrations of 10 mg L⁻¹ not be exceeded due to the tendency of concentration: emission intensity to be nonlinear beyond that concentration range.(Morrison et al., 2020) The three most important considerations in sample preparation are the following: digestion tube composition, closed versus open digestion tubes, and correct choice of digestion reagents.(Morrison et al., 2020; Koons, 2003)

Morrison et al.(Morrison et al., 2020) used two types of digestion-tubes namely borosilicate and high-density polyethylene (HDPE). In order to determine which digestion tube could have given the best results, {CdSe[n-octylamine]_{0.53}}, which has a Cd:Se ratio of 1:1, was synthesized and then digested so as to establish which digestion tube gave results closest to the known 1:1 Cd:Se values. It was found that

better results were generated when using HDPE versus borosilicate.(Morrison et al., 2020; Koons, 2003)

Next the authors tested the concept of analyte digestion of both open and closed digestion. Better results were found when digestion was conducted in closed HDPE tubes. The hypothesis for this was that semiconductors which contain sulfur and selenium, and therefore which may produce volatiles H₂S and H₂Se, respectively, are prone to loss during digestion. Such loss would result in higher metal:sulfur and metal:selenium ratios. It was found that closed digestion tubes (made of HDPE and digested with H₂O₂/HNO₃) achieved the Cd/Se ratio closest to the theoretical and known one.(Morrison et al., 2020)

Lastly, digestion with three separate reagent digestion protocols was determined. The three reagent digestion protocols were the following: HNO₃, H₂O₂ + HNO₃, and H₂O₂. The poorest results were found when H₂O₂ was used solely. The reagent HNO₃ alone provided satisfactory results while the best results (most closely matching the Cd:Se ratio of 1:1) were found when both digestion reagents H₂O₂ + HNO₃ were applied.(Morrison et al., 2020) ICP-OES presents an alternative, as sample digestion occurs before analyzing, and ICP-OES is capable of detecting in the mg kg⁻¹ range. The precise detection of lighter elements and volatile components is a challenge in all techniques, as high energy photons may eject components, cause a change in oxidation state and to the crystal structure. For example, in X-ray photoelectron spectroscopy (XPS), there has been found to be up to a 46 % difference in initial and final measurements of the metal ions due to the aforementioned causes.(Saparov et al., 2015) In addition, many of the techniques have strict requirements for the samples, such as how thick the sample is, or concerning its homogeneity.(Morrison et al., 2020)

2.5. Dietary supplements

In 1994, the US Food and Drug Administration (FDA) revised the Federal Food Drug and Cosmetic Act to include botanical products, complementary nutritional's, and micronutrients under the category of dietary supplements. These products can lead to unintended adverse effects if they are contaminated with heavy metals, microbial contaminants, pesticides, and other toxins. There are thirty-five metals that, if found in food products and ingested, can potentially lead to health problems such as lung damage, gastrointestinal symptoms, and detrimental effects to the nervous system, cardiovascular system, and several other major organ systems.(Canbay and Doğantürk, 2017)

Canbay et al.(Canbay and Doğantürk, 2017) used ICP-OES to detect the concentration of some mineral elements, such as Al, Cu, Fe, Mn, and Zn, and some toxic elements which included Pb, Cd, Hg, As, Cr, Co, and Ni. A Perkin Elmer Optima 8000 ICP-OES was used for the detection of metals and metalloids was performed in supplements.

Ten distinct dietary supplements and diet products were analyzed in this study, two of which were in the form of a pill, while the other eight were found to be in powder form. Prior to digestion, the samples were prepared as follows; first they were homogenized, and then 0.5 g of sample was added to 9 mL of 65 % w/v HNO₃ and 3 mL of 10 M HCl into a TFM digestion tube. The samples were digested in a microwave oven and the resulting digest was transferred to a 50 mL acid washed volumetric flask and diluted up to 50 mL using ultrapure water. Each sample was analyzed in triplicate. The least sensitive element, manganese, was used to optimize the measurement conditions. The emission of the analytes was based on the difference of measured emission intensity of the top peak and the background near said peak.

The results of Canbay et al.(Canbay and Doğantürk, 2017) showed that the mean levels of the metal(loid)s were as follows: Ni $3.34 \pm 0.01 \mu\text{g g}^{-1}$, Zn $41.24 \pm 0.63 \mu\text{g g}^{-1}$, Mn $23.27 \pm 0.25 \mu\text{g g}^{-1}$, Fe $221.10 \pm 1.53 \mu\text{g g}^{-1}$, Al $18.46 \pm 0.14 \mu\text{g g}^{-1}$, and Cu $7.76 \pm 0.15 \mu\text{g g}^{-1}$. No other metals and heavy metals were found in significant concentrations. The ranges for each metal concentrations were as follows: Zn was between 11.61 and 41.24 $\mu\text{g g}^{-1}$, Ni was between 1.34 and 3.34 $\mu\text{g g}^{-1}$, Mn was between 1.53 and 23.27 $\mu\text{g g}^{-1}$, Fe was between 19.14 and 221.10

$\mu\text{g g}^{-1}$, Al was between 5.21 and 18.46 $\mu\text{g g}^{-1}$, and finally, Cu was between 3.33 and 7.76 $\mu\text{g g}^{-1}$. (Canbay and Doğantürk, 2017) Recent data suggests the importance of macro- and microelements to adrenals function, while some elements inflict harmful effects. (Canbay and Doğantürk, 2017)

2.6. Human tissue and bodily fluids

2.6.1. Adrenal adenomas

The adrenal glands, small glands located at the top of each kidney, consist of a cortex and a medulla which are used to produce hormones. (Pignatti et al., 2017) Additional functions of the adrenal gland include regulation of the immune system, energy metabolism, the homeostasis of body fluids and electrolytes. (Pignatti et al., 2017) Recent literature suggests that the chances of adrenal masses increase with age. (Jagodić et al., 2021) Most adrenal tumors diagnosed are benign, but larger masses (>4 cm) increase the risk of adrenocortical carcinoma. (Chatzellis and Kaltsas, 2019) Recent data suggests the importance of macro- and microelements to adrenals function, while As, Cd, Cr, Hg and Pb inflict harmful effects. (Lauretta et al., 2019; Rana, 2014; Stojsavljević et al., 2019)

Jagodić et al. (Jagodić et al., 2021) focused on the amounts of micro- (Mn, Co, Cu, Zn, As, Se, Cd, Pb, U) and macroelements (Ca, Na, K, Mg) in healthy adrenal tissue (HAT) and adenomatous adrenal tissue (AAT) samples using ICP-OES and ICP-MS. A comparative determination of macro- and microelements in healthy blood (HB) and adenomatous blood (AD) as well as a chemometric analysis inferring the elemental profile changes of adrenal adenoma (AA) accompanied the results. (Jagodić et al., 2021)

25 AA patients (f/m ratio = 14/11; average age: 57 ± 7) and 30 healthy blood volunteers (f/m ratio = 16/14; average age: 54 ± 4) fasted overnight then had 5 mL of peripheral venous blood collected using the BS 368381 vacutainer trace element plastic blood collection tubes. All patients underwent the planned AA surgical treatment. (Jagodić et al., 2021) After the laparoscopic adrenalectomy, well-demarcated AAT and normal HAT were excised in each patient. Using a histopathological (HP) examination and AA diagnosis, all tissue was confirmed viable by pathologists. Patient numbers decrease due to other chronic diseases, which might have caused alterations to target element levels (Jagodić et al., 2021).

Sample preparation consisted of two stock solutions (10 mg L^{-1} for microelements and 1000 mg L^{-1} for macroelements) prepared using ultrapure water obtained using the Milli Q Plus System. An approximate mass of 0.5 g was taken from each sample. An ETHOS 1 System (Milestone, Italy) microwave digestive system was used in decomposing the samples with the microwave digestion protocol as follows; 2 min. Heating to 85 °C, 5 min. Heating to 135 °C, 5 min. Heating to 180 °C and maintained for an additional 15 min at 180 °C. Samples were then diluted to 25 mL with ultrapure water. An ICP-OES iCAP 6500 Duo Spectrometer (Thermo Scientific, UK) and an ICP-MS iCAP Q (Thermo Scientific, UK) were used to determine the concentration levels of each element. ICP-MS analyzed elements were quantified in an optimized mode according to the principle of kinetic energy discrimination (KED). Microelements were determined in the range from 1 to 250 $\mu\text{g L}^{-1}$, whereas the macroelements were determined in the range from 1 to 25 $\mu\text{g L}^{-1}$. Six calibration solutions were used in both methods and correlation coefficient (R) was >0.998 for each element, the percent recoveries ranged from 89.4 to 106 %. (Jagodić et al., 2021) To further confirm the accuracy, five blood samples and five tissue samples were spiked with a standard solution of each element (10 and 25 $\mu\text{g L}^{-1}$ for microelements, or 10 and 25 mg L^{-1} for macroelements): the results were relatively close to the predicted amount. The Shapiro-Wilk's and Mann-Whitney U tests were performed using IBM SPSS Statistics Software v.20. A PLS ToolBox was used to examine the principal component analysis (PCA); $P < 0.05$ was the degree of statistical significance. (Jagodić et al., 2021) Zn was the dominant microelement in the AAT

samples, followed by Cu, Mn, Se, Cd, Pb, As, Co, and U; the results for HAT were nearly identical, except for As, and Pb. Tissue and blood samples showed similar microelements distribution; the highest amounts were found for K, Na, Ca, and Mg. The highest macroelements in both HB and AB samples were Na, K, Ca, and Mg. A multivariate analysis was used to do additional analysis of the obtained results. Two PCAs were applied to detect trends, explain characteristics, and decrease the extent of the data set. The results from the first PCA followed the results of the Mann-Whitney U test. The second PCA was performed to gain criteria for separating HATs from AATs. HATs and AATs contained similar amounts of Co, As, Cd, U, Ca, and Na, which suggests the elements were not significant for their separation. (Jagodić et al., 2021)

The findings from Jagodić et al. (Jagodić et al., 2021) suggest the regulation of adrenal steroidogenesis has a close relation to Mn in terms of functioning as a cofactor of mitochondrial superoxide dismutase (SOD). Mn adrenal tissue amounts were reported as 0.20 $\mu\text{g g}^{-1}$ and 0.69 $\mu\text{g g}^{-1}$, which agreed with the results from this study. (Jagodić et al., 2021; Miller and Miller, 2018) Cu and Zn are components of cytoplasmic SOD, which look for superoxide free radicals. Cu has been mentioned to have harmful effects on the endocrine system and stress response. Zn has an inhibitory effect on cortisol secretion. Deregulation of the adrenal gland occurs with the production of free radicals; these are removed by antioxidant enzymes dependent on Se. Using ICP-based techniques, the examination and Mann-Whitney U test AATs showed significantly higher Mn, Cu, Zn, Se, Pb, K, and Mg levels than the HATs. In opposition, adenomatous blood samples indicate benign adrenal masses can withdraw target elements from circulation (Jagodić et al., 2021).

2.7. Dietary habits and human scalp hair

To determine the quantities of pollutants that bioaccumulate in food, water, or the environment, various biological monitors, including microbiological, plant, animal, or human character, have been used. (González-Muñoz et al., 2008) Biomarkers of exposure of humans include invasive (blood and other internal tissues/organs) and non-invasive (excretory routes – urine and keratin materials hair and nails) the non-invasive biological monitors are preferred because of ethical controversy. (Goullé et al., 2005; Kazi et al., 2009; Ponce et al., 1998; Spallholz et al., 2005; Torrente et al., 2005) Hair is a preferable biomarker because the elements are deposited permanently in the shaft as it grows, and the mineral content has had long-term exposure to toxicants or pollutants (Foo and Tan, 1998; Sela et al., 2007).

Chojnacka et al. (Chojnacka et al., 2010) focused on how dietary habits are reflected by multi-elemental analysis of human scale hair. The content of 39 elements (Ag, Al, As, B, Ba, Bi, Ca, Cd, Ce, Co, Cr, Cu, Fe, Hg, K, La, Li, Mg, Mn, Mo, Na, Ni, P, Pb, Pt, Rb, S, Sb, Se, Si, Sn, Sr, Ti, Tl, V, W, Y, Zn, and Zr) in hair was determined by a ICP-OES Varian-Vista MPX (Australia) with a pneumatic nebulizer (macroelements) and a Thermo Fisher Scientific ICP-MS (microelements and toxic elements), as described previously. (Chojnacka et al., 2005; Chojnacka et al., 2006a; Chojnacka et al., 2006b)

The study was carried out using 117 participants involving 41 males and 76 females, with a uniform age 21–22 years with similar environmental and occupational exposure. The participants were given a questionnaire that specifically asked questions regarding dietary habits. The participants cut hair from their nape of the neck directly after washing their hair four times consecutively with Johnson's Baby shampoo and drying. The cutting of the hair was done utilizing stainless steel surgical scissors.^[91] After the samples were cut 0.5 g was solubilized using nitric acid (69 %; m m^{-1}) suprapur grade from Merck. After microwave digestion Milestone (USA), samples were diluted to 50 g using ultrapure water deionized by Aquadem 50 L, WilhelmWerner GmbH, and Millipore Simplicity UV. For macroelement content, samples were analyzed directly using ICP-OES Vista MPX (Australia) with a pneumatic nebulizer. After ten dilutions, samples were analyzed using

ICP-MS Thermo Scientific (Germany) for microelements, toxic elements, and other trace elements. *Statistica ver 8.0* was used to elaborate results statistically. (Chojnacka et al., 2010) The hair of the individuals who consumed low-processed food contained 15 % more V, three times less Sr, 30 % less P, 40 % more Ni, two times less Na, three times more Mo, and 10 % less Co; the differences were not statistically significant ($P < 0.1$). The content of the following elements increased with frequent intake and were found to be statistically significant: Al never-frequently $P = 0.00107$, Al never-rarely $P = 0.00255$; Cr between all the groups $P = 0.000113$; Fe never-frequently $P = 0.0042$; K never-rarely $P = 0.077$; Na never frequently $P = 0.042$. Samples from those who consumed slimming preparations (about 10 % of participants) contained two times higher levels of Fe, five times of Cr, and 3.5 times of Al than subjects without. Pb levels are 40 % higher in people linked to laxatives. Analgesic agent consumers contained two times more Si than those that did not take the medication. It was concluded that human hair is, in fact, a useful biomarker of the elemental status of humans. The mineral content of hair reflected the dietary habits of the individual (Chojnacka et al., 2010).

2.8. ICP-OES for semiquantitative analysis and speciation in food, dietary supplements, microplastics, electronic and biological materials

ICP-OES is a powerful analytical technique widely used for semiquantitative analysis in various fields. Semiquantitative analysis refers to the estimation of elemental concentrations in samples without the use of external calibration standards. (Choi et al., 2007) In ICP-OES, the emission signals from the plasma are used to determine the relative concentrations of elements present in the sample. (Smoliński et al., 2022) By comparing the intensity of the emission lines from the unknown sample to those of known standards, it is possible to obtain semiquantitative information about the elemental composition of the sample. Although semiquantitative analysis does not provide precise quantitative measurements, it is often valuable in preliminary screening, trend analysis, and comparative studies. Additionally, the ability of ICP-OES to simultaneously analyze multiple elements makes it an efficient tool for semiquantitative analysis in various applications, such as environmental monitoring, geological studies, and quality control in industries (Sharma, 2020; Granell et al., 2022).

ICP-OES can be hyphenated to an LC (Liquid Chromatography) method for chemical speciation analysis in various materials, including food dietary supplements, microplastics, and electronic and biological materials. (Granell et al., 2022; Li et al., 2021) By combining these two techniques, researchers can obtain valuable information about the elemental composition and speciation of target compounds present in these samples. LC allows for the separation and purification of complex mixtures, while ICP-OES provides sensitive and selective detection of trace elements. (Montes-Bayón, 2003) This hyphenation enables the identification and quantification of specific chemical species, such as metal ions or organic compounds, within the complex matrices of these materials. (Brewer and Marcus, 2007) The combined approach of ICP-OES with LC holds significant potential for ensuring the safety, quality, and compliance of these products, as well as for studying the behavior and fate of microplastics in different environmental and biological systems (Prakash et al., 2022; Raji et al., n.d.; Nimbkar et al., 2023; Wuilloud and Altamirano, 2006).

3. Limitations of ICP-OES: Solutions and future developments

The fact that ICP-OES suffers from a number of recognized limitations has led to the development of alternative performance-enhancing sampling accessories and in many cases, other plasma spectrochemistry emission techniques. Taking a closer look at some of those developments as well as how creative practitioners and instrument vendors have developed optimized sampling techniques and innovative hardware and software solutions to mitigate the impact of these

drawbacks, we can suggest the following solutions to address the recognized limitations of ICP-OES.

3.1. Detection capability

Because ICP-OES is a technique developed for liquids, solid samples such as soils and rocks have to be digested using concentrated mineral acids and microwave dissolution systems. Once in solution the samples have to be diluted to a known volume, which degrades the practical limit of quantitation in the sample by the dilution factor used. In addition, detection limits for some elements important to environmental monitoring and clinical toxicology applications are on the edge of the capability of ICP-OES, but do not need the increased performance of an ICP-MS. In both these scenarios, the use of an ultrasonic nebulizer (USN) can improve the limit of detection by 5–10-fold, allowing ICP-OES to meet the required detection limits, without the need for ICP-MS. (Boss and Fredeen, 2004)

In ultrasonic nebulization, the liquid sample is pumped onto an oscillating piezoelectric transducer. The oscillations break the sample into a fine aerosol so that aerosol formation is independent of nebulizer gas flow. The efficiency of an ultrasonic nebulizer is typically between 10 % and 20 %, at least 10-fold greater than typical pneumatic nebulization. As a result, more sample will reach the ICP, providing detection limits which are usually 5–10 times lower than pneumatic nebulization. The higher efficiency of the ultrasonic nebulizer increases the water loading to the ICP, so a desolvation unit is added after the nebulizer. The cooling portion of the desolvation unit is typically a Peltier cooling device. Autotuning circuitry has greatly improved the short- and long-term stability of the ultrasonic nebulizer allowing the system to be used for routine, high throughput work. However, the ultrasonic nebulizer is still susceptible to matrix effects, is not HF resistant and is therefore more suited to clean samples, with low dissolved solids. A schematic of a USN is shown in Fig. 6.

3.2. Solid sampling capability

ICP-OES is a technique primarily designed for analyzing liquids, although there has been some success for characterizing solid samples by coupling the technique with a laser ablation system to pass the ablated sample aerosol into an ICP-OES for analysis. However, a novel emission technique has now been developed which uses a high energy laser to ablate solid samples and to look at the emission profile of ablated material with an emission spectrograph. The technique is called LIBS which stands for laser induced breakdown spectrometry and has been commercially available since the early 2000s, but it has only been in the past 5 years where its application potential has been fully explored. Initially developed by a group of government scientists in the early 1980s. (Radziemski et al., 1983) it was first applied to the analysis of soils and hazardous waste sites, because of its remote sampling capabilities. (Yamamoto et al., 1996) However, since it has been in the hands of the routine analytical community, it is now being used to solve real-world application problems. (Harmon et al., 2013) Although the analytical capability, performance and elemental range of LIBS compares quite favorably with other AS techniques, it should be considered complimentary (and a competitor) to both ICP-OES, and XRF. The unique benefits of LIBS are in its ability to sample a very diverse range of matrices, both in a laboratory environment and at remote locations out in the field.

Laser induced breakdown spectrometry is an atomic emission spectroscopic technique that utilizes a small plasma generated by a focused pulsed laser beam (typically from a Nd:YAG laser) as the emission source. The plasma formed is about ten times hotter than inductively coupled plasma and as a result will vaporize just about any material it comes in contact with. The energy from the plasma excites the vaporized sample which results in a characteristic emission spectrum of the elements present in the sample, which is then optically dispersed and

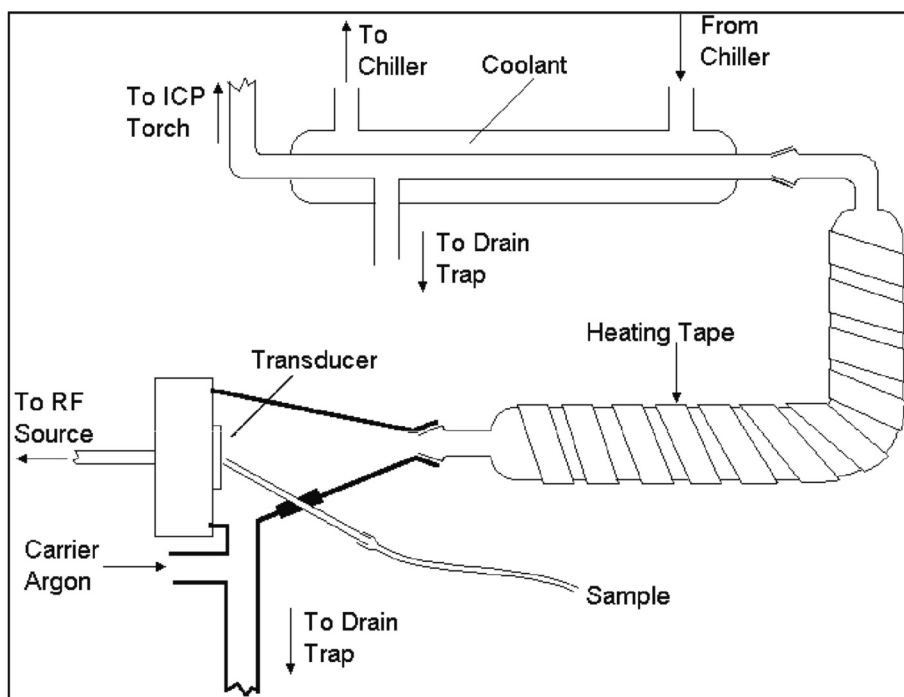


Fig. 6. USN schematic (Boss and Fredeen, 2004).

detected by optical components traditionally used in an emission spectrometer. (Cremers and Radziemski, 2013) A typical optical layout of a LIBS system is shown in Fig. 7.

3.3. Spectral interferences

Spectral overlaps are a way of life in ICP-OES. There are literally tens of thousands of emission lines that could potentially interfere with any of the analyte wavelengths depending on the sample matrix being analyzed. However, by utilizing a suitable simultaneous spectrometer,

with a suite of optimized emission lines based on the spectral complexity of the sample matrix or a sequential spectrometer, where the best emission line can be selected a suitable analyte wavelength can be used for quantitation.

However, under normal circumstances if the analyte concentration is high enough and the sample matrix is spectrally clean there is typically an abundant choice of emission lines available for quantitation. However, when working with analyte signals at or near the detection limit or the sample matrix is spectrally complex it becomes more problematic to select the optimum wavelength. The traditional way of dealing with

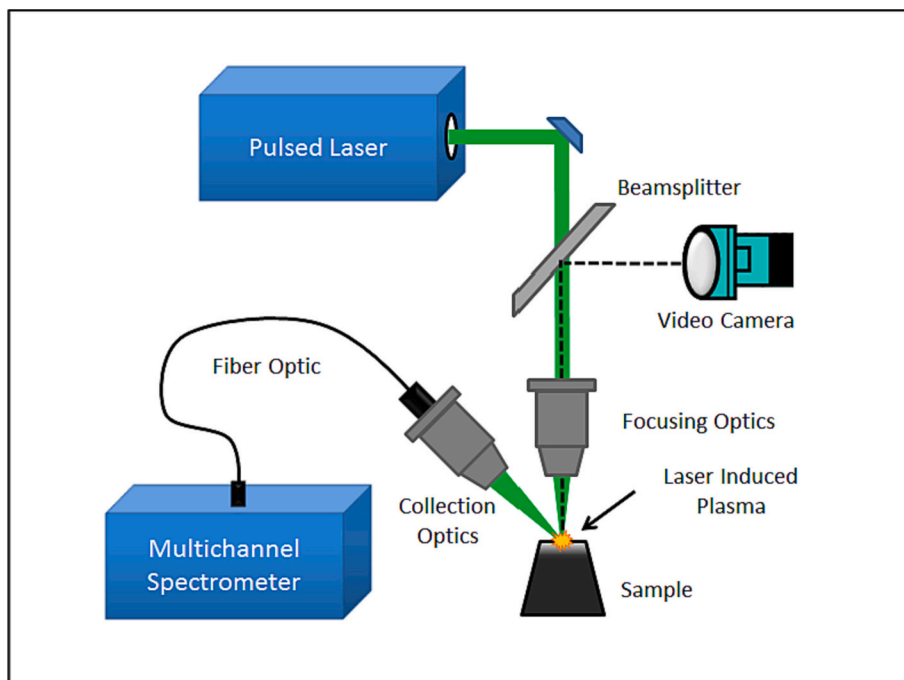


Fig. 7. Optical configuration of a LIBS system. (Cremers and Radziemski, 2013)

these complex spectral situations is to use of interelement correction (IEC), which uses intensity measurement at the analyte emission wavelength and compares the emission intensity of the interfering element with the analyte. This works quite well as long as the concentration of the interfering element remains within the linear concentration range, the matrix components are similar and the plasma conditions remain constant, which is not always the case.(Gaines, 2011)

3.4. Spectral correction software algorithms

A more accurate method for performing spectral interference corrections uses the wealth of information obtained with advanced detector systems that capture the entire emission spectrum and are known generically as Automated Background Correction Software Algorithms (ABCA). Ordinary IECs attempt to correct for interferences by making a single measurement of the interferent and, from that, creating a mathematical factor that is applied to subsequent measurements of the analyte. ABCA rather than relying on a simplistic assumption, measures not only the interferent but also the background contribution from the matrix, thereby creating a software correction formula. The result is an improvement in accuracy and detection limits. There are many types of ABCA, including Fast Automated Curve Fitting Technique (FACT), Fitted Background Correction (FBC), and Multicomponent Spectral Fitting (MSF) but they all utilize mathematical modeling typically using multiple linear least squares model based on an analysis of the pure analyte, the matrix and the blank.(Corp, n.d.) They create an interference-corrected mathematical model and allows the determination of the analyte emission in a spectrally complex matrix with improved detection limits and accuracy. An example of this is shown in Fig. 8 which shows 1 mg L⁻¹ B (black) in the presence of 100 mg L⁻¹ Fe (blue). It can be seen that by automatically applying the correction, the peak for 100 mg L⁻¹ Fe would be mathematically subtracted, ensuring the 1 mg kg⁻¹ B (red) would be quantified free of the Fe interference.(Thomas, 2023)

3.5. High cost of operation

Even though ICP-OES is a multielement technique, it is expensive to run. It consumes 15–20 L min⁻¹ of gaseous argon, which translates into approximately \$2500 per year for a lab that is running their instrument

for 1000 h (2.5 days a week).(Thomas, n.d.-b) This has benefits over flame atomic absorption (FAA) even though the cost of gases such as acetylene and nitrous oxide are much higher, AA is a single element technique, therefore the cost of carrying out multielement analysis is significantly higher and much slower, particularly with regard to electrothermal atomization (ETA). However, when compared to ICP-MS, the cost of ICP-OES is more attractive because of the higher cost of ICP-MS consumables such as interface cones and ion detectors. Table 2 gives a summary of the running costs of the major AS techniques.

The high running costs of ICP-OES opened up an opportunity for the development of microwave induced plasma (MIP) technology in the early-mid 2000s. Microwave generated plasmas using air or nitrogen have been used as gas chromatography detectors for decades and were explored as potential excitation sources for emission studies back in the 1970s, when ICP was being investigated. However, it was found that they had limited applicability, because they were not considered robust enough for introducing liquids. As a result of this limitation in MIP technology, ICP became the dominant excitation source. However, many of the earlier limitations were addressed by solid state RF technology, which was not around when MIPs were first developed. As a result, MIP technology became a viable alternative to ICPs. To better understand this technology, a closer look at an MIP is generated must be taken (Jankowski, 1999).

Microwave-induced plasma technology basically consists of a quartz tube surrounded by a microwave waveguide or cavity. Microwaves

Table 2

Annual Operating Costs (\$US) for the Four AS Techniques for a Laboratory Running an Instrument 1000 h per Year (20 h per Week). (Note: ¹ using acetylene and nitrous oxide, ² using gaseous argon, ³ using liquid argon supply, ⁴ using a helium collision/reaction cell, ⁵ hollow cathode lamps and tubing, ⁶ graphite tubes, ⁷ plasma torches/nebulizers/spray chambers, ⁸ interface cones/detectors).(Thomas, n.d.-b)

Technique	Gases (\$)	Power (\$)	Consumable supplies (\$)	Total (\$)
FAA	5000 ¹	100	1800 ⁵	6900
ETA	200 ²	300	5500 ⁶	6000
ICP-OES	2500 ³	500	3100 ⁷	6100
ICP-MS	3000 ^{3,4}	500	10,000 ^{7,8}	13,800

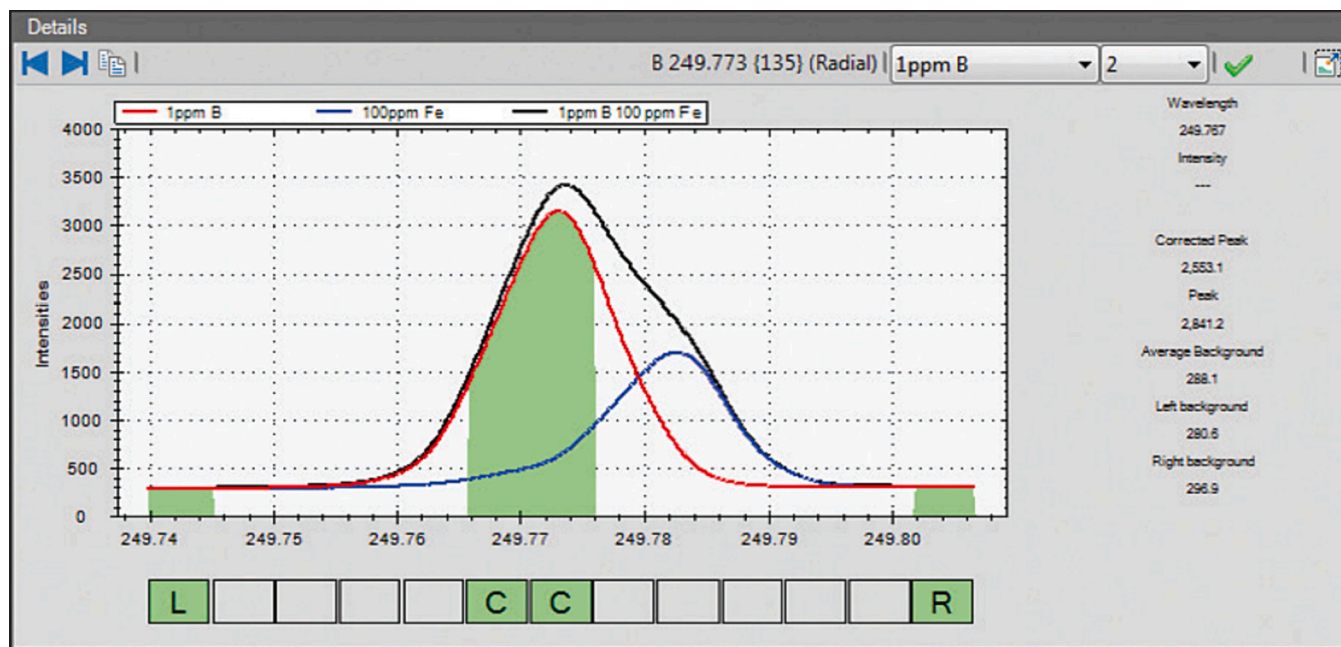


Fig. 8. 1 mg L⁻¹ B in the presence of 100 mg L⁻¹ Fe (shown by the black peak with a shoulder). By mathematically subtracting the iron (blue peak), the 1 ppm B (red) peak can be quantified using an automated background correction algorithm (ABCA).(Thomas, 2023)

produced from a magnetron fill the cavity and cause the electrons in the plasma support gas to oscillate. The oscillating electrons collide with other atoms in the flowing gas to create and maintain a high-temperature plasma. As in the inductively coupled plasmas, a high voltage spark is needed to generate the initial electrons to create the plasma, which achieves a temperature of approximately 5000 K, slightly less than an argon based ICP.

At the heart of this technology is a 2.5 GHz magnetron coupled into nitrogen plasma, which is created using compressed air and a nitrogen generator. By using the magnetic field rather than the electric field for excitation, extremely robust plasma is formed, which is capable of handling much higher dissolved solids than previous MIP designs. The microwave waveguide concentrates both the axial magnetic and radial electrical fields around the torch, which creates a conventional-looking plasma, allowing for a traditional inert concentric nebulizer and double pass spray chamber to be connected to the torch. The optical system in the first commercial-available instrument is a conventional scanning monochromator based on the Czerny-Turner optical design and a thermoelectric-cooled CCD array detector. (Elliot, n.d.)

Because of lower excitation temperatures in an MIP-OES, the detection capability is typically slightly inferior to conventional ICP-OES, although for some elements they are very similar. However, the real benefit of MIP-OES is that it is much less expensive to run because it does not require the use of argon. Therefore, as long as its detection limits meet the demands of the application, the cost of analysis is significantly lower. Table 3 provides a comparison of detection limits between ICP-OES and MIP-OES.

MIP-OES technology has been used since 2012, where it has achieved reasonable success in the marketplace as a low-cost option for applications requiring a small group of elements requiring ICP-OES/FAA detection limits. However, at the 2023 Pittsburgh Conference, a more advanced version of microwave-induced plasma technology was introduced. (RADOM, n.d.-a) This innovative design called the MICAP-OES 1000 (microwave inductively coupled atmospheric plasma – optical emissions spectrometer) utilizes a nitrogen plasma using Cerawave™ ring technology that provides highly focused RF energy which does not require air or water cooling. Coupled with a high-resolution Echelle-based CCD detector it provides rapid, simultaneous measurement of the full wavelength range of elements. This approach offers benefits over the existing MIP-OES technology, which uses scanning Czerny-Turner optical technology, which means that each wavelength is measured sequentially. Due to its compact design, the MICAP technology is well-suited for remote field-based analysis, as well as laboratory installation. MICAP technology provides similar detection capability to existing MIP-OES instrumentation, but because the spectrometer has high resolution (5 picometers at 200 nm), it is ideally suited for real-world samples with spectrally-complex matrices as demonstrated by Table 4 which shows quantification and recoveries of Au at 267.60 nm in a series of geological CRMs (RADOM, n.d.-b).

4. Conclusions

ICP-OES has emerged as a pivotal spectroscopic technique for the analysis of multiple elements, providing scientists, including chemists,

Table 3
Detection limit comparison ($\mu\text{g L}^{-1}$) of MIP-OES with ICP-OES (Cauduro, n.d.).

Element	ICP-OES	MIP-OES	Element	ICP-OES	MIP-OES
K	1.0	0.65	As	1.0	50
Ca	0.05	0.04	Cd	0.1	1.4
Mg	0.04	0.09	Cr	0.2	0.3
Na	0.5	0.12	Mn	0.1	1.0
Au	1.0	2.1	Pb	1.0	2.5
Pt	1.0	6.1	Sb	2.0	12
Pd	2.0	1.6	Se	2.0	77
Ag	0.6	1.2	Zn	0.2	3.1

with a powerful tool to perform elemental analysis at the parts per million (ppm) and parts per billion (ppb) levels. This comprehensive review showcases the diverse recent applications of ICP-OES in various scientific fields and highlights its notable advantages over alternative analytical methods, especially when dealing with complex samples requiring trace element analysis. Some notable areas where ICP-OES has been successfully employed include analyzing trace elements in the human brain, characterizing the chemical composition of cigarettes, pesticide analysis, and assessing the purity of pharmaceutical compounds. While ICP-OES has conventionally found application in the analysis of drinking water, alcoholic beverages, and petrochemicals, its decreasing capital costs have made it more accessible to undergraduate/graduate programs and small businesses in need of trace elemental analysis for their clientele. This review highlights the intriguing and expanding range of applications for ICP-OES, ensuring its continued relevance and continued interest within the scientific community for the foreseeable future.

Although ICP-OES is a powerful analytical technique with a wide range of applications it does have some limitations, including poor detection limits for solid samples, spectral interferences, and a high cost of operation. To address these limitations, researchers have developed a number of new techniques, including ultrasonic nebulizers, LIBS, ABGA, and MIP technology. These new techniques have helped to improve the performance of ICP-OES to make it a more versatile and powerful analytical technique. However, there are still some challenges that need to be addressed, such as the development of more sensitive and selective detection methods for solid samples, and the development of more robust and user-friendly software algorithms for spectral interference correction.

Future prospects of ICP-OES involve the advancement of intelligent instruments capable of identifying and rectifying potential errors without the need for an expert operator. Additionally, ongoing research is focusing on developing new atomic emission sources that offer higher sensitivity and lower continuum background emission. If successful, these novel sources could greatly improve the detection limits achievable with ICP-OES, surpassing current capabilities.

One particularly promising area of research is the development of MIP. MIP utilizes microwave radiation to generate plasma and boasts several advantages over ICP, such as lower operational costs, higher sensitivity, and reduced continuum background emission. However, MIP does have some drawbacks, including a smaller plasma volume and narrower emission bandwidth. Due to these limitations, the widespread adoption of MIP technology has been hindered. Nevertheless, ongoing research in this domain holds the potential for MIP to become a more viable alternative to ICP-OES in the future.

In conclusion, the future of ICP-OES appears bright, with several promising research areas that may lead to significant enhancements in its performance. As these advancements materialize, ICP-OES will evolve into an even more potent and versatile analytical tool.

Author contributions statement

Chris Douvris: Conceptualization, Writing - Original Draft, Supervision.

Trey Vaughan: Writing - Original Draft, Graphics.

Derek D. Bussan: Conceptualization, Funding acquisition, Writing - Original Draft, Supervision, Project administration.

George Bartzas: Writing - Review & Editing.

Robert Thomas: Writing - Original Draft, Reviewing and Editing and Graphics.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Table 4
Quantification and recoveries of Au at 267.60 nm in a series of geological CRMs.(RADOM, n.d.-b)

Analyte	Wave-length	CRM ID	Certified Value	Preparation 1	Preparation 2	Dilution	Recovery 1	Recovery 2
Au, mg L ⁻¹	267.60	238	2.95	2.99	2.84	1×	101 %	96 %
		242	8.33	6.95	7.28	1×	83 %	87 %
		255b	4.08	3.82	3.77	1×	94 %	92 %
		256b	7.58	7.61	7.13	1×	100 %	94 %
		257b	14.17	14.55	15.42	1×	103 %	109 %

Data availability

Data will be made available on request.

Acknowledgements

We are grateful to Liliya Snaychuk for reviewing the paper and giving viable suggestions. We would also like to thank Kimberly Savaglio for her work with the graphical abstract. We would like to thank Syed Fawaz for his contributions. The authors would like to express their sincere thanks to the Editor and the three anonymous reviewers for their constructive comments, which significantly improved the quality of the manuscript.

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Related ARS Project # 3062–51,000-056-00D.

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