

Influence of matrix effects in the study of chemical elements in biological fluids by inductively coupled plasma mass spectrometry

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Received February 6, 2023

Revised May 11, 2023

Accepted June 5, 2023

In the work, we studied the influence of matrix effects on the detection limit of individual components, and the dilution and mineralization method carried out a comparative analysis of the results of sample preparation. Inductively coupled plasma mass spectrometry studied a number of elements in solutions for analysis. It was found that the decrease in the throughput of a number of parts of the analyzer is a decrease in the diameters of the sampler and skimmer holes due to organic solvents. Two methods to reduce the influence of organic components of analyzed solutions on the results of the analysis were proposed -microwave decomposition and simple decomposition. We showed the advantage of simple dilution. However, in the analysis of biological fluids (mainly whole blood), oxidative mineralization can remove complex organic matrix and reduce biohazard. The article also considers the possibility of using an internal standard in order to obtain correct results by eliminating matrix effects. The article may be useful for an experimental analyst to assess (even increase) the degree of accuracy of the results obtained and allow doctors to restore important elements lost during dialysis in the patient's body.

Keywords: Biological fluid, inductively coupled plasma mass spectrometry, spectral and non-spectral matrix effects, internal standard.

DOI: 10.61011/TP.2023.08.57276.17-23

Introduction

Most recently, more and more attention in medicine is paid to studying the role of microelements in the human body, since an excess of microelements in the human body or their deficiency in the diet causes serious diseases [1]. Microelements are found in proteins, fats, and are involved in carbohydrate metabolism and immune reactions. Conducted studies show that an increase in the amount of macro- and microelements in soil, water and atmospheric air corresponds to increase in the level of elements in human hair and biological fluids [2].

Inductively coupled plasma mass spectrometry (ICP-MS), which is one of the medical diagnostic methods, allows you to identify a number of diseases by studying the level of microelements concentration in biological fluids of the human organism. Currently, ICP-MS occupies a leading position in the field of elemental analysis of biological objects due to the high sensitivity of the method, as well as the possibility of conducting multi-element analysis in a wide range of concentrations.

The advantages of ICP-MS — multi-element analysis, low detection limits, short analysis time, small volume of analyzed samples — make it indispensable in the analysis of biological fluids. The latter is associated, on the one hand, with the greater accessibility and productivity of the method,

and on the other hand — with a extra low detection limit of chemical elements and their isotopes, which is required when studying analytes with very low concentrations in the sample [3].

However, like any analytical method, ICP-MS has its drawbacks, such as spectral and non-spectral matrix effects that directly affect the analysis results. These effects when analyzing samples of complex composition significantly increase the lower limit of the elements being determined and complicate the correct determination of them in complex biological samples [4,5]. In recent years (10–15 years), many papers were published relating the study of options for analyzing various biological samples by ICP-MS method [6,7]. Depending on the type of sample, its composition and sample preparation many specific problems can arise in ICP-MS that lead to distortion of the results obtained. The main goal of this paper is to study and to eliminate interference during the analysis of blood and urine samples from patients with renal failure using ICP-MS method.

Thus, this paper relates to the chemical elements determination in biological samples of complex composition using ICP-MS, as well as these samples preparation using various methods (direct dilution and acid mineralization), consideration and reducing matrix effects that arise when analyzing the biological fluids.

1. Experimental conditions

1.1. Equipment

The measurements were carried out on ICP-MS from Agilent Technologies 7700 (USA) under stable operating conditions of the device [7–9].

The ICP-MS method is based on the use of an argon ICP as an ion source and a quadrupole mass spectrometer.

Fig. 1 shows a diagram of the main parts of the instrument using the ICP-MS Agilent 7700 as an example. The sample introduction system includes a peristaltic pump, an atomizer, and a spray chamber. The solution of the studied substance is sucked in by the peristaltic pump at a speed of 0.1 ml/min. An aerosol is obtained from the sample solution and passed through a two-pass spray chamber. The fine aerosol obtained from the sample (leaving the spray chamber) directly enters tube that directs the aerosol into a horizontally mounted plasma burner. The gas entering the three-cylinder plasma burner is called plasma, auxiliary gas and carrier-gas (supplied to the atomizer). A four-turn coil (inductor) is attached to the end of the burner, a high-frequency signal (27.12 MHz) is supplied to it. After the plasma is enriched with electrons in a strong high-frequency field, the collisions of argon atoms are ensured (i.e., plasma „combustion,, is supported). At the plasma center the temperature reaches the range of 8000 to 10 000 K. The aerosolized sample is instantly freed from solvent and ionized. Further, a beam of ions from the analyzed sample is formed and introduced into the mass spectrometer through a system of cones and lens. The ions then enter the quadrupole analyzer. Only ions with a specific mass-to-charge ratio (m/z) are able to pass through the center of the quadrupole under a specific combination of applied voltages.

The quadrupole provides a very fast (sawtooth) change in voltage, due to which it can scan the entire mass range (from 2 to 260 Da) in 100 ms. As a result, mass-spectra displaying the intensity vs. mass can be recorded for all elements virtually simultaneously. After passing through the quadrupole, the ions are detected by an electron multiplier.

Table 1. Experimental mode

Plasma, generator power, W	1450
Argon flow rate, l/min	1.2
Sample supply rate, l/min	1
Mass-spectrometer resolution, Da	0.2
Vacuum without plasma, Torr	$4 \cdot 10^{-4}$
Dynamic cell, gas	Helium
Time of measurement, s	0.1–0.5

Table 1 shows some ICP-MS setting data in experimental mode.

1.2. Sample preparation

The samples were mineralized in a microwave oven „Speedwave Xpert“ (Germany) with the ability to monitor the temperature, equipped with small-volume vessels for work with micro-samples. During the experiment, dispensers with a volume of 100–1000 μ l and 1–10 ml produced by Pipet4u and Eppendorf (Germany), one-use tips and polypropylene tubes with volume of 15 and 50 ml were used.

Reference solutions were prepared by serial dilution of the basic solution. Standard solutions containing 32 elements with a concentration of 10 mg/l (manufactured by High Purity Standards, USA) were used as a basis. When studying the influence of matrix elements, standard Na, K, Ca single-element solutions were used. Internal standards Rh, In, Sc, Ge (High Purity Standards, USA) were prepared with a concentration of 1 mg/l.

For samples mineralization and preparation of calibration solutions, 65% nitric acid (HNO_3) and 30% hydrogen peroxide (H_2O_2) produced by Suprapuz (Merck, Germany) were used. All solutions were diluted with deionized water (18.2 $\text{M}\Omega\cdot\text{cm}$).

The device was calibrated with calibration solutions Calibration Standards at a given volume from 1 to 50 ppb, and the corresponding straight lines were obtained at the output.

Blood and urine samples were collected in one-use polyethylene tubes from patients aged 30–40 years with renal failure who frequently undergo hemodialysis. Urine was diluted with nitric acid (concentration of HNO_3 is 0.4 ml per 20 ml of sample).

Whole blood is the most complex biological fluid in composition with a high content of both inorganic and organic substances. For blood preservation, a mixture of EDTA – HNO_3 was used. Urine and blood samples after sampling were stored for several days in a refrigerator at a temperature of 2–4°C, then analyzed, and the dialysis fluid was dissolved in 0.2% nitric acid.

Blood (0.5–1 ml) and urine (1–2 ml) samples were decomposed in the microwave oven (MW) using concentrated HNO_3 and H_2O_2 . Mineralization modes are presented in Table 2.

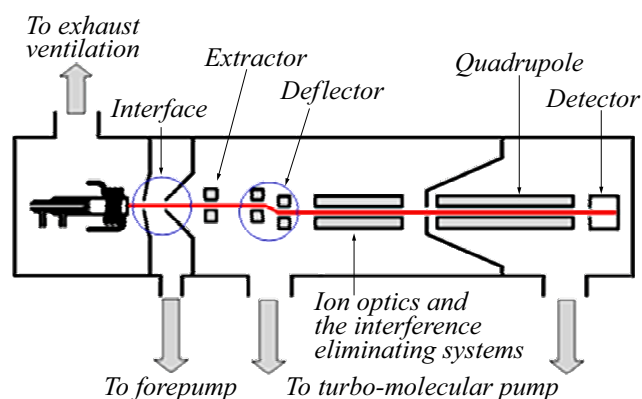


Figure 1. Diagram of ICP MS Agilent 7700.

Table 2. Mineralization mode for urine and blood samples

Step number	Temperature, °C	Time, min
1	15–80	4
2	80–160	3
3	160–190	5
4	190–210	14

The studies showed that at high temperature and with a long time of sample mineralization, some highly volatile elements evaporated, so the optimal operating mode for sample mineralization was chosen: for blood — step number 3, and for urine — 2.

Internal standards with the concentration of the corresponding element 20–50 µg/l were added to the solutions prepared for measurement.

2. Results and discussion

As it is known, blood is a substance consisting of a large number of organic compounds, and various sample preparation methods are used for its analysis by ICP-MS. However, regardless of the sample preparation methods, not all organic mass is decomposed into its components, which, in turn, causes the precipitation of salts or oxides in the ion-optical system of the mass-spectrometer, including on the surface of the cones and burner. Salts adsorbed on the surface of the cones primarily reduce the diameters of their holes, which leads to a decrease in the throughput capacity of the device [3]. Besides, excessive ingress of organic solvents (above 0.2%) can cause a significant change in the thermal characteristics of the plasma, primarily a decrease in its temperature, since additional energy is spent on the evaporation and dissociation of these substances.

Therefore, to reduce the effect of the components, two different sample preparation methods were studied: direct dilution and microwave decomposition of the analyzed samples. The direct dilution method has a number of advantages: easy sample analysis in a short time, low cost, minimal sample contamination, etc. However, this type of sample preparation can lead to failure of some parts of the mass-spectrometer, fist of all of the sampling hoses, and blockage of the cone holes. All this enhances the action of matrix effects (spectral and non-spectral) due to the components of insoluble salts [10,11]. However, despite these disadvantages, this method of sample preparation is rather often used in practice, due to the possibility of preparing in a short time many samples required in medical laboratories [12–14]. Oxidative mineralization is also widely used during the elemental analysis of biofluids [15–18], primarily whole blood [19,20], due to the ability to remove complex organic matrix and to reduce the biological hazard when working with such objects. However, this type of sample preparation also has a number of disadvantages: different software for a specific sample, long sample

preparation times (3–4 h), increased sample contamination when adding additional solutions, use of a large amount of analyte, loss of some elements, primarily volatile ones, etc.

The studies shown that during both sample preparations in dialysates the concentration of some elements with low atomic mass does not change, and the concentration of elements with higher atomic mass increases by 2–3 times. It was found that compared with the analysis of microwave decomposition with simple dilution, the concentration of copper increased by more than 2 times, of zinc by more than 1.6 times, and of strontium by 2 times (Fig. 2, a), which is explained by the presence of spectral matrix noise affecting the analysis results.

In general, spectral matrix effects most often manifest themselves during sample preparation, and therefore, in most cases, to eliminate this effect the devices equipped with collision cells located after the ion-optical system of ICP-MS are used. Collision cells are often enriched with helium (He) gas, rarely with hydrogen (H₂) or ammonia (NH₃) is used.

Spectral matrix effects can be divided into:

- 1) isobaric interferences — superposition of signals from isotopes of various elements close to each other in mass;
- 2) multiple charged atoms corresponding to the m/q value of the masses of atoms of other elements;
- 3) polyatomic (multiatom) ions, i.e. superposition of analytical signals of polyatomic ions on the signal of analytes of the same mass. The strongest spectral effects in ICP-MS are created by polyatomic (multiatom) ions, the elimination (or reduction) of which is an urgent task of mass-spectrometry.

Inductively coupled plasma contains various types of polyatomic ions that cause spectral interference:

- 1) background polyatomic ions formed exclusively by components of plasma gas, adjacent atmospheric air and water (Ar, C, H, O, N);
- 2) polyatomic ions formed only by components of the dissolved sample. First of all, this group should include oxide MO⁺, hydroxide MOH⁺ and hydride ions MH⁺ of elements included in the sample (M — element included in the analyzed sample);
- 3) polyatomic argon-containing ions formed by the components of the sample and plasma gas (argides): ArCl⁺, ArS⁺, ArF⁺, ArM⁺, etc.

For example, the formation of oxide polyatomic ions is explained by the fact that oxygen atoms coming from air and acids, used in dissolving the sample and located in the sample itself, subsequently enter the inductively coupled plasma, where at high temperature (10 000 K) combine with argon atoms or with other ions whose mass is similar to the atomic masses of analytes (hydrides, oxides, etc.). For example, for a signal ⁶³Cu the interfering interferences can be ²³Na⁴⁰Ar⁺, ⁴⁷Ti¹⁶OIFx20x E [21–23]; on ⁶⁶Zn — ³²S¹⁶O¹⁸O, ³²S¹⁷O₂⁺ [21,22]; on ⁸⁸Sr — ⁷²Ge¹⁶O⁺, ⁴⁰Ar⁴⁸Ca⁺ [22] etc.

Fig. 2 shows the concentration of elements in dialysates without and with the use of the collision cell, depending on

the sample preparation conditions. The best way to suppress spectral interference is to use helium gas as a buffer in the collision cell. The optimal helium flow rate was also determined, which was 3 ml/min. From Fig. 1, *b* it is clear that after adding helium gas to ICP-MS, the decrease in the effects of interference of several signals was obtained (Fig. 2). The essence of the method is that before the ion beam enters the mass-analyzer, they collide with helium ions, where the latter collide with large molecular ions present in the beam, and less often with metal ions with a smaller diameter, resulting in the decrease in intensity of the flow of molecular ions entering the detector.

From the experiments conducted, it was also revealed that during dialysis a large number of important elements, such as copper, zinc, iron, etc., are washed out of the human body. The release of these elements from the human body in large quantities will lead to their deficiency, which can primarily affect the weakening of the patient's immune system. Copper is an essential element for human life, and most of it is found in the heart, kidneys and liver. Copper also helps the body to absorb iron and plays an important role in energy production, and a lack of copper in the body increases the likelihood of cold-related and other diseases, brittle bones and problems with movement. With a lack of zinc in the body a neurological disorder occurs, visual acuity decreases, and the condition of the skin deteriorates [24]. The results obtained will enable doctors to restore the content of elements lost during dialysis in the body of patients, and at the same time it becomes possible to avoid side effects during hemodialysis.

Urine is a highly concentrated saline solution with a noticeable content of salts of organic acids. During work the urine was prepared in two ways. Studies shown that the results of both methods are almost the same, which once again proves the practicality of the direct dilution method. Urine samples were collected from volunteers of three different age groups in one-use polypropylene tubes, and then 65% nitric acid was added, thereby diluting them by 10–20 times with deionized water and then analyzed.

As we mentioned above, the disadvantage of direct dilution is the presence of carbon deposits on the surface of the burner, sampler and skimmer. This is because the incomplete dissolution of the components in the urine and blood creates a dielectric layer of positive ions on the surface of the cones, which, in turn, distorts the trajectory of the ions passing through these cones. To eliminate this effect, it is enough to add 1–5% oxygen gas to the argon plasma. During the experiments it became clear that by adding oxygen gas it was possible to eliminate the non-spectral matrix effect and to increase the operating time of the cones. The fact is that oxygen added to the argon plasma reacts with organic compounds, destroying them and creating compounds with a lower atomic mass, which easily pass through the holes of the sampling cones and enter the ion-optical system.

Fig. 3 shows the results of analysis of urine composition of three patients before (Fig. 3, *a*) and after (Fig. 3, *b*) oxygen

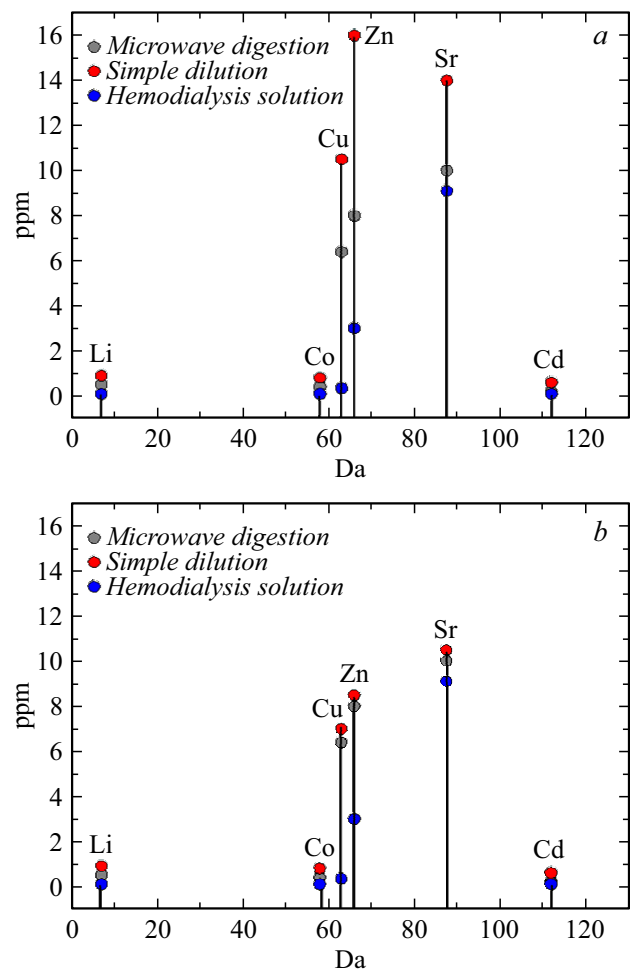


Figure 2. Concentration of elements in dialysates depending on the sample preparation conditions without (*a*) and with the use of the collision cell (*b*).

addition. The Figure shows that after the oxygen addition the concentration of elements increased. This means that the number of ions passing through the cones has increased, and the amount of organic compounds deposited on the surface of the cones decreased.

It is known that the blood is the traditional biomaterial used in biomedical studies. Several methods for blood preparation for analysis are described in the literature [10,25,26]. As you know, blood is enriched with many organic compounds, and it would be wrong to analyze it directly. Therefore, to obtain a more accurate result and to reduce the influence of non-spectral matrix effect in ICP-MS, it is recommended to analyze blood with internal standards (IS) [27]. The main criteria for IS selection are:

- 1) its absence in the analyzed sample;
- 2) mismatch of the atomic mass of the isotope with the mass of the analyte;
- 3) the proximity of its ionization potential (IP) to the IP of the analyte;
- 4) absence of its isotope in the analyzed substance, etc.

This indicates the difficulty of IS selection, especially when analyzing biological fluids. Therefore, compromise must be made.

Adding more IS can also contaminate the sample and cause spectral and mostly non-spectral interference. The authors of papers [28,29] who sometimes recommend the use of multiatom ions formed from the plasma gas or the matrix of the analyzed solution, such as Ar^{2+} , ArO^+ , N^{2+} , ClO^+ , SO^+ , MO^+ , where M is the atom of the analyzed element, a group of IS is used. Due to the fact that complete refusal from IS can lead to instrumental drift, the use of at least one IS is recommended. Since it is difficult to select one IS for analytes with different atomic masses, some authors recommend changing the device parameters by increasing the generator power and decreasing the argon flow rate through the atomizer, depending on its model, in order to obtain more accurate results [25]. From the experiments performed it became clear that after setting up the device it is possible to select one IS for analytes with different atomic masses, regardless of their physicochemical properties. Rhodium (Rh) is often chosen as IS, since it is not very common in nature and is free

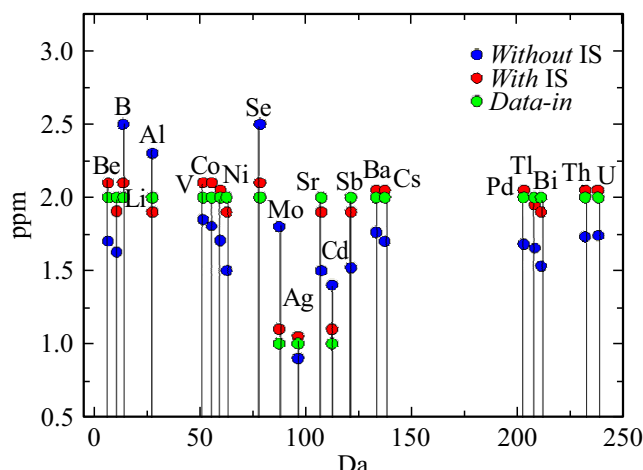


Figure 4. Measurements of elements in blood „introduced-found“ both with and without the IS (Rh) use.

from isobaric superposition. Natural rhodium consists of one stable isotope ^{103}Rh . Thus, natural rhodium is an almost isotopically pure element.

Fig. 4 shows measurements of elements in blood „introduced-found“ both with and without the IS (Rh) use. From Fig. 4 it follows that for a number of elements, such as Mn, Ag, Cd, Sb, Pb, Bi, underestimated results were obtained without IS use, which is apparently due to the manifestation of the spectral matrix effect. To verify the correctness of the results, we selected two elements as IS.

In the first case, the sodium Na element at a concentration of 100 mM was added to the sample as IS. As a result of the experiment, it was revealed that these additives did not lead to any changes in the results. In the second case, rhodium was added to the sample, and the results obtained were close to the true composition of the calibration solution. This phenomenon can be explained by the fact that the introduction of a large amount of sodium primarily changes the temperature of the plasma; in addition, sodium atoms have a low ionization potential and, when entering a high-temperature plasma, are quickly ionized, thereby increasing the electron concentration. In this case, the plasma is enriched with electrons, neutralizing through recombination ions of elements with higher ionization potential, resulting in decrease in the plasma temperature and the number of positive ions.

3. Conclusions

The analysis results showed that:

- Spectral matrix interference occurred in the analysis of biological fluids can be eliminated, or at least accounted for, by adding helium gas to the ICP-MS. This leads to approximation of the results of samples obtained both by microwave and by simple dilution;
- the leaching of certain elements (for example, copper and zinc) from the human body during hemodialysis can

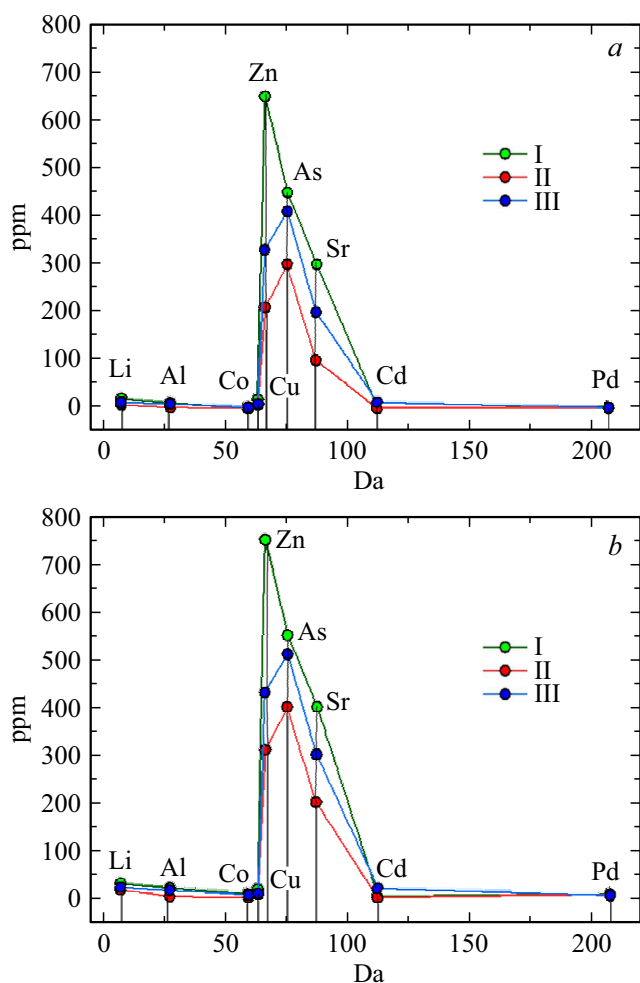


Figure 3. Results of analysis of urine composition of three patients before (a) and after (b) oxygen addition.

lead to weakened immune system. The results obtained in the paper make it possible to restore lost elements in the patients' bodies;

- urine can be analyzed without mineralization, and before measurements the sample shall be diluted by 10 times with deionized water;

- elements of organic substances deposited on the surface of the cones create a field that changes the trajectory of the ions;

- adding 1–3% oxygen to argon plasma minimizes non-spectral matrix interference;

- blood is the main biomaterial in biomedical study of organic substances, therefore, to obtain accurate results when preparing analyzed solutions, it is necessary to use IS (for example, rhodium).

Conflict of interest

The authors declare that they have no conflict of interest.

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Translated by I.Mazurov