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ABSTRACT

of the dissertation submitted for the degree of
Doctor of Physical Sciences

PHYSICAL PRINCIPLES OF THE LIMITATION RELATIVE SENSITIVITY COEFFICIENT OF ELEMENTS AND MATRIX EFFECTS IN THE ANALYSIS OF SUBSTANCES BY THE MASS SPECTROMETRIC METHOD

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GENERAL DESCRIPTION OF THE WORK

Relevance and development of the topic. Mass spectrometers solve many analytical problems; widely use spark discharge, laser beam, and secondary ion emission methods as ionization methods. Recently, many articles have been published on the mechanisms of ion formation by these ionization methods. The interest of specialists in this field has two main goals. The first is of scientific interest from studying the sequence of processes in a substance during ionization by these methods. Their effect on the measured composition of a sense (mass spectrum) proves the theory of mass spectrometry as a scientific direction. The second is experimental and improves the analytical characteristics of the mass spectrometry method, the reproducibility, and the accuracy of the results.

So far, in quantitative analysis carried out by mass spectrometry, the measured composition of a substance in most cases does not coincide with its true composition.

On the one hand, it is due to the relative yield of elements with different physical and chemical properties during ionization and the discrimination of features by mass in the analyzer and detector systems. On the other hand, the relative sensitivity coefficient (RSC) is commonly used to overcome this. For this, a substance called an "internal standard" is added to the test sample, the composition and amount of which are known in advance, and its physical and chemical properties are close to the elements of the test sample. In this case, the sample's composition is determined following the internal standard.

$$\frac{J_x}{J_{in.st.}} = K^{x}_{in.st.} \cdot \frac{N_x}{N_{in.st.}}$$

here J_x and $J_{d.st.}$ - signals registered at the output of the determined and reference element, Nx and $Nd.st.$ is the concentration of these elements in the sample, and - is RSC.

Can be determined the RSC value experimentally by analyzing samples with internal standards. However, the complexity of the homogeneous and uniform addition of internal standards to the sample and its homogeneous distribution is preferable to calculate the RSC theoretically using empirical formulas. However, since currently used, each of more than 20 empirical and semi-empirical formulas is based on a different ion formation mechanism. The systematic error in their use exceeds 100% because they can apply these empirical formulas only under the device and experiment conditions[1,2,3].

On the other hand, the composition of the samples under study is sometimes so complex and varied that the experimental determination of the RSC becomes unrealistic[4,5].

In this regard, developing new ionization models for determining the RSC, simplifying existing formulas, and, finally, studying ways to abandon it and use a "nonstandard" method of analysis is one of the urgent problems of modern mass spectrometry. All stages of the mass spectrometry method contribute to RSC formation during measurements. The most important of them are the stages of atomization (dissociation), ionization, decomposition of the resulting plasma, and the formation of ion packets.

Subsequent steps include discrimination when passing ions through the ion-optical system, separating them in a mass analyzer, and detecting. In other words, can write the expression for the

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relative sensitivity coefficient as the product of several RSC (corresponding to each stage).

Calculation of each factor separately, included in the expression of RSC, somewhat simplifies finding its general value. Therefore, we can solve each aspect theoretically. Thus, modern physics, chemistry, biology, pharmacy, geology, metallurgy, ecology, and medicine need a great need to develop susceptible devices with high resolution to minimize the impact of RSC and study the chemical and elemental composition of substances.

$$RSC_i = RSC_{dis} \cdot RSC_{ion} \cdot RSC_{rek} \cdot RSC_{an} \cdot RSC_{det}$$

On the other hand, modern medicine is showing increasing interest in the life of human activities. This interest is based on the functional effects of chemical elements on the human body since clinical specialists' and ecologists' research has been based on environmental risk assessments for many years. In this regard, one of the most critical issues is a high-precision analysis of the environment and the composition of natural food products.

The detection of inorganic toxicants in biological samples during large-scale monitoring and the study of the monotonic dependence of the number of vital elements on external factors can give a new impetus to the development of medical methods of diagnosis and treatment (basic diagnostics).

During large-scale monitoring, detects inorganic toxicants in biological samples. Furthermore, the study of the monotonic dependence of the number of vital elements on external factors gives a new impetus to the development of medical methods of diagnosis and treatment (basic diagnostics).

The main task in achieving high results in the areas mentioned above is the correct and quick analysis of the elements of a substance with a comprehensive content in various biological fluids (blood, its plasma, urine).

Modern mass spectrometers, including inductively coupled plasma mass spectrometers (İCP-MS), play an essential role in solving this problem.

Over the past 30 years, these mass spectrometers have held the leading positions in this field due to their high sensitivity, wide concentration range (10^{-8}-10^{-9}%), high resolution (10000-30000), accuracy, and precision. However, despite these advantages, like all measuring devices, İCP-MS also has drawbacks. One of the reasons limiting its technical characteristics is matrix effects (spectral and nonspectral matrix effects).[6,7,8]

Elimination of nonspectral matrix effects remains a problem. However, over the past 20-30 years, some experience has been accumulated in combating spectral matrix effects in the study of biological samples by the ICP-MS method. One of the methods in this series, as mentioned above, is to add one (or several) internal standards (IS) to the test substance, the composition and amount of which are close to the physicochemical properties of its elements. In this case, the concentration of elements in the mass spectrum is relative to the internal standard. Unfortunately, the same application of this method complicates the solution of several problems, such as choosing the correct internal standard. These features make it challenging to analyze biological samples without a specific research method on any device.

Based on the above, a promising method for eliminating the nonspectral matrix effect should be developed, which minimizes the limiting impacts of studying biological objects in any modern mass spectrometers.

Object and subject of research.

Solids (Fe, Cu, Cr, etc.), including stainless steel, marble, biological materials of healthy people, drinking and wastewater, soils, cores, stones, etc., were used as the studied objects and materials.

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- "Yenimed" clinic is provided blood and urine samples by the laboratory of the;
- In the area of the Araz River in the Imishli region were taken water and bottom sediments;
- SOCAR provided core samples.
- SEM-AZ purchased standards, acids, and model solutions.

Elemental analysis of solids (e.g., stainless steel, marble, Fe, Cu, Cr, etc.) was measured using a time-of-flight mass spectrometer with an axially symmetric electric field developed in the laboratory of high voltage physics and technology. Elemental analysis of biological fluids, including cores, water, and bottom sediments, was carried out on an ICP-MS-7700 quadrupole inductively coupled plasma mass spectrometer manufactured by Agilent Technologies, USA. Use ICP-MS ChemStation software (version G1834B) from the Autotune package to control, tune and process the results.

The goals and objectives of the study. The theoretical and experimental study of the influence of systematic errors on the relative sensitivity of elements in the mass spectrometric analysis of the elemental and isotopic composition of solids by laser, spark discharge, and secondary ion-emission ionization. Elimination of the influence of spectral and nonspectral matrix effects on the measurement results arising in the analysis of biological solutions and biologically active components by mass spectrometry with inductively coupled plasma.

The following issues were raised and attempts were made to address them to achieve this goal.

1. Study of the dependence of the relative yield of ions on their coefficient of relative sensitivity;
2. Experimental estimation of the coefficient of the relative sensitivity of mixed (additive) elements from the spectrum of metals by the method of laser, spark discharge, and second ion-emission ionization;
3. The role of recombination in the formation of the ionic composition of the plasma in the mass spectrometry analysis of solids;
4. Assessment of the influence of the spectral matrix effect on the mass spectrum when analyzing solutions using a quadrupole mass analyzer;

5. Assessment of the levels of nonspectral matrix effects when diluting biological fluids;

6. Ability to eliminate the nonspectral matrix effect by choosing the operating mode of the device;

7. The role of the internal standard in the limiting effect of the nonspectral matrix effect in different modes of operation of the mass spectrometer.

8. The role of electron concentrations in the attenuation of analytical signals in the presence of matrix elements with different primary ionization potentials in plasma;

9. Possibility of improving the accuracy of results in the exploration of oil and gas fields using the ICP-MS method;

10. Application of the ICP-MS method in environmental monitoring.

Research methods. Mass spectrometry methods with laser, spark discharge, secondary ion emission, and inductively coupled plasma ion sources.

Basic provisions of protection

1. Methods for regulating the degree of ionization and ionic composition of the plasma formed during the ionization of organic and inorganic substances by methods of laser, spark discharge, and secondary ion emission;

2. Experimental results of the dependence of the relative sensitivity of elements on their energies of atomization and ionization and their theoretical explanation;

3. The role of ionic recombination in the formation of the ionic composition of plasma using a laser (or spark discharge, secondary ion emission);

4. Dependence of the relative yield of various elements on their ionization potential during the second ion emission.

5. Results of elimination of the nonspectral matrix effect by choosing the design and operating mode of the mass spectrometer;

6. Criteria for the selection of internal standards for the analysis of biological solutions in the operating mode of the device;

7. Optimal conditions for the selection of internal standards for the analysis of biological solutions in various modes of operation of the mass spectrometer;

8. The role of electron concentrations in the attenuation of analytical signals in the presence of matrix elements with different primary ionization potentials in the analytical zone;

9. Possibility of improving the accuracy of results in the exploration of oil and gas fields using İCP-MS method;

10. Results of the method of environmental monitoring.

The scientific novelty of the research. An empirical formula is obtained to determine the relative sensitivity coefficient in the mass spectrometric analysis of solids by laser, spark discharge, and secondary ion emission methods.

The mode and parameters of the laser ionization method, which bring the value of the coefficient of the relative sensitivity of the element to a minimum, are determined.

It has been experimentally established that in the case of a standardless analysis of elements in mass spectrometers with a spark discharge and secondary ion emission, the relative ion yield is higher for elements with a low ionization potential and lower for elements with high atomization energy.

The role of recombination in the ionic composition of the resulting plasma is revealed, regardless of the ionization method (laser, spark, secondary ion emission).

Studied the conditions for forming the nonspectral matrix effect and its main features during the analysis of biological solutions in the ICP-MS.

The analysis of Agilent Technologies-7700 examined the reasons that weaken (or amplify) the analytical signal of several processes: sampling processes (sample penetration into the sprayer, aerosol formation, and transmission, etc.) and argon plasma processes (evaporation), atomization, ionization, etc.).

The spectral and nonspectral matrix effects cause a relative increase or decrease in the analytical signal, depending on changes in the operating parameters of the device (high-frequency generator power, the rate of propagation of argon passing through the injector). It has been shown that the decrease in the sensitivity of the device is mainly due to the change in the potential of the lens extractor and the velocity of the argon gas passing through the sprayer. Thus, there is a direct link between the different operating modes of the device and the criteria for selecting the internal standard.

The presence of elements with different primary ionization potentials in inductively coupled plasma determined the role of electron concentrations in the attenuation of signal intensities.

An inductively coupled plasma mass spectrometer studied the depth dependence of hydrocarbon gases and trace elements in solid rocks. It has been shown that hydrocarbon gases migrate along with the depth. Under the influence of penetrating water and soluble gases, the composition and properties of rocks change, and their partial dolomitization occurs. Studied the method of increasing the accuracy of the results in exploring oil and gas fields with the help of the technique of ICP-MS.

Noted that the use of ICP in the analysis of various objects (natural and drinking water, sediments, and soils) would further expand the range of identified elements, increase the reliability of the analysis, and solve almost any problem of elemental analysis of the environment.

Theoretical and practical significance of the research. The dissertation results showed that the mass spectrometry method could determine the composition of an element or isotope of a solid without using an internal standard (without a standard) with high accuracy. The practical value of these results lies in the fact that the composition of solids consisting of mixed elements with different physical and chemical properties, measured in this way, is close to its actual composition and is free from many complex mathematical calculations.

The main result of the dissertation is that all experimental conditions are determined for each of the lasers, spark discharges, and other methods of analysis. The parameters of the investigated ions were determined by laser, spark discharge, and the second mode of ion emission. With the help of mass spectra of hundreds of samples, tables were constructed reflecting the relative sensitivity of substances. The use of these tables proved the possibility of studying the elemental composition of some dielectric and semiconducting substances.

Universal methods have been developed for approximating a simple procedure for mass analysis of samples, regardless of their specific composition and origin, to eliminate the nonspectral matrix effect in solutions prepared by different methods. During the investigation of biological solutions, determined the possibilities of these approaches and the scope of their application. It was confirmed that any standard solutions analyzed by the proposed fitting method could be compared, regardless of when they were prepared.

Approbation and application.

Thesis materials were discussed at the following international and national conferences: XVI International Conference on Mass Spectrometry, held in Edinburgh from August 31 to September 2, 2013, in 2008 in Romania, in 2009 in Spain, in 2010 IV, V, VI, VII, International conferences on the topic "Technical and physical problems of electrical engineering" held in Iran (Tabriz), in Turkey in 2016, 2019, in Nakhchivan in 2017, as well as in 2011 are presented at the IV All-Russian the conference "Mass Spectrometry and Its Applied Problems" which took place in Moscow, were discussed at a joint seminar of the laboratories.

The results of the work are used in the project "Development of chromo to the mass-spectrometric method to improve the accuracy of forecasts in the exploration of oil and gas fields of the Scientific Fund of the State Oil Company of the Azerbaijan Republic" (No. 01 LR - ANAS).

Publications. 57 works, including 41 articles in foreign ("Science Citation Index") and republican scientific journals, conference proceedings, including 25 foreign (21 with an impact factor), 16 local journals, 2 abstracts, and 10 materials of the conference, 1 preprint was published, including 4 patents based on the main results of the dissertation.

On the topic of the dissertation in the republican ("Physics", "Energy Problems", "News") and foreign journals (“Приборы и техника эксперимента”, “Журнал технической физики”, “Письма в Журнал технической физики” “Электронная обработка материалов”, “Физика и химия обработки материалов”, “International Journal of Modern Physics B”, International Journal on

“Technical and Physical Problems of Engineering” (IJTPE)") 57 articles and conference proceedings were published.

The name of the organization in which carried out the dissertation work. Performed the dissertation was at the Institute of Physics of Azerbaijan National Academy of Sciences in the laboratory "Physics and technology of high voltages."

The structure and scope of the thesis. The dissertation consists of an introduction, 6 chapters, a conclusion, a result, and a list of references. The dissertation consists of the introduction of a text of 19,078 symbols, the first chapter with 2 tables, 15 figures, and 51,925 symbols, the second chapter with 7 tables, 21 figures, and 69,914 symbols, the third chapter with 5 tables, 1 figure and 51,709 symbols, the fourth chapter 5 tables, 10 figures and 31,496 symbols, the fifth chapter 9 tables, 17 figure, and 81,482 symbols, the sixth chapter 11 tables, 10 figure and 49,456 symbols, the conclusion of 45,114 symbols, the result consists of 4,837 symbols of the text. The total volume of work consists of 39 tables, 74 figures, and 405,011 computerized text, 294 pages, 10 appendices, and a list of used literature in 203 titles, including 12 local and 191 foreign authors.

THE CONTENT OF THE WORK

The **introduction** substantiates the relevance of the topic, formulates the purpose of the study, and provides scientific innovations, the main provisions, and their practical significance that need to protect.

Chapter 1 gives a brief overview of the analytical application of mass spectrometers with various ion sources and gives some characteristics of mass spectrometry and their development over the past 30 years.

The development of physics, chemistry, biology, medicine, and other scientific fields is closely related to the study of objects at the molecular level. This research method allows you to study the micromolecular properties of some substances. In many cases, the properties of solids, liquids, gases, and plasma are determined by their quantitative and qualitative composition, structure, and particles' interaction inside the substance. The most sensitive method for studying these characteristics is the mass spectrometry method, which occupies one of the top places in modern measuring technology from this point of view due to its comprehensive capabilities.

The investigations show that there are several advantages of the mass spectrometric method when studying the elemental composition of substances: no restrictions on the physical form of the sample: consisting of a metal, semiconductor, or dielectric (compact or powder form); simplicity of the sample preparation process; high-quality and accurate analysis of the sample; no prior sample information is required; The ability to determine about 60 elements in pure substances and 35-40 elements in complex and natural compounds during research; high relative (10^{-6} - 10^{-8} percent by weight) and absolute (10^{-7} - 10^{-15} g) sensitivity, etc.

These advantages create a wide range of possibilities for mass spectrometry analysis of natural objects and technical materials. However, recently, new, very "stringent" requirements have been presented to this method. These conditions apply to lower further the detection limit of the number of mixed elements found in substances and to increase further the repetition rate, resolution, and sensitivity of the results. For example, the recent development of modern electronics requires detecting elements with the lowest concentrations in small quantities (especially in rocks of space objects).

The use of new ionization methods based on radical improvements in mass spectrometry has played an important role. In this sense, both laser and spark discharge and secondary ion emission and, finally, inductively coupled plasma mass spectrometry have significant advantages.

We mention a mass analyzer with an axially symmetric electric field among the time-of-flight mass spectrometers. According to this theory, the calculation gives the ion-optical properties of a mass spectrometer with an axially symmetric electric field in an electric and magnetic field. In this case, after calculating the trajectory of ions of a certain mass in electric and magnetic fields perpendicular to each other, the flight time of ions moving along this trajectory is determined. The values of the electric and magnetic fields are chosen so that ions with a particular scattering in initial energy, angle, and coordinate simultaneously reach the focal plane. An example is a time-of-flight mass spectrometer with an axially symmetric electric field, developed and operating now in the Laboratory of Physics and Technology of High Voltage to determine solids' chemical and elemental composition (Fig. 1).

Fig. 1. Photo of a flight mass spectrometer with an axial-symmetric electric field

Although mass spectrometry is used in all fields of science (physics, chemistry, biology, medicine, medicine, pharmacy, metallurgy, etc.), it is also used in geophysics and geochemistry. Furthermore, the study of the age of geological objects, called the isotope method of mass spectrometry, is given a special place. Finally, the discovery of new oil and gas fields using mass spectrometry and other methods (chromate-graphic method) can improve the forecasting accuracy of these fields.

At present, mass spectrometers with a laser, spark discharge, secondary ion emission, and other ion sources are used widely in analytical practice. Inductively coupled plasma mass spectrometers (ICP-MS) have found widespread application and versatility over the past 30 years. Over the years, the technical parameters of this serial device have become an invaluable method for studying the elemental and isotopic analysis of technical, biological, and pharmaceutical substances.

Chapter II discusses the determination of the relative sensitivity coefficient (RSC), which occurs during an elemental and isotopic analysis of solids, as well as ways to reduce his calculated (or measured) value. Most of the material in this chapter is original and results from published experimental and theoretical work. At the beginning of the chapter, the physical processes that occur on the surface of solids by a bright, intense laser beam are studied, and the main parameters of the laser beam are selected. Found that by changing, several laser beam parameters (the strength of its intensity, diameter, and exposure to the sample at different angles), one can decrease the CRS of elements and the introduction of as many singly charged ions into the analyzer as possible.

As a result of the interaction of the laser beam with the surface of the sample, at high temperatures, where the local surface of the sample is solid, light quanta are absorbed by the electrons of the substance. Thus, it heats the surface of the sample. Depending on the intensity of the radiation, this interaction occurs by different mechanisms. However, the main problem in analytical experiments is determining the elemental composition of ions formed by this interaction.

Suppose the intensity of the incident laser beam is more significant than any value of q. In that case, the plasma temperature will increase due to the excitation coefficient, ionization, and absorption of atoms. In this case, the ion pair will completely absorb the incident radiation, which characterizes the processes there.

The theory makes it possible to determine the value of q with sufficient accuracy. However, of course, the experiment results provide more information that is accurate. Research has shown that high-energy ions include multi-ionized ions. The increase in single-ion ions is due to the recombination of most multi-ion ions, which accelerate when plasma propagates in a vacuum. As mentioned above, one of the factors that discriminate the relative yield of ions of mixed elements of solids is the difference in the degree of ionization of their atoms themselves and the difference in the degree of ionization of the plasma. Therefore, when calculating the relative yield of ions of the elements under study, we considered the effect of the degree of ionization of atoms (1-2-3 times) on their relative product under the action of laser radiation.

In this case, using two methods to calculate the relative yield of single ionized atoms:

- Based on the Saha-Eggert equation (the ionization process takes place in plasma);
- Based on the Saha-Langmuir equation (ionization occurs in a sample heated by a laser on the surface of the sample).

Numerous experiments show that the dependence of the relative yield of singly charged ions on the intensity of the laser beam is close to the dependence $N \sim q^{0.8}d^2$ (where d is the diameter of the laser beam). In this regard, the dependence of the relative yield of ionized atoms of various layers of stainless steel Cr, Mn, Fe, Ni, Cu on the intensity of the laser beam was investigated. In this case, the range of laser beam intensity was 10^8-10^{10} W/cm^2.

The investigation has shown that at high values of the laser beam intensity $q \sim 10^6$-10^7 W/cm^2, the number of singly charged atoms emitted from the sample is greater than the number of multiple charged particles. However, at low intensities, the relative yield of elements is small; therefore, the number of numerous charged atoms there is more significant, and multiple charged atoms of elements enter the analyzer. It violates the primary condition of the mass spectrometer (the requirement that singly charged atoms enter the analyzer). Experiments show that at low values of the intensity of laser radiation, the number of atoms formed during the evaporation of a substance is determined by its latent evaporation temperature and not by the thermal conductivity of the solid.

Thus, the study of the dynamic processes occurring in the mass of the laser-plasma shows that ionization, acceleration, or recombination prevail in the plasma formed because of the interaction of the laser beam with the target. These processes strongly affect the formation of plasma and the relative sensitivity of the mixed elements.

One of the parameters of a laser beam is its diameter. The dependence of the number of single- and multi-ionized atoms of stainless steel on the diameter (d) of the laser beam (Fig. 2) shows that z = 1.2, (3) multiply ionized atoms predominate in the mass spectrum. As the diameter of the laser beam increases, higher levels of ionized atoms appear in the range.

The results show that when the laser beam diameter is less than 0.2 mm, the RSC of the elements of this matrix is more than 90% of the singly charged atoms of the mixed elements. However, increasing the laser beam diameter to 0.2-0.8 mm increases the number of multiple ions in the plasma. The smaller the diameter of the laser beam, the more charge atoms of the elements are emitted from the sample.

The following parameter is the influence of the laser beam on the sample at different angles. In this case, the grades are calculated concerning the perpendicular plane drawn on the sample. The action of the laser beam on the sample is viewed at two angles: 20^0 and 85^0. The plasma produced by the laser beam, acting on the sample at a low angle, consists mainly of singly charged ionized atoms. As the angle increases, the atoms of the emitted elements become multiply ionized. From the data obtained from the experimental table, it is clear that the value obtained with a 10-fold pulse of the laser beam acting on the sample at an angle of 85^0 corresponds to the value of one vibration of the laser beam working at an angle of 20^0.

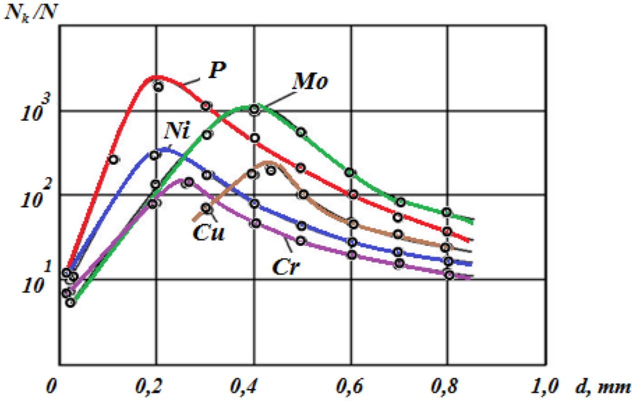


Fig 2. Dependence of normalized output of mixed ions of stainless steel on the focal diameter of the laser beam ($q = 5 \cdot 10^9$ W/sm^2)

Thus, we can conclude that by changing the laser beam parameters, i.e., at high laser intensity values, small diameter, and slight angle of incidence, it is possible to predict the plasma composition, i.e., plasma can be enriched with single atoms.

The second ionization method was secondary ion emission. In this case, taking measurements without reference analysis and Fe (iron) was adopted as an internal standard in the elements used as samples.

In addition to other methods, the secondary ion emission method (SİE) is a direct measurement method for studying the chemical composition of solids. This method, like others, has specific analytical characteristics that characterize the unambiguous relationship between the concentration of the measuring element and the recorded signal.

The experiments were carried out on relatively common isotopes of 27 pure metals using a second ion-emission mass spectrometer. In the calculations, iron was taken as an external standard. Ar^+, O^+ and Xe^+ ions were used as bombarding ions. Experiments have shown that it is more expedient to use Ar^+ ions as the first ions since the ionization potential of the Ar atom is higher than the ionization potential of the other two elements. When the sample is bombarded, it does not participate in the reaction, i.e., it does not ionize or enter the analyzer.

First of all, we should note that the second ion emission is very sensitive to structural changes in solids since it depends both on the structure of the substance and on the properties of the metal. It means that, depending on the nature of the target, the intensity of the second ions (in other words, RSC) can differ by two orders of magnitude for different elements. Based on the results of experiments, the dependence of the relative coefficient of sensitivity of elements on their atomization (dissociation) energy and ionization potential was established in the analysis of elements by the secondary ionized emission method (Fig. 3).

As can be seen from the graph, the relative ion yield is quadratic and depends on the first ionization potential (φ) RSC. The dependence of the RSC on the atomization energy shows the effect on the relative yield of secondary ions, the processes of atomization (the rate and energy of atomization). Large values of the RSC are obtained at low values of the ionization potential of the elements but high values of the atomic energy of the elements. The dependence of these elements on the sublimation energy shows the effect of the atomization energy on the relative yield of secondary ions.

Thus, during the second ion emission, the relative yield of various elements is large for ions with a low ionization potential and small for ions with high atomization energy.

Based on the data obtained during plasma ionization under the action of a spark discharge of several pure substances using a time-of-flight mass spectrometer with an axially symmetric electric field, it was possible to calculate the RSC of a mixed element without using an internal standard. Furthermore, it showed that the amount of substance released from the sample periodically depends on the atomic mass of the element. Most likely, this is due to an increase in the atomic masses of the elements of the periodic table and a decrease in the atomization energy.

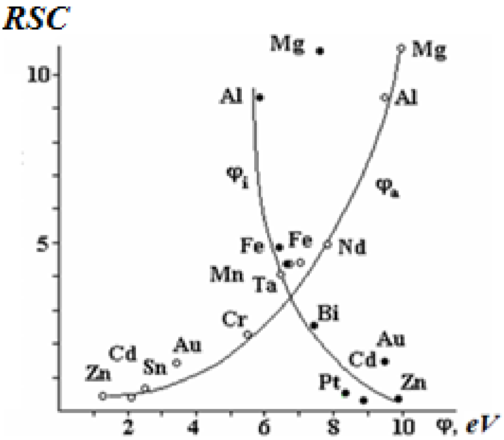


Fig. 3. Dependence of the relative output of ions on their -single ionization potential and -atomation (dissociation) energy

Experiments have also shown that the degree of ionization of the main element (matrix) depends on the relative concentration of the mixtures held in it. Similar experiments were carried out mainly on copper, aluminum, and steel samples.

This chapter also presents the results of experimental studies of ion recombination in a vacuum-dispersed plasma on the CRS of elements.

Found that electrons and ions undergo recombination after the complete expansion of the plasma. However, the recombination rate is reduced drastically due to decreased particle density and load. At a particular time, $t = 4^{-5} \cdot 10^{-5}$ sec. after the termination of inelastic processes, the plasma temperature continues to decrease (Fig. 4). Thus, when a plasma is distributed completely in a vacuum, it becomes thermodynamically unbalanced. Calculations show that in this case the recombination process can be specified with the following condition:

$$l_p(z)=t_p(z)\sqrt{T_0/M}$$

here, $l_p\ (z)$ -recombination distance, T_0-plasma initial temperature, t_p(z) -plasma departure time, M - molar mass of element

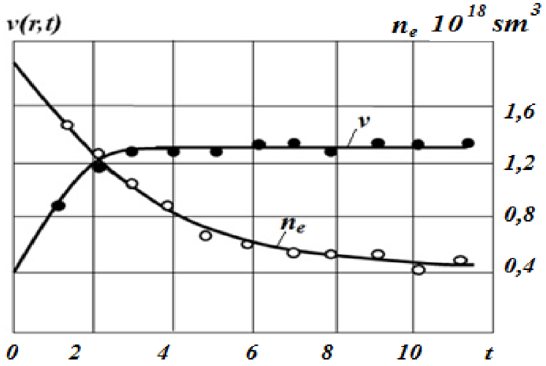


Figure 4. Changes in the velocity and concentration of electrons masι during the dispersion of plasma in vacuum
$n = 10^{19}\ sm^{-3}$; $R_0 = 3 \cdot 10^{-2}$ sm; $T_0 = 10^5$ K.

The time dependence of the ratio of the number of double atoms to the number of singly charged atoms (Fig. 5) shows that the temperature nonlinearly depends on the second ionization potential at 5 eV. With an increase in time, the conversion rate of doubly charged ions into singly charged ions decreases. The ions of certain elements do not recombine from a particular moment, while most of the ions continue to ionize. Thus, the kinetic energy of electrons is converted into potential, that is, ionization.

Thus, it is necessary to calculate complex mathematical models of an expanding plasma bunch or to create a simplified expansion model for a multicomponent plasma. There are two ways to do this. First, singly and can determine doubly charged ions (with the spectrometric ratio of the recorded mass) from the initial density and temperature of the plasma. Secondly, can determine the mixed composition of the sample (using mass spectrometry analysis) from the composition z = 1.2 multiple ions.

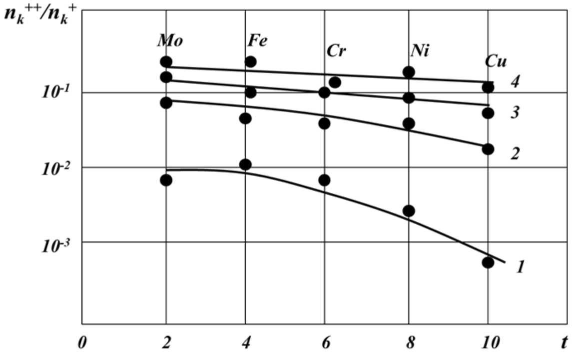


Figure 5. Time dependence of the ratio of residual double-charged ions to single-charged ions during the distribution of plasma mass with radius $R_0 = 3 \cdot 10^{-3}$ sm; $N_0 = 10^{19}$ sm^{-3}. 1-T_0=5·10^{4}K; 2 -10·10^4 K; 3 - 15·10^4 K; 4 - 20·10^4 K.

The study showed that experimental measurement (or rather, calculation) of RSC is a challenging task since the relative sensitivity of elements is influenced by all stages of the experiment, regardless of the method of ionization of the solid. First, the steps combine the processes of atomization, ionization, and recombination of various elements, and secondly, the separation of ions, the movement of ions in the optical system, and discrimination in the detector. Consequently, RSC should be considered as the interaction of various processes. In our opinion, the search for a solution to the CRM in this way, both theoretically and practically, simplifies the problem. Because for each type of discrimination, there is a specific physical process that can be studied.

Chapter III is based on the application of inductively coupled plasma mass spectrometry (ICP-MS) in medicine, biology, pharmaceuticals, geology, and other environmental fields. This analysis method has been applied successfully in these areas for over 30 years.

Inductively Coupled Plasma Mass Spectrometry (İCP-MS) has been used long to analyze biological objects and clinical drug preparation laboratories. At that time, the main reason for limiting the widespread use of this method was its high cost and complexity. Today ICP-MS occupies one of the leading positions in this area. The main reason for maintaining this position for a long time is, on the one hand, the preservation of its advantages as a mass spectrometer, and, on the other hand, a decrease in its cost due to the expansion of its production. The reason for the widespread use of this method lies in its following advantages over other methods:

- a minimal lower limit for the detection of chemical elements and their isotopes (nq/l, sometimes pc/l);
- the possibility of multi-element analysis;
- having a comprehensive (10 collections) dynamic range of masses;
- having a minimal setting limit for the measurement background (0-10 pulses/sec);
- the relative simplicity of the spectra and the ease of interpretation of the results obtained (explanation);
- minimal volume and mass of the analyzed substances: (~ 0.1 ml and ~ 0.1 mg).

However, ICP-MS, like other instrumental methods, is not without drawbacks that limit its use. The most important of these disadvantages are spectral and nonspectral matrix effects. The matrix refers to the primary substance in which the investigated component (analyte) is dissolved, and the analyte relates to the mixed ingredients. It is important to note that these effects on test results depend on the sample type and how it is prepared before analysis.

This chapter also focuses on the preparation conditions for biological solutions (blood and urine) and explores overcoming its nonspectral matrix effect. However, in the cited scientific articles, proposals for solving this problem are not systematized. The criteria for choosing an internal standard (IS), the similarity of the atomic masses of the analyte and IS, and the primary ionization potential (φ_i^+), which play a decisive role in overcoming these disadvantages, is not substantiated.

In this regard, this chapter discusses three main reasons for the nonspectral matrix effect: the action of the acid, the role of the elements participating in the reaction (accompanying), and the presence of organic matter. In work, it was investigated and noted the presence of these elements, the complexity of the mechanisms of their occurrence, and alternative ways of eliminating their effect were shown (mainly by changing the operating mode of the device). Therefore, this chapter discusses the ISP method in detail. In this regard, a comprehensive study of both spectral and nonspectral matrix effects was chosen as a standard internal method to eliminate the causes that distort the technical characteristics of the device. Showed that such mechanisms as the recombination of matrix and analyte ions in argon plasma and the positive space charge created by ions in a high vacuum contradict each other.

The influence of the components of the analyzed solutions on the intensity of the signals received at the output was evaluated using the following expression:

$$\gamma(An)_{Mt} = S(An^+)_{Mt}/S(An^+)_{m\ddot{u}q} \cdot 100\%$$

$\gamma(An)_{Mt}$ - calculation of the change in the modulus of the analyte signal intensity in the studied matrix relative to the comparative matrix:

$S(An^+)_{Mt} -$ the intensity of the analyte signals in the matrix under study; $S(An^+)_{m\ddot{u}q}$ −the intensity of the signals of the comparative matrix;

A medium in which all graduated solutions are prepared with a concentration of 1% by volume is meant by a comparison matrix.

As already noted, the nonspectral matrix effect is quite complex. This effect is due to the variety of its appearance, the type of the mechanism of action, and the variety of device design and its adjustment methods. From the above, we can conclude that the influence of the matrix effect cannot be predicted, and even by adjusting the device, it is impossible to reduce it ultimately. Therefore, it is always necessary to look for new ways to minimize this effect. If it is not needed to select a particular matrix during sorting, then the most tried and tested method is the internal standard method mentioned above. However, studies show that the criterion for choosing an internal standard or the ability to select only one standard (without using mathematical equations) is also a big question.

In other words, when working with biological objects, it is necessary to develop any method to obtain the correct result. It makes it possible to create new, most simple forms of mass analysis of biological samples of various compositions.

The end of the chapter also contains a description of the reagents, materials, instruments, and research methods used in work.

The work used a solvent HNO_3 (65%) produced by Merck from deionized water with a specific resistance of 18.0 MΩ · cm; composition of a standard multi-element solution: *Li, Be, B, Na, Mg, Al, P, K, Ca, Sc, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, As, Pb, Sr used, Y, Cd, Jn, Cs, Ba, Kc, Th*, ICP-MS Multi-Element Standard, and High-Purity *Bi*, *Hg*, *Rh*, *La*, *Sn*, and *Ge* single element standard elements. Prepared essential working solutions were from 2% HNO_3 solutions, for the preparation and storage of solutions, used test polyethylene and polypropylene containers of 10 and 40 ml. The solution was soaked in 10% HNO_3 4-5 days before the experiment and washed in deionized water during the investigation.

The experiments were performed on an ICP-MS-7700 series instrument manufactured by Agilent Technologies. In this case, the operating mode of the device is selected as follows: the power of the high-frequency generator W = 1400-1500W; the flow rate of the plasma-forming gas Ar 1.3 l/min; auxiliary gas (He) speed 0.9 l/min, argon flow rate in the nebulizer 0.95 l/min; sample use rate no more than 0.8 ml/min. The level of oxide ions in each measurement did not exceed 3% CeO^+/Ce.

Chapter IV. The significance of the levels of vital or toxic elements in biological objects, the change in their amount in the human body is of great interest in modern medicine. However, as shown in the third chapter of the study of nonspectral matrix effects that occur during the analysis of ICP-MS, somewhat complicate this work. Therefore, this chapter is devoted to exploring ways to eliminate these distortions quickly by measuring the technique and instrumental tuning of the device in the processing of analytical signals. In this case, the elements *J, Mg, Ni, Cu, Zn, Ga, As, Se, S, Sb, Pt,* and *Pb* were taken as analytes. We chose these elements because they belong to a set of elements currently being studied in medicine and pharmacy.

This chapter presents simple techniques for eliminating nonspectral matrix effects in the mass spectrometry analysis of biological solutions. This type of experiment shows the influence of the spectral effects of the matrix on the intensity of the analytical signals. Solvents were selected to prepare solutions and, based on the data obtained, determined the sources of discrepancies. Deviations were observed in the maximum sensitivity of the mass spectrometer in the "standard" mode (generator power 1450 W, argon flow rate in the injector 1.2 l/min, the potential on the extractor lens -200 V, and Rh was adopted as an internal standard).

The effect of spectral interference created by matrix components in solutions showed that when using Ga and Zn in quadrupole mass spectrometers without collision chambers, the interferent's $^{40}\mathrm{Ar}^{23}\mathrm{Na}^{+}$, $^{138}\mathrm{Ba}^{++}$, and $^{40}\mathrm{Ar}^{37}\mathrm{Cl}^{+}$ distorted the analytical signals of these isotopes (Figure 6).

Signals generated around masses 69 a.m.u. in deionized water or urine solution belong to the double ionized isotopes $^{138}\mathrm{Ba}^{++}$, $^{138}\mathrm{La}^{++}$ and $^{138}\mathrm{Ce}^{++}$. However, this high-resolution mass spectrometer cannot determine which doubly ionized isotopes belong to the spectral background.

The elements *La* and *Ce* have a poor concentration compared to *Ba*. Can say that the ion generating the background signal is the element $^{138}\mathrm{Ba}^{++}$. Can conclude from the studies that after adding *He* gas to the collision chamber of a quadrupole mass spectrometer, the determination limit of the Ga element (in biological solutions, blood, and urine) is determined not by the element itself in the solution or the number of reagents used. It will be determined by the background signal generated by the matrix components.

This chapter also discusses the dissolution of biological solutions in various solvents (e.g., EDS, Triton X-100, 1-butanol). At the first stage of the experiments, prepared artificial model solutions from 4 solvents; their content was 100 µg/l *J, Mg, Ni, Cu, Zn, Ga, As, Se, Sb, Pt, Pb*, as well as 20 µg/l Rh as an internal standard (İS). These solvents include:

I - 1 vol.% Triton + 1 vol.% HNO_3
II - 1 vol.% Triton + 1 g / l EDS + 1 vol.% HNO_3
III - 1 vol.% Triton + 1 vol.% 1- butane + 1 vol.% HNO_3
IV - 1 vol.% Triton +1 g / l EDS + 1 vol.% 1- butane +1 vol.% HNO_3

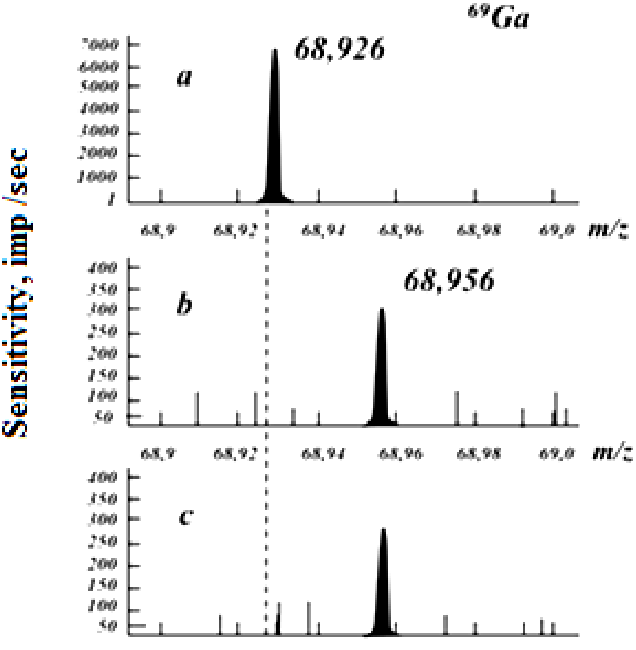


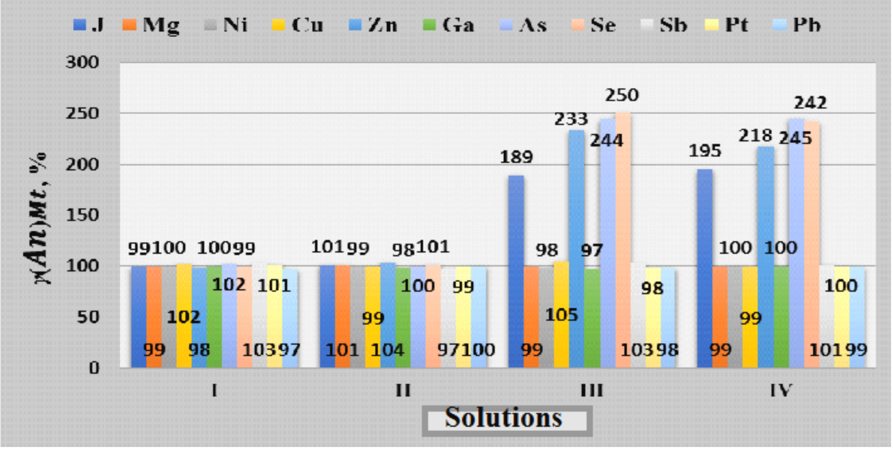
Figure 6. Mass spectra of the element Ga with 69 isotopes in 3 different samples: a) 1 µg / l Ga in standard solution, b) in deionized water and c) in 50 times diluted urine

In this case, choosing the element Rh as İS is not present in the solution and is not subject to spectral interference.

It has been shown that each solvent has a different effect on the sample. For example, the presence of 1-butanol in solution doubles the analytical signals of some analytes (J, As, Zn, Se) because the carbon ion carries an electron charge from analytes with a low ionization potential (Table 1).

Table 1

Values of quantity $\gamma(An)_{Mt}$for elements studied in solvents of different composition



In connection with the results obtained in this chapter of the dissertation, the main attention is paid to the interpretation of several approaches to eliminating the influence of the nonspectral matrix effect on the experimental results. These approaches include such proposals as, for example, the choice of operating modes of the device, the proximity of the internal standard to the corresponding physical properties of its atomic mass and ionization potential, the choice of ion optics, the choice of the rate of transfer of the sample into the plasma, etc.

It should note that the model solutions were dissolved mainly in two matrices: 5% HCl, 15% HNO_3. Furthermore, it should add no internal standard to the selected solutions. The reason was to evaluate the role of the device in minimizing the negative impact on the test results only by changing the parameters of the device. For ease of use, the elements of the model, soluble in the selected matrices, are divided into two groups: elements with a low ionization potential (φ<9.0 eV) *Mg, Ni, Cu, Ga*, and *Pb* and elements with a relatively high ionization potential (φ>9,0eV). eV) *J, Zn, As, Se, Sb*.

All parameters were left in the "standard" mode and changed. Only the generator power *As* expected, a decrease in the intensity of analyte signals was observed with a reduction in plasma temperature at generator values below 1430 W under the accepted optimal sensitivity value.

In this case, in the entire power range from 1430 W to 950 W, the intensities of elements begin to decrease gradually in solutions of 5 volumes of HCl and 15 volumes of HNO_3. Therefore, at the lower limit of the generator power (at the level of 950 W) in both solutions, the signal intensity of the elements decreases by 10-20 times. When the generator power increases to 1550 W, they do not increase (Figure 7).

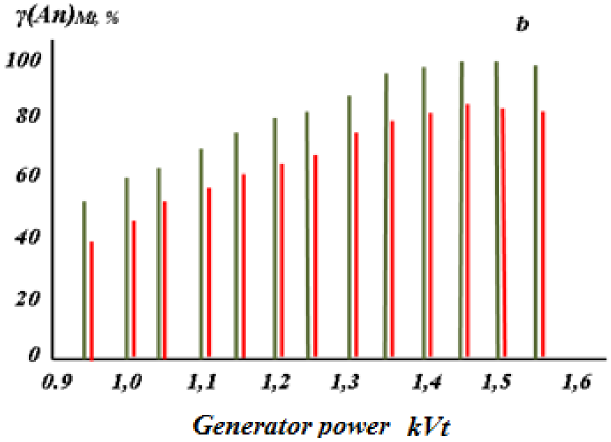


Figure 7. Dependence of $\gamma(An)_{Mt}$ values for generator power for φ_i+ <9.0 eV (blue) and φ_i + > 9.0 eV (red) elements 15 volumes % HNO_3 solution (n = 3)

The possibility of eliminating nonspectral effects by changing this parameter corresponds to the maximum value, which characterizes the depth of this effect regardless of the nature of the solution matrix, but only at high values of the generator power. Most likely, this is due to both an increase in the plasma temperature and the transfer of plasma energy from the periphery to the center. In this case, can change the elements to the ionization potential (φ^+) in parallel for the dependence $\gamma(An)_{Mt}= f$ (W) for both matrices and the first approximation for both groups of elements.

Considering this, we can say that the power of the "stable" generator was adopted at 1430 W since there is no difference between the sensitivity of the accompanying components in the range of 1430-1550 W and at high values of the generator power, the number of double ionized ions increases.

Nonspectral matrix effects for all elements do not eliminate by simply changing the generator power. Therefore, we decided to change the flow rate of argon gas supplied to the nebulizer at the next stage, keeping all the mass spectrometer parameters constant. To prove that a decrease in this parameter eliminates distortions, both a decrease and an increase in argon gas consumption are considered (by the way, confirmed this method in the literature).

The study results show that the device's sensitivity changes almost the same when changing the flow rate of gaseous argon for both matrices of the analyzed solution (i.e., HCl and HNO_3). The possibility of relative compensation for nonspectral effects is associated with a decrease in the flow rate of argon gas passing through the injector (Figure 8).

In this case, for each component of the matrix, there is a value of, at which the discrimination of elements concerning φ_i^+ is eliminated. This value corresponds to an argon flow rate of 1.00l/min in 5 volumes of HCl and 15 volumes of HNO_3 solutions. Most likely, this is due to the small number of matrix components in the plasma and an increase in its temperature, on the one hand, and the fact that the sample has been in the high-temperature zone for a long time. On the other hand, this is due to the more efficient ionization of elements with a high ionization potential (φ_i^+) in the analysis of complex solutions and a decrease in ion-electron recombination of analytes in the presence of easily ionized elements.

As in the previous study, one of the other parameters that play a crucial role in minimizing the effects of a nonspectral matrix is the potential of the lens extractor. The study results showed that a change in the potential of -100 and -200 V in a given range did not affect the value of all elements, regardless of the matrix. However, when the potential of the lens extractor changes from 0 to -50 V, the signal intensity of the elements increases, especially for the elements *Ni* and *As*, where the most significant change in intensity dependence is observed (Figure 9).

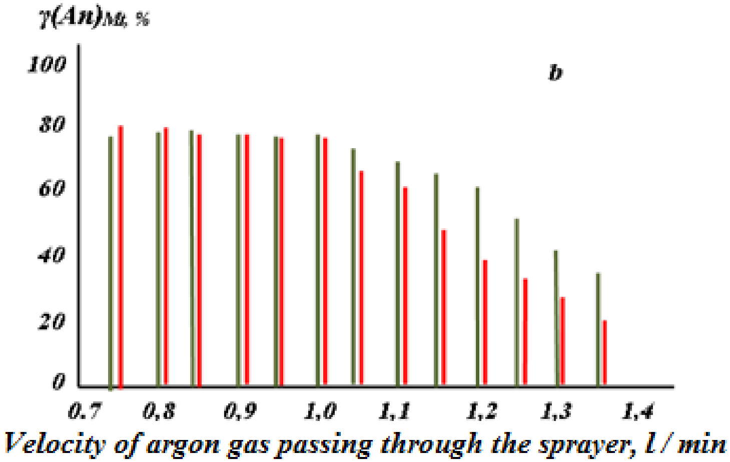


Figure 8. Dependence of $\gamma(An)_{Mt}$on the velocity of argon gas for the elements φ_i^+ <9.0 eV and φ_i^+ > 9.0 eV in a solution of 15 vol.% HNO_3 at a constant value of voltage and other parameters.

As noted in Chapter III of the dissertation, the internal standards are those elements close to the analyte's atomic mass and the ionization potential (satisfying all general requirements). However, some researchers disagree. Therefore, a wide range of elements with different ionization potentials (Be, Co, As, Rh, Bi) was used as an internal standard in matrices. At the same time, the physical properties of the fiber should not be overlooked since the ionization potential of the element comes to the fore. Research shows that it is much easier to select aircraft in "stable" mode. In this case, only one element can be selected as a İS (regardless of the ionization potential).

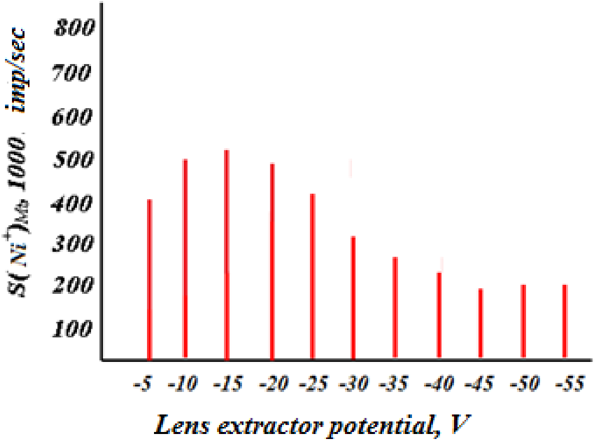


Fig. 9. Dependence of the intensity of ^{64}Cu (blue) absolute signals on the lens-extractor potential in a 15% volume HNO$_3$ solution (n = 3)

Experiments show that in the "standard" mode of the mass spectrometer, it is incorrect to select İS by masses, since if the pack of the İS is close to the mass of the analyte, isobaric spectral interference will occur, which, in turn, will distort the analytical signals. Therefore, it is more expedient to choose an internal standard close to the ionization potential of the analyte. However, in the "stable" mode, the internal standard has selected any element, regardless of ionization potential or atomic mass, and does not distort the analytical signals of the elements.

In general, the influence of the components of the analyzed solvents on the output signals is determined not only by the processes occurring in the plasma (evaporation, atomization, ionization) but also by the processes associated with the introduction of the sample into the system. (ingress the sample into the nebulizer, formation, and aerosol transportation). Therefore, it is necessary to consider the last process, which does not depend on the physicochemical properties of the analytes, since it directly depends on the physical properties (viscosity, surface tension, density, and variability) of the analyzed solvents.

The main disadvantages of natural disintegration of biological solutions include blockage of the spray outlet, injector, sampler, and skimmer openings. One of the most frequent cases in our experiments is forming a dielectric layer on interface cones due to the incomplete combustion of organic matter in solution. After analyzing 30-35 biological fluids, a sufficient carbon layer formed on the skimmer (Fig. 10, b). We decided to add 1-5% O_2 to argon to solve this problem.

Studies have shown that it is enough to add 1-2% oxygen to argon to extend the life of the skimmer and sampler (Fig. 10, a).

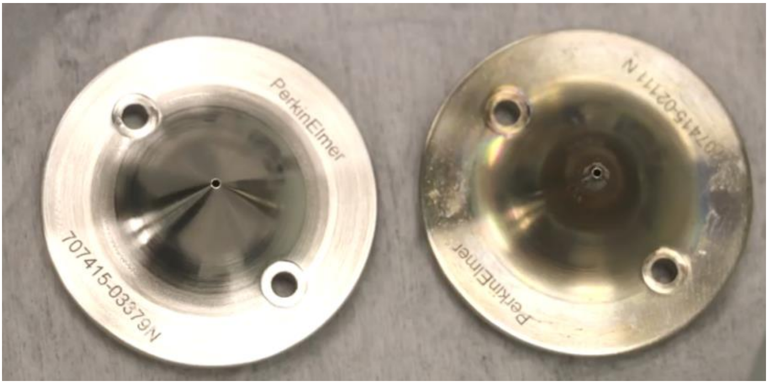


Fig. 10. Conditions of skimmer and sampler after analysis of 25-30 blood samples with (a) addition of 2% oxygen and (b) failure

In this case, the gas flow composition does not affect either the intensity of the output signals, the value of, or the formation of oxide ions.

In other words, when looking for "stable" device parameters, we saw that by decreasing the velocity of argon gas through the nebulizer, nonspectral effects are minimized. Furthermore, reducing the Ar velocity reduces the matrix effect and eliminates element discrimination according to φ+. In this case, the primary mechanism influencing these processes is, on the one hand, a decrease in the ionization effect of elements and an increase in ion-electron recombination. In addition, research shows that one of the critical factors in increasing device sensitivity is to optimize the lens extractor's potential further.

Chapter V explored the theoretical and practical foundations of the formation of doubly charged ions (M^{++}) of several elements using inductively coupled plasma mass spectrometry. The efficiency of the building of singly and doubly charged ions with the lowest values of the second ionization potential was calculated using the field equation and thermodynamic modeling method. The experimental and theoretical results of the obtained inductively coupled plasma mass spectrometry (ICP-MS) were compared. In addition, the results of calculations and their application in ICP-MS to predict the efficiency of the formation of M^{++} ions showed that the reasons for nonspectral matrix effects in the analysis of biological solutions are caused by organic substances included in the sample, as well as the content of acid and salt in them. Therefore, it determined that should select the first ionization potential of the internal standard based on the proximity to the ionization potential of the element.

Experiments have shown that the increase in the M^{++}/M^{+} ratio is the pinch discharge between the plasma and the grounded structures of the device. In this case, an increase in the plasma potential occurs due to the argon flow rate passing through the injector chamber. Therefore, in our study, we considered the dependence of the M^{++}/M^{+} ratio on the flow rate of gaseous argon. Figure 11 shows this relationship for four key elements.

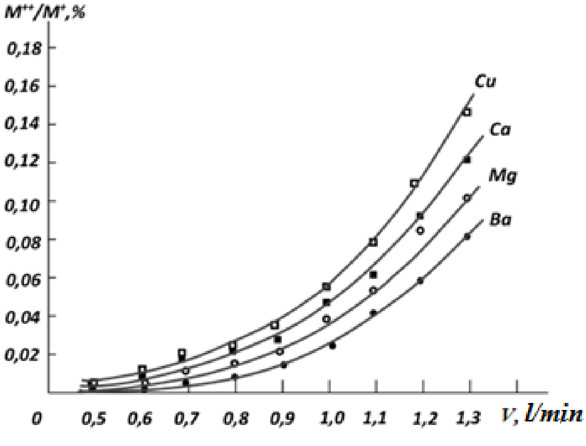


Figure 11. Dependence of the M^{++}/M^{+}ratio on the flow velocity of the argon stream T = 8000K, n = 0.64 • 1021 m^{-3}

It can see from the graph that the efficiency of the formation of double ions (M^{++}/M^{+}) almost doubles with an increase in the argon flow rate to 0.6-1.0 l / min. It should note that the theoretical value of the M^{++}/M^{+} ratio obtained from the field equation is much higher than the value obtained experimentally.

Thus, a study of the physicochemical characteristics of doubly ionized elements shows that their ionization potentials are less than argon's first ionization potential. These properties are suitable for *Be, Mg, Ca, Cu, Sr, Ba, Pb*, and all rare earth. Therefore, the first thing to pay attention to is the presence of these elements in the solution.

Studied the influence of nonspectral matrix effects on the results of the analysis of biological fluids and showed that the dependence of this effect on the salts and acidity of the matrix and the operating mode of the device is additive.

Investigated the possibility of developing a standard-free analysis of solids by the mass spectrometry method and showed the influence of each stage of laser-plasma expansion on the formation of the coefficients of the relative sensitivity of the sample elements theoretically and experimentally. It was determined that the construction of ions and the stages of their registration play a vital role in the formation of the relative sensitivity coefficient, and it was proposed to separate the processes of dissociation and ionization from each other both in time (or) and in space (Figure 12).

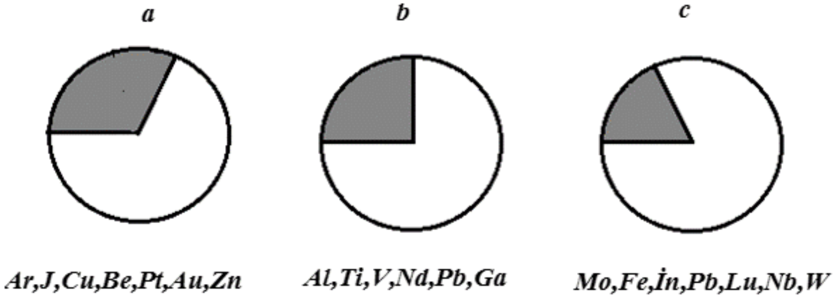


Figure 12. Nomograms of energies of elements with close ionization potential:
a – $\varphi_a+\varphi_i$=20 – 30 eV; b – 20 - 25 eV; c – 20 - 22 eV

In fig. 12 shows a nomogram of elements divided into three groups (a, b, c), close to each other in the sum of the energies of dissociation and ionization. The fields of the circles are the energy W0 received by each atom; the shaded parts are the energy spent on ionization and atomization), and not the shady part is the residual energy of the particle spent on the kinetic energy of the ion. The figure shows that the residual energy of the ions of the first group (a) after the expansion of the plasma is 0.8 W_0, the second (b) -0.75 W_0, and the third (c) - 0.6 W_0.

It shows that ions have 30% energy dissipated when they leave the ion source, resulting in discrimination in the ion-optical path and the analyzer. This process shows itself in mass spectrometers (such as flight time analyzers, radiofrequency and quadruple analyzers), where ion energy plays a crucial role. From this, we can draw the correct conclusion: to overcome these disadvantages, and it is necessary to separate the processes generated by dissociation, ionization, and recombination.

The effect of ionization events on analyte signals was taken into account by inductively coupled plasma mass spectrometry with a high-temperature ion source. The dependence of the decay rate of ion signals on the concentration of electrons for matrix ions and mixed elements is calculated and experimentally determined. Found that the degree of signal attenuation depends on the concentration of electrons in the analytical zone in the presence of matrix elements with different primary ionization potentials. The experimental results showed that weakening the analytical signals obtained at the output is the ion-electron recombination of ions in the plasma (both matrix and analyte).

To study the influence of various elements on the electron concentration in the analytical zone, the composition of more than 30 matrix elements with different ionization potentials (φ_i^+) was calculated at an ICP plasma temperature of 7500 K and its equilibrium state. Performed the calculation was for the average $M(H_2O)/M(Ar)$ molar ratio of water vapor and argon in the mixture. Figure 13 shows the dependence of the ionization probability of atoms on their ionization potential. In this graph, single ionization can be divided into three groups depending on the ionization efficiency: light ionized $\left(\varphi_i^+(M_e) < 8eV\right), \delta(M_e) > 90\%$), medium ionized $\left(\varphi_i^+(M_e) = 8 - 12{,}2eV\right),\ \delta(M_e) > 10 - 20\%$ and hard ionized elements $\left(\varphi_i^+(M_e) > 12{,}2eV\right), \delta(M_e) > 10\%$).

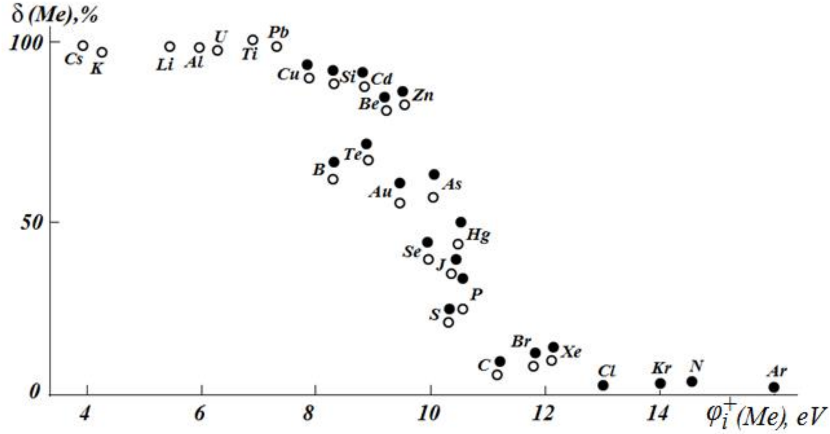


Fig. 13. Temperature $T_e = 7500K$ concentration $n_e = 10^{15} sm^{-3}$ The dependence of the degree of ionization in plasma on the single ionization potential of the elements $\varphi_i^+(Me)$.

The relative scattering of points on the graph depends on the density of electrons arising from the ionization of matrix elements, both on their ionization potential and the ratio of the sum of states of their ions and atoms.

This chapter also discusses the efficiency of doubly charged ion production in an inductively coupled plasma. Showed that the formation mechanism of doubly charged ions depends on many experimental factors, including the change in the plasma temperature in the analytical zone. However, during the experiment, the efficiency of the formation mechanism of M^{++} ions does not depend on the potential of secondary ionization of atoms of elements (Figure 14).

The processes of ion formation during plasma expansion were studied using inductively coupled plasma mass spectrometers (ICP-MS). The relative sensitivity coefficients of more than 20 elements were calculated at a plasma temperature of 5-25 eV, which showed that the density and temperature of the electron and ion gas in inductively coupled plasma are the same. Furthermore, it is shown that after the recombination of multiply charged ions in the plasma, a nonthermodynamic equilibrium is formed, which depends on the ratio of the degree of ionization and the length of the recombination distance of ions to the charge to the plasma size l_{rec}/R_0. In the case of the model under consideration, when expanding into plasma into a vacuum, it can be characterized by the following parameters $n_e \leq 10^{20} sm^{-3}$, $T_e \geq 5 - 10\ eV$; $R_0 < 10^{-2} sm$, and l_{ei}" R_0.

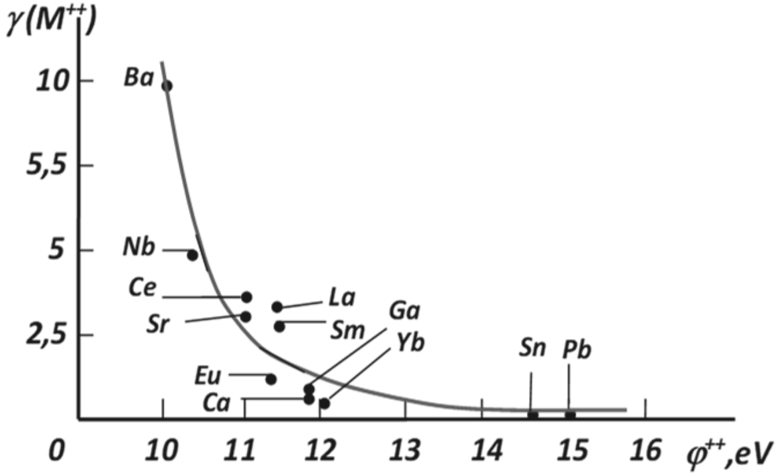


Figure 14. The dependence of the calculated ionization efficiency of double-charged ions on the double ionization potential.

It means that electrons and ions exchange energy through mutual heat exchange, during which the temperature of the plasma is not equal through energy exchange. It means that the electronic and ionic components of the plasma mass are subjected repeatedly to energy exchange during the time required for heating the plasma bunch due to thermal conductivity, and the contribution of thermal conductivity to the temperature equalization process is relatively small.

Table 2 shows the theoretical and experimental values of CRS calculated by the formula $NHƏ_{DS}^{x} = exp\ exp\left(-\frac{\varphi_x^+ - \varphi_{DS}^+}{kT_u}\right) \cdot \left(\frac{m_x}{m_{DS}}\right)^{\gamma}$

We measured the signals of more than 30 single-element analytes of the same concentration (10 µg/l) to calculate the relative sensitivity coefficient.

As can be seen from Table 2, the relative error of the experimental values of the RSC significantly differs from the theoretical value (~ 0.5). The average value of the dependence of this difference lg (RSC) = $f(\varphi_i^+)_x$ is equal to 0.52. It shows that in theoretical calculations, the chosen model temperature ($T_u = 70000$ K) is higher than the actual temperature of the ICP-MS (10,000 K).

Table 2

Calculated RSC and experimental values of RSC Relative sensitivity of RSC and various elements $\Delta = \left|\frac{CRS^{tәc} - CRS^{nәz}}{CRS^{tәc}}\right|$

Element	CRS^{theo}	CRS^{pr}	Δ	Element	CRS^{theo}	CRS^{pr}	Δ
Li	1,00	0,99	0,01	**Co**	0,97	1,10	0,37
Be	0,86	0,18	3,78	**Ni**	0,96	0,90	0,07
Na	1,00	1,20	1,70	**Zn**	0,85	0,50	0,70
Mg	0,95	1,00	0,50	**As**	0,66	0,10	5,60
Al	1,00	1,10	0,09	**Se**	0,67	0,10	5,70
Cr	1,00	1,20	0,17	**Sr**	1,00	1,20	0,17
Mn	0,99	1,20	0,25	**Nb**	1,00	0,80	0,25
Fe	0,99	1,20	0,25	**Mo**	1,00	0,90	0,11
Rh	0,97	1,10	0,12	**Nd**	1,00	1,00	0,00
Sb	0,89	0,60	0,49	**Pb**	0,99	0,90	0,10
Ag	0,98	1,10	0,11	**Lu**	0,99	1,00	0,10

In the next experiment, we studied the effect of electron density on the analytical signals of elements in ICP-MS (Fig. 15).

It is shown that with an increase in the electron concentration, the amplitudes of the intensities of large-mass elements (Cd, In, Ba, Pb) weaken more than those of low-mass elements (Li, Ca, Co, Ni, Cu, Sr). Furthermore, experiments show that the electron density depends on the degree of ionization of argon in the absence of matrix components at a certain (specific) temperature.

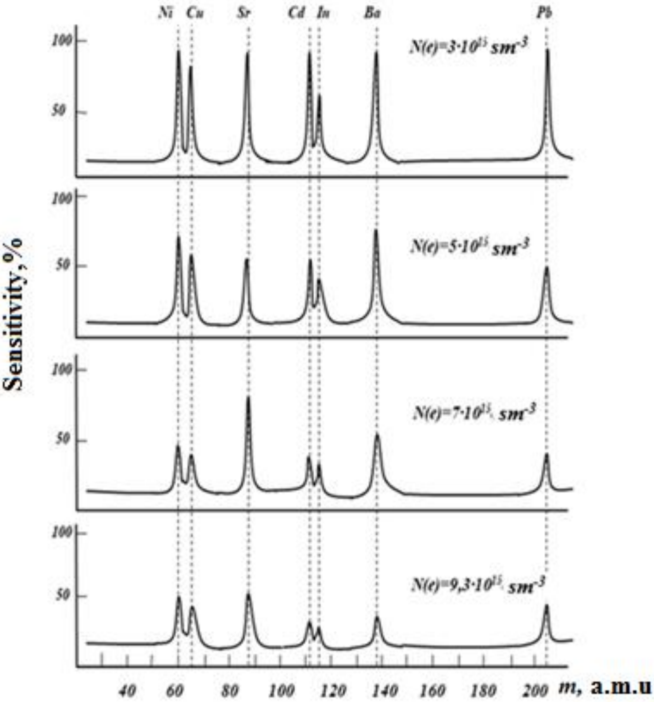


Fig. 15. Dependence of the sensitivity of the analyzer on the atomic mass of the mixed element at different values of T = 7500 K and W = 1450 Vt and the density of electrons.

Chapter VI. Prospecting and exploration for oil and gas wells have faced several complex challenges in recent years. Among the issues that need to be resolved in this case are the development of profound and complex deposits, the location of consumer territories away from production sites, and, therefore, the conduct of geological exploration, requiring significant capital investments, which further increases the risk of decision-making. As a result, traditional methods such as top-down sampling for oil and gas fields no longer work. Therefore, in addition to the experience accumulated over the years before geological exploration, it is essential to create various models for solving several geological and economic problems, test them, and obtain experimental confirmation.

One of the main issues considered in this chapter of the dissertation is the creation of massive data using modern analytical tools (gas chromatography, mass spectrometry, and other physical methods) to increase the efficiency of geological exploration, their high-speed primary processing based on computer technologies and justification of correct interpretation of the results (Figure 16).

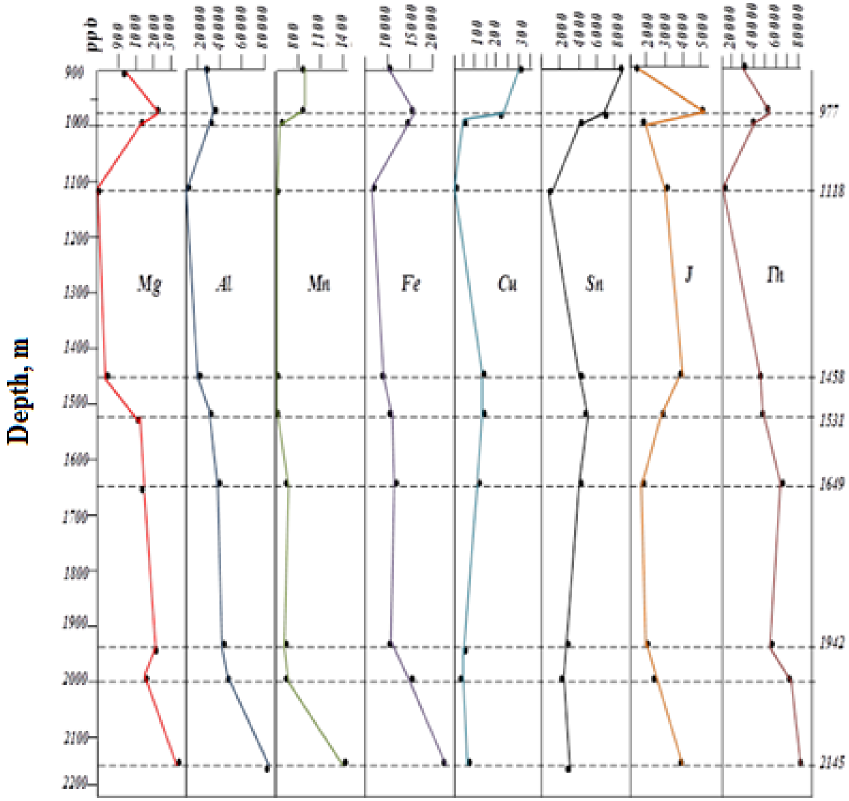


Figure 16. Results of the analysis of rocks taken from different depths by mass analyzer

In this regard, in addition to the elemental composition of rocks, we also studied the ratio of their constituent elements: Mg/Al, Al/V, Fe/Cu, Sn/I, etc. (Figure 16). In fig. 16, curves are plotted according to the algorithm shown in Table 3.

Table 3

Algorithm for calculating the ratio of trace elements in a sample taken from the same depth (900 m).

○	$\frac{M_2}{M_1}$	$\frac{M_3}{M_1}$	$\frac{M_4}{M_1}$	$\frac{M_5}{M_1}$	$\frac{M_6}{M_1}$	$\frac{M_7}{M_1}$	$\frac{M_8}{M_1}$	$\frac{M_9}{M_1}$	$\frac{M_{10}}{M_1}$
$\frac{M_1}{M_2}$	○	$\frac{M_3}{M_2}$	$\frac{M_4}{M_2}$	$\frac{M_5}{M_2}$	$\frac{M_6}{M_2}$	$\frac{M_7}{M_2}$	$\frac{M_8}{M_2}$	$\frac{M_9}{M_2}$	$\frac{M_{10}}{M_2}$
$\frac{M_1}{M_3}$	$\frac{M_2}{M_3}$	○	$\frac{M_4}{M_3}$	$\frac{M_5}{M_3}$	$\frac{M_6}{M_3}$	$\frac{M_7}{M_3}$	$\frac{M_8}{M_3}$	$\frac{M_9}{M_3}$	$\frac{M_{10}}{M_3}$
$\frac{M_1}{M_4}$	$\frac{M_2}{M_4}$	$\frac{M_3}{M_4}$	○	$\frac{M_5}{M_4}$	$\frac{M_6}{M_4}$	$\frac{M_7}{M_4}$	$\frac{M_8}{M_4}$	$\frac{M_9}{M_4}$	$\frac{M_{10}}{M_4}$
$\frac{M_1}{M_5}$	$\frac{M_2}{M_5}$	$\frac{M_3}{M_5}$	$\frac{M_4}{M_5}$	○	$\frac{M_6}{M_5}$	$\frac{M_7}{M_5}$	$\frac{M_8}{M_5}$	$\frac{M_9}{M_5}$	$\frac{M_{10}}{M_5}$
$\frac{M_1}{M_6}$	$\frac{M_2}{M_6}$	$\frac{M_3}{M_6}$	$\frac{M_4}{M_6}$	$\frac{M_5}{M_6}$	○	$\frac{M_7}{M_6}$	$\frac{M_8}{M_6}$	$\frac{M_9}{M_6}$	$\frac{M_{10}}{M_6}$
$\frac{M_1}{M_7}$	$\frac{M_2}{M_7}$	$\frac{M_3}{M_7}$	$\frac{M_4}{M_7}$	$\frac{M_5}{M_7}$	$\frac{M_6}{M_7}$	○	$\frac{M_8}{M_7}$	$\frac{M_9}{M_7}$	$\frac{M_{10}}{M_7}$
$\frac{M_1}{M_8}$	$\frac{M_2}{M_8}$	$\frac{M_3}{M_8}$	$\frac{M_4}{M_8}$	$\frac{M_5}{M_8}$	$\frac{M_6}{M_8}$	$\frac{M_7}{M_8}$	○	$\frac{M_9}{M_8}$	$\frac{M_{10}}{M_8}$
$\frac{M_1}{M_9}$	$\frac{M_2}{M_9}$	$\frac{M_3}{M_9}$	$\frac{M_4}{M_9}$	$\frac{M_5}{M_9}$	$\frac{M_6}{M_9}$	$\frac{M_7}{M_9}$	$\frac{M_8}{M_9}$	○	$\frac{M_{10}}{M_9}$
$\frac{M_1}{M_{10}}$	$\frac{M_2}{M_{10}}$	$\frac{M_3}{M_{10}}$	$\frac{M_4}{M_{10}}$	$\frac{M_5}{M_{10}}$	$\frac{M_6}{M_{10}}$	$\frac{M_7}{M_{10}}$	$\frac{M_8}{M_{10}}$	$\frac{M_9}{M_{10}}$	○

The mass spectra of ions of various elements obtained using ICP-MS of rocks taken from different depths are presented (Table 3). Preliminary results indicate that changes in element concentrations provide hope for these studies. However, the same can say about the difference in the proportions of these elements, shown in Figure 17.

Thus, the study results show that rocks' elemental-mineralogical composition and physical properties in the entire geochemical zone are subject to specific changes. In this case, the information content of these and other indicators depends on the geological and geochemical characteristics of the exploration area, the depth of the field, and the phase state of the field.

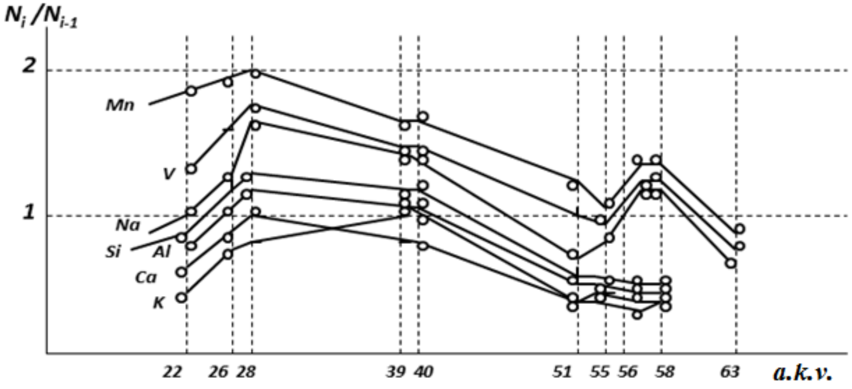


Fig.17. The ratio of rock elements

The depth distribution of elements and changes in their proportions can form the average composition of the rock cross-section. We then calculated the ratios of the ingredients and plotted the distribution of these values in the cross-sectional area and the study area. The data obtained together make it possible to determine the zone of migration of fluids from oil and gas fields, which provides additional information on assessing the potential of geological exploration areas.

Geochemical prospecting indicators are based on the interaction of hydrocarbon (HC) and their components with the environment during subvert migration from oil and gas fields. Theoretically, we can assume that at a particular value of the concentration of gases migrating to the upper layer, "syngeneic gases of rocks - organic matter - mineral part of the rock" can violate the regularity of the gas ratio. Thus, in principle, studying the nature of this disorder can solve a significant problem - the diagnosis of the genetics of hydrocarbons and their components by breed.

Experience has shown that during migration, part of the hydrocarbons is sorbed, dissolving in the water part of the rock and bitumen, and gets into the microreliefs of the rock. The rest of the migrated hydrocarbons are scattered over different layers, which leads to a change in the mineral composition of rocks, abnormal accumulation of their products, and the development of a unique microflora.

This chapter is also devoted to studying the composition of samples of natural drinking water and soil taken from different regions of Azerbaijan, especially along the Araz River. Finally, it discusses some possibilities to overcome the ICP-MS method's matrix effects limitations. During the experiment, we found that when added the analytical solution to the samples, the analytical signals either decreased or increased or had no effect on the sample.

In fig. 18 shows the curve of the change in the sensitivity of the mass spectrometer in the ^{6}Li-^{238}U range depending on the amount of calcium (Ca) in water. The figure shows that the sensitivity of light atoms (such as Na) decreases more than the sensitivity of heavy particles in the analyzed sample as the matrix element (Ca) increases.

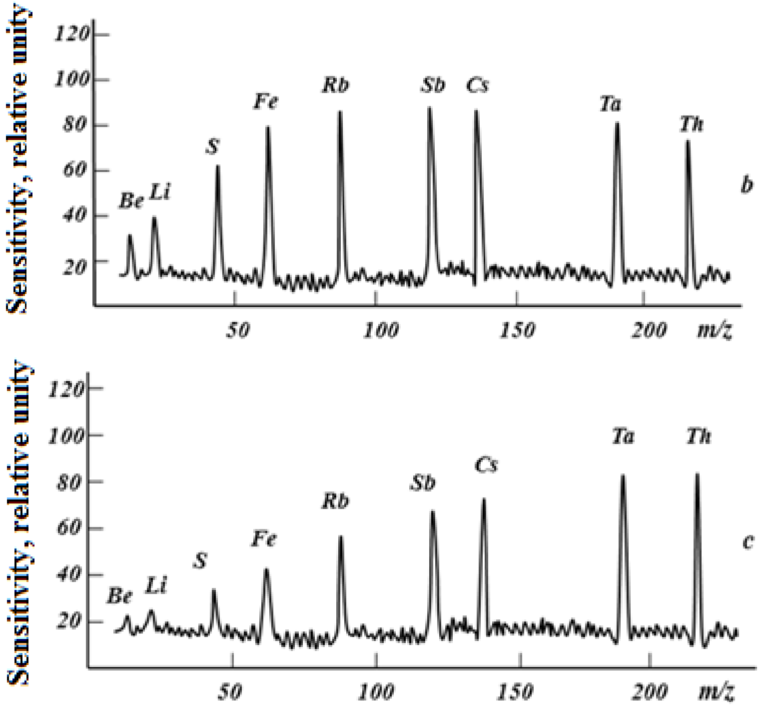


Figure 18. The effect of the amount of calcium in water on the sensitivity of the device b) n_{Ca} = 300 mg / l, c) n_{Ca} = 900 mg / l

It means that the matrix effect depends both on the number of elements in the water and on the atomic number of the mixed elements. We also determined the effect of increasing the atomic number of the matrix element on the mass spectrum.

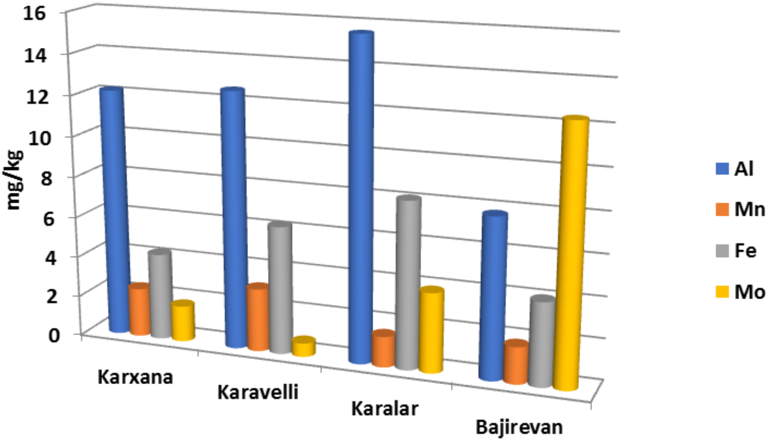
The composition of arable land irrigated with water from the Araz River and pastures flooded by frequent floods was studied using ICP-MS. The study's primary goal is to check the composition of water and soil along the river and identify sources of heavy metal pollution. It has been found that processing plants, metallurgical plants, and mines can be sources of water pollution with high copper and molybdenum content.

The study was carried out in the "standard mode" of the ICP-MS instrument.

When studying the composition of bottom sediments of the Araz River in the villages of Badzhiravan and Garalar, Imishli region, the amount of heavy metals has increased. As a result, the amount of Mn, Mo, Cu, Al in the waters of the Araz River exceeds the maximum permissible concentration (MPC). In addition, the elements Fe, Mn, and Mo were higher than usual in groundwater and wells (Table 4).

Table 4

Amount of heavy metals in the sediments of Araz river in Karavelli, Karalar, Baciravan and Otuzikilar (Imishli region) villages



Some water samples from the Araz River showed that the aluminum content is 3-5 times higher than the MPC. We knew that high levels of copper and molybdenum could be sources of water pollution. In the villages of Badzhiravan and Garalar, we observed an increase in the content of molybdenum in the sediments of the river. In some samples, the Mo concentration is ten or even one hundred times higher than in the MPC. The amount of copper in the water samples taken from the wells was average. However, the amount of copper on arable land and in samples of pastures from the village of Badzhiravan was found four times more than in the MPC.

In some wells, molybdenum in water is 50-100 times higher than the MPC. At present, the problem of a significant excess of the permissible values of molybdenum content in water bodies is becoming more urgent. A certain amount of this element in biological processes is necessary for plants, animals, and humans. Still, it tends to accumulate in biogeocenoses, and its concentration can reach dangerous values even at low levels.

The quantitative composition of heavy metals and radionuclides on agricultural land and pastures has been studied, and the chemical composition of plants grown in these territories has been studied. According to the study, we can consider that the continued pollution of the Araz River in the study areas in the future may cause serious harm to the health of the population.

THE MAIN RESULT PRESENTED FOR DEFENCE

1. Although the plasma formed by the laser, spark discharge, and secondary ion emission consists of single and multiple ions, the composition of a substance is more accurately reflected by single ions of each element [23,28,42].
2. Experimentally has been shown that it is possible to predict any degree of laser-plasma ionization based on the correlation between the diameter and intensity of the laser beam and the maximum yield of single or multiple ionized atoms of mixed elements and [6, 25, 26].

3. It has been established that the influence of the recombination process on the ionic composition of the plasma during vacuum decomposition is significant since, during the expansion of the plasma, the ionic composition is formed due to recombination and ultimately consists mainly of single and double charged ions. It, in turn, brings the RSC of elements closer to unity [33, 37].
4. It has been established that in the case of a laser-plasma (or spark discharge) one of the reasons for discrimination of elements depends on the duration of their stay in the plasma region, i.e., the mass of the atom. [26.28].
5. Showed that in the case of a standardless analysis of elements in spark discharge and secondary ion emission (SİE) mass spectrometers, the relative yield of various elements is high for ions with a low ionization potential and low for ions with high atomization energy. It turned out that it is more expedient to use ions of Ar atoms as the first ion in the SİE method. This element's ionization potential is higher than that of atoms of other factors [22, 37, 24].
6. The contributions of nonspectral matrix effects that distort the analysis results of biological fluids have been identified and investigated. It turned out that eliminating the nonspectral matrix effect is possible only by adjusting the device's operating parameters. We determined that eliminating this effect was based on parameters such as increasing the generator power and decreasing the argon flow through the nebulizer. It has been found that it is possible to increase the sensitivity of the elements by further optimizing the potential of the extractor lens. It is not recommended to use only the instrumental method to achieve this goal [47, 55].
7. It was found that there is a direct relationship between the various modes of operation of the device and the choice of internal standards. Based on this, two equally combined approaches were proposed to eliminate the studied nonspectral matrix effect: 1) measurements performed in the "standard" mode of operation of the device using an internal standard (IS) selected based on the proximity of the primary ionization potentials (PI) of the element

and the analyte, or 2) analysis of parameters in a "stable" mode using a single element, such as a IS, regardless of the atomic mass and PI [35, 50].

8. The dependence of the degree of ionization of matrix elements and analytes on the concentration of electrons has been determined theoretically and experimentally. Showed that the attenuation of the output signals in the presence of matrix elements with different primary ionization potentials in the analytical zone strongly depends on the electron concentration [37, 53].
9. It has been established that the reason for the discrimination of ions formed during laser and spark discharge is that they have different energies of atomization (dissociation) and ionization. Thus, although all elements receive the same point during one pulse, they enter the analytical zone with foreign powers. It showed that dividing these two processes in time and space could bring the RSC closer to unity [36].
10. Using an inductively coupled plasma mass spectrometer, we studied the depth distributions of hydrocarbon gases and trace elements in solid rocks. It is shown that during the vertical migration of hydrocarbons, the composition and properties of stones change under the influence of water and soluble gases, and dolomitization occurs in them. Considering this effect makes it possible to increase the accuracy of forecasts when searching for oil and gas fields [41, 44, 49, 51].
11. Environmental monitoring of the environment (especially around the Araz River) was carried out, and the ecological state of arable land, pastures, and crops are grown in some areas was studied. It has been shown that the use of ICP-MS in the analysis of various objects (natural and drinking water, bottom sediments, and soils) will further expand the range of determined elements, increase the reliability of the analysis and solve almost any problem of elemental analysis of the environment [39, 56, 57].

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