Direct Multi-element Analysis of Liquids (Water) in Glow Discharge Mass Spectrometry

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Abstract: Attempts to conduct direct mass spectral elemental analysis of liquids have been made many times. ICP mass spectrometry used for elemental analysis of liquids has a significant drawback — a large matrix effect, which limits its use for the analysis of liquids with a high content of impurities. The paper considers the possibility of direct multi-element analysis of water in glow discharge mass spectrometry. To carry out such an analysis, an ion source based on a hollow cathode was used. The method is based on the phenomenon of physical adsorption and desorption of water and its components on a metal surface. A capillary is inserted into the hollow cathode of the ion source, through which water with impurity elements is introduced into the source using a peristaltic pump. Water spreads and wets the metal surface; impurities are adsorbed on the metal surface around the capillary. Water evaporates in a vacuum. The glow discharge is excited in water vapor. Ions are pulled out of the negative glow, bombard the cathode-metal surface and desorb water molecules and impurities contained therein. Several designs of a source for supplying water to the spray area are given. In steady-state mode, the rate of water input into the source is less than 1 mm^3/min, the adsorbed liquid layer is constantly updated. If the water flow rate is too high, an ice plug forms at the end of the capillary, which is sprayed in the discharge. To test the source, various elements were introduced into the analyzed water. At the same time, ICP mass spectrometry standards were used. Mass spectra of elements contained in water are obtained. Elemental sensitivity at the ppb level is achieved. The absolute sensitivity of the method is 3-4 orders of magnitude higher than the absolute sensitivity of the ICP mass spectrometry method. In the glow discharge, the matrix effect is absent, or is insignificant. Solutions of caustic sodium and caustic potassium with a concentration of components up to 20% were introduced into the ion source. Even with such a high concentration of components, the source continued to function. The proposed method is completely new, and obviously needs further research and improvement. In turn, the author is ready to provide consulting services to all interested persons and organizations.

Keywords: Ion Source, Glow Discharge, Adsorption, Desorption, Capillaries, Sputtering, Elemental Analysis

1. Introduction

Attempts to determine the content of various impurities in the liquid (in water) have been made repeatedly. About 30 years ago, a method for analyzing liquids using a high-frequency spark source was proposed [1]. According to this method, the analyzed liquid was frozen with liquid nitrogen, and the ice turned into ions in a high-frequency vacuum spark. Several samples of Antarctic ice were analyzed by this method, but the method was not developed. A method using a high-frequency vacuum spark was proposed in [2]. In this method, not the liquid itself was analyzed, but the impurities in it. A drop of the analyzed liquid was placed on a flat surface (usually on a silicon substrate), the liquid evaporated, and all impurities remained on the substrate. The substrate was then scanned using a metal counter electrode (usually tantalum). This method achieved record detection limits of several ppb at that time. Variants of liquid analysis methods were proposed using one of the types of glow discharge – a

hollow cathode in [3-6]. Several drops of the analyzed liquid were placed in a hollow cathode. Then the liquid was evaporated. The dry residue in the glow discharge turned into ions. The detection limit of several ppb was reached, but the instability of the signal and the high background did not allow the use of mass spectrum electrical registration. Currently, these methods are not used in analytical practice.

Due to the rapid development of new instrumental methods of analytical chemistry, ICP spectroscopy and ICP mass spectrometry are currently used for direct multi-element analysis of water. The methods are widely used due to their high analytical characteristics. ICP mass spectrometry is currently the best and practically the only analytical method for quantitative elemental analysis of liquids with high sensitivity and performance. Such a proliferation of ICP mass spectrometry occurred due to the lack of other methods with similar characteristics.

An attempt to develop a new method for direct multi—element analysis of liquids - glow discharge mass spectrometry was carried out in this paper.

2. Research Results

The main task in the analysis of a liquid by the glow discharge method is to introduce a liquid into a vacuum on any surface, hold it on this surface in an adsorbed form, vaporize the excess liquid, then spray the dry residue with ions and inject the atomized atoms into the glow discharge plasma, and for using this method in mass spectrometry with electrical registration of the mass spectrum this process should be continuous. Naturally, the implementation of this process is associated with limitations. It is obvious that a liquid in a vacuum cannot remain in a stable state for a long time, some part of the liquid can be adsorbed and retained on the surface, but most of it quickly evaporates, while it cools, the excess liquid freezes, forming icicles of various configurations. In a vacuum discharge, these ice floes are sublimated or can be sprayed with ions. But in principle, for the elemental analysis of a liquid, the presence of the liquid itself in a vacuum is not necessary, and is not even necessary. We only need the analyzed elements that are contained in the liquid and one or more label elements introduced into the liquid at the preliminary stage. The liquid in such an analysis plays the role of only the carrier of the analyzed elements. It is the analyzed elements that must be introduced onto a substrate, be sprayed and directed into the glow discharge plasma. It is well known and confirmed by numerous experiments that the matrix effect in the glow discharge is absent or insignificant. From this point of view, the concentration of impurities in the liquid does not affect the results of the glow discharge analysis. On the contrary, the analysis of liquids with a high concentration of impurities is preferable for glow discharge, since it reduces the load on

the vacuum system (unlike ICP mass spectrometry). Moreover, liquid vapors cool the plasma, its heating requires additional power, which, in turn, requires additional heat removal, etc. The liquid itself does not carry any information during its elemental analysis. Unlike ICP mass spectrometry, where the introduction of the analyzed elements into the plasma of a high-frequency burner is carried out using a dual carrier: argon (or other inert gas) is the carrier of micron droplets of liquid, and the liquid is the carrier of the analyzed elements and label elements. In the glow discharge method, the number of carriers is half as much.

The required rate of liquid entry into the ion source is determined by the rate of its pumping through the hole in the discharge chamber. The diameter of this hole in glow discharge mass spectrometers:

$$Q = \sqrt{\frac{kT}{2\pi M}} \ (p_1 - p_2) \cdot S$$

or for air:

$$Q = 11.6 \cdot (p_1 - p_2) \cdot S$$

where Q is the pumping speed l/sec, p_1 and p_2 are the gas pressure on both sides of the hole mm Hg, S is the area of the hole cm^2. At a gas pressure in the discharge chamber of 0.1 mm Hg, the pumping speed will be ~ 0.01 l/sec. For water vapor, the same pumping rate can be assumed.

Water evaporates intensively in a vacuum. Therefore, the rate of water entering the ion source should be significantly limited. The evaporation process of volatile liquids is described by the Langmuir—Knudsen equation [10]:

$$W = -\frac{dm}{dT} = kP_1\sqrt{\frac{M}{2\pi RT}} \cdot S$$

where W is the evaporation rate; m is the mass of evaporated water; τ is the evaporation duration; S is the evaporation surface; P_1 is the vapor pressure of the liquid; M is the molecular weight; T is the evaporation surface temperature; 0 <k <1 is the correction factor.

Or for water:

$$m = \frac{SP_1}{\sqrt{2\pi MRT}}$$

where m is the evaporation rate g-mol/sec, S is the surface of the liquid cm^2, P is the vapor elasticity of the evaporated water bar at a temperature of T0K, M is the molecular weight of the liquid, R is the gas constant - erg ·g-mol^{-1}·deg^{-1}.

As a result of the experimental work carried out, it is generally accepted that the evaporation rate of water in vacuum is ~ 1 kg/m²· hour ≈ 0.3·10^{-3} mg/mm²·sec. Table 1 shows data on water vapor pressure at different temperatures.

Table 1. *Water vapor pressure at temperature t, °C.*

t, °C	p, Pa	t, °C	p, Pa	t, °C	p, Pa	t, °C	p, Pa
0	$6.1 \ 10^2$	16	$1.8 \ 10^3$	32	$4.8 \ 10^3$	48	$1.1 \ 10^4$
4	$8.1 \ 10^2$	20	$2.3 \ 10^3$	36	$5.9 \ 10^3$	52	$1.4 \ 10^4$
8	$1.1 \ 10^3$	24	$3.0 \ 10^3$	40	$7.4 \ 10^3$	56	$1.7 \ 10^4$
12	$1.4 \ 10^3$	28	$3.8 \ 10^3$	44	$9.1 \ 10^3$	60	$2.0 \ 10^4$

A glow discharge source with a hollow cathode was chosen as an ion source for converting a liquid into a low-temperature plasma [8]. The liquid can be injected into the discharge chamber using a capillary. In this work, capillaries from medical needles with an internal diameter of 0.3-0.7 mm were used. The rate of liquid entry through the capillary can be determined from the expression (Poiseuille formula) [9]:

$$Q = \frac{V}{t} = \frac{\pi r^4}{8\eta L} \cdot (p_2 - p_1)$$

where Q is the volumetric velocity of the liquid flow through the capillary of radius r, L is the capillary length, n is the viscosity of the liquid, (p2-p1) is the pressure difference at the ends of the tube. Dynamic viscosity of water = 1.004 (N • c/m²) • 10^3.

When water is introduced into a vacuum, it evaporates. The amount of water vapor formed should not exceed the pumping speed of the discharge chamber. Calculations show that the pumping rate of water vapor 0.01 l/sec at a pressure of 0.1 mm Hg is equivalent to the rate of 0.1 mm³ of water entering the discharge chamber, which is much less than the rate of water entering through a capillary with a diameter of 0.3-0.7 mm due to the pressure difference. When 1 mm³ of water is injected into a vacuum at a pressure of 0.1 mm Hg, ~ 1 liter of water vapor per second is formed. Therefore, the rate of water entering the vacuum and the capillary conductivity should be significantly reduced.

Methods for reducing the capillary conductivity are shown in Figure 1 where the cross section of the capillaries is presented.
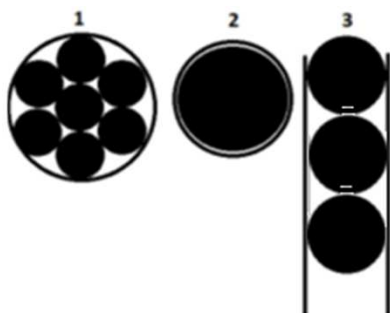

Figure 1. *Options for reducing capillary conductivity.*

1-several delays are introduced into the capillary.
2-one wire is inserted into the capillary.
3-a ball is inserted into the capillary.

A lot of thin wires are inserted into the capillary, filling the inner space of the capillary. In this case, a system of several dozen micron capillaries connected in parallel is formed

(option 1). You can insert one wire with a diameter close to the inner diameter of the capillary (option 2). Or one or more balls (from a ballpoint pen) are inserted into the top of the capillary (option 3). Obviously, other options for reducing the capillary conductivity are also possible. The use of capillaries with a diameter of 0.3 mm or more is possible if a wire with a diameter close to the inner diameter of the capillary is inserted into the capillary (in some cases, the capillary will be called the liquid emitter). In this case, the conductivity of the emitter can be determined from the expression:

$$G = 3.27 \cdot 10^2 \frac{(D_2 - D_1)(D_2 + D_1)^3}{L\sigma}$$

where D_2 is the inner diameter of the capillary, D_1 is the diameter of the injected wire. A 0.2 mm diameter wire in a capillary with an internal diameter of 0.3 mm (Figure 2) reduces the capillary conductivity by more than an order of magnitude, which is quite enough to solve the problem.

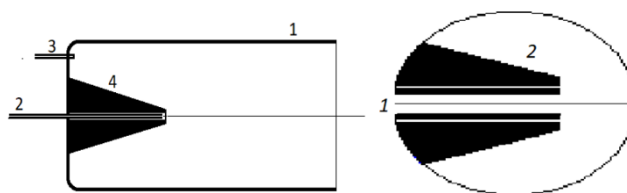Figure 2 shows a diagram of a hollow cathode with a capillary and a metal cone.

Figure 2. *Hollow cathode with capillary. 1-hollow cathode, 2- capillary for liquid injection, 3-capillary for argon injection, 4-metal cone.*

Capillary 2 is inserted into the hollow cathode through a metal cone (Figure 2).

A metal cone is needed to cool the capillary. Without cooling the capillary, the discharge current should not exceed 2-3 mA so that the capillary does not heat up. With cooling, the discharge current can be increased to 15-20 mA. The capillary should fit tightly into the cone. Then the liquid from the capillary spreads along the top of the cone. To inject water into the capillary, it is necessary to use a peristaltic pump with low performance: *BIO.PROP* with a liquid input rate of 2.5-25 ml/hour, or *LabK10*, with a liquid input rate of 0.04-149 ml/min, etc.

The main task in the analysis of a liquid by the glow discharge method is to introduce a liquid into a vacuum on any surface, hold it on this surface in an adsorbed form, then spray it with ions and inject atomized atoms into the glow discharge plasma, and to use this method in mass spectrometry with electrical registration of the mass spectrum, this process must be continuous.

Aqueous solutions cannot be in a vacuum in a free state

due to the high pressure of water vapor. On the other hand, water is always present in a vacuum in a bound state. Water is well adsorbed on any metal surface. The amount of water associated with the surface depends on many conditions: material and surface quality, temperature, vacuum degree, etc. In the case of polymolecular adsorption occurring at saturated vapor pressures, a liquid film (adsorption polymolecular layer) is formed on the surface of the adsorbent. During the adsorption of polar liquids (water), the polymolecular layer has a finite thickness. At the same time, a special oriented structure is formed near the surface of a solid in a thin layer of liquid. This layer with a thickness of 10^{-6}-10^{-5}cm is called the boundary phase, it is separated from the usual (bulk) liquid phase by a sharp boundary. When liquid appears at the end of the capillary, it wets the surrounding surface and the tip of the cone and spreads over it. Together with spreading, liquid adsorption occurs ahead of the wetting perimeter [11]. The wetting mechanism can be seen in Figure 3.
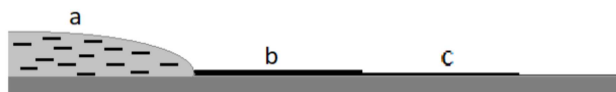

Figure 3. *Spreading of a drop of water on the surface of a solid.*

a is the initial drop of liquid, c is the primary spreading layer, b is the secondary spreading layer.

It can be assumed that the capillary surface in vacuum is sufficiently clean and the liquid moistens this surface. On the other hand, any surface that has been in the atmosphere is always covered with a polymolecular layer of water, and a drop of liquid a that appears on the surface spreads into a thin film. This means that the forces of attraction of a liquid to a solid body prevail over the mutual attraction of liquid molecules. In this case, the equilibrium edge angle is not set. The forces of molecular attraction from the solid body pull a thin layer of liquid c from the lower layer of the injected drop. The thickness of this layer does not exceed the radius of action of the forces of molecular attraction. This is the primary spreading layer. The formation time of this layer is 10^{-3} - 10^{-4} seconds. The thickness of this layer may not exceed 10-5 cm. Following the leading layer, the next, thicker layer b of secondary spreading is pulled out of the liquid. Its thickness can be several tens of microns. The liquid spreading rate is tens and sometimes hundreds of cm/sec. After the formation of these layers, the entire liquid enters into motion.

On the metal surface, the liquid and its components are adsorbed. Adsorption is a process of spontaneous increase in the concentration of a substance at the interface of phases. There are two types of adsorption: physical adsorption and chemical (chemisorption).

Physical adsorption is caused by the forces of the intermolecular Van der Waals interaction. It is non-selective, flows at a high speed, has a low heat of adsorption from several kilojoules/mol to several tens of kilojoules/mol (no

more than 50 kJ/mol of adsorbate). Adsorption proceeds molecularly, i.e. the compounds are adsorbed in an undissociated state [12-14].

During physical adsorption, molecules are attached to the surface and held on it by intermolecular interactions (Vanderwaals forces). This process is reversible — it is desorption. Metals, glass, salts, oxides are hydrophobic, i.e. they are well wetted with water. During adsorption from aqueous solutions, both molecules and atoms of the absorbed substance and water are absorbed by the adsorbent. If the rates of adsorption and desorption are equal, then this indicates the establishment of adsorption equilibrium. The adsorbed molecules move freely on the surface and in the layer. The adsorbed molecules sooner or later leave the surface and are desorbed. In the state of equilibrium, the number of adsorbed and desorbed molecules is constant.

During chemisorption, a chemical interaction occurs between the adsorbent and the adsorbing surface, while the composition of the adsorbent surface changes. However, in the case under consideration, chemical adsorption does not take place.

Adsorbed substances are difficult to remove from the surface of the adsorbate even when it is heated more than 1000°C, but they are very effectively removed by ion bombardment of surfaces.

Vanderwaals forces act at distances of much larger sizes of molecules, so the number of adsorbed layers on the surface can reach up to 20 monolayers. With the heating of the adsorbing surface, the number of these layers rapidly decreases, at a temperature of ~ 800°C, only 2-3 molecular layers of water remain on the metal surface.

In the case of polymolecular adsorption occurring at saturated vapor pressures, a liquid film (adsorption polymolecular layer) is formed on the surface of the adsorbent. During the adsorption of polar liquids (water), the polymolecular layer has a finite thickness. At the same time, a special oriented structure is formed near the surface of a solid in a thin layer of liquid. This layer with a thickness of 10^{-6}-10^{-5}cm is called the boundary phase, it is separated from the usual (bulk) liquid phase by a sharp boundary.

The adsorption process is reversible, the particles in the adsorption layers are not rigidly fixed, they make oscillatory movements, approaching and moving away from the surface of the adsorbent.

Obviously, along with the liquid, all the impurities contained in the liquid also spread over the solid surface. And they are also adsorbed on the surface. The water then easily evaporates into vacuum, the evaporation rate of water in vacuum = 0.01 g/cm^2 sec, however, the water adsorbed on the surface cannot evaporate, because the binding energy is high. Adsorbed water and its components can only be sprayed by ion bombardment of these surfaces [15-18].

In the presence of a liquid, a smoldering discharge is excited in its vapors, which penetrate into the hollow cathode. A dark cathode space is adjacent directly to the walls of the hollow cathode. Its length is 2-4 mm (with an internal diameter of the hollow cathode ~ 25 mm). There is a

negative glow behind the dark space. The greatest intensity of the glow is on the discharge axis, as in a conventional glow discharge. With distance from the axis, the intensity of the glow decreases. At a low rate of liquid vapor entering the hollow cathode, there may be no discharge at all. After the liquid enters the hollow cathode, the pressure in the hollow cathode and the discharge chamber increases sharply. The rate of liquid entry into the hollow cathode is 0.5–1.0 mm³/min. The width of the dark cathode space is reduced to 0.5-1 mm. The negative glow penetrates into the hollow cathode. The depth of penetration of the glow is determined by the discharge current and the voltage at the gap. The material adsorbed on the walls of the hollow cathode and on the cone is sprayed.

The evaporation process of volatile liquids is described by the Langmuir—Knudsen equation 18]:

$$W = -\frac{1}{s}\frac{dm}{d\tau} = kP_1\sqrt{\frac{M}{2\pi RT}}$$

where W is the evaporation rate; m is the mass of the evaporated liquid; τ is the evaporation duration; s is the evaporation surface; P_1 is the vapor pressure of the liquid; M is the molecular weight; T is the evaporation surface temperature; $0 < k < 1$ is the correction factor. Due to the heat of evaporation, the surface of the liquid cools, which introduces an error in determining the evaporation rate. The decrease in the evaporation surface temperature depends on the volatility of the solvent (Figure 2): the higher the volatility of the solvent, the greater the decrease in surface temperature. When experimentally determining the volatility of solvents, it is necessary to take into account the transfer of heat from the air and from the substrate. With this in mind, the decrease in the temperature of the evaporating surface can be expressed by the following formula:

$$\Delta T = \frac{k}{c_n h}\Delta H = \Delta H_{evap}(p_{i0} - p_{i00})$$

where h is the heat transfer coefficient; k is the thermal conductivity; ΔH_{evap} is the heat of evaporation; p_{i0} is the pressure of saturated solvent vapor; p_{i00} is the solvent vapor pressure above the surface; C_n is an experimental coefficient that takes into account heat transfer from the substrate; C_n can be calculated based on experimental results; for acetone, $C_n = 4.8$. The calculated results have good convergence with experimental. Thus, when water evaporates at 25°C, its surface cools to 15.6°C. At the same time, the vapor pressure decreases from 3.20 kPa (24 mm Hg) to 1.73 kPa (13 mm Hg). At a high rate of water entry into the capillary, the water on its top freezes during evaporation, an ice plug forms. The discharge voltage increases sharply, but the high-voltage glow discharge continues. The ice plug sublimates quite quickly, sprays and collapses. To speed up this process, another capillary is inserted into the hollow cathode, through which argon or air is supplied to the hollow cathode for a short time. The ice plug collapses quickly and argon injection can be stopped. The discharge takes place exclusively in the vapors of water

injected into the source. Argon injection can also be used to clean the cone and hollow cathode in a glow discharge after analysis from the remains of the analyzed sample. To clean the capillary, distilled water is injected into it between analyses. However, flushing the capillary from the previous analysis is a rather lengthy process due to the low rate of fluid entry. This disadvantage can be eliminated by using replaceable, pre-cleaned capillaries.

In principle, an additional capillary for the introduction of argon in this source is not required, the capillary is effectively cleaned from the ice plug when discharged in water vapor. Argon is used only to speed up the process. Practically an ion source of glow discharge for the analysis of liquids is arranged as follows:

In the center of the discharge chamber (Figure 3) there is a metal capillary 1 with an inner diameter of 0.25-0.7 mm. The capillary is electrically isolated from the discharge chamber through a ceramic insulator. One end of the capillary is located 10-20 mm from the outlet of the discharge chamber, the other is discharged into the atmosphere. The diameter of the hole in the discharge chamber through which the ions are drawn is 1.0 mm. Vacuum pumping of the discharge chamber is carried out through the same hole. The second end of the capillary is discharged into the atmosphere and connected to a device that regulates the flow rate of liquid through the capillary – a low-performance peristaltic pump. There is no need to inject argon into the discharge chamber - the smoldering discharge is excited only in the vapors of the liquid and its components.

Figure 4 shows a diagram of an ion source with a hollow cathode. The distance between the hollow cathode and the walls of the discharge chamber does not exceed 1 mm to exclude discharge on the outer surface of the hollow cathode.
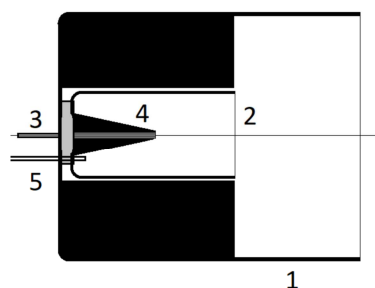

Figure 4. *Diagram of the ion source.*

1-discharge chamber, 2-hollow cathode, 3- capillary for liquid injection, 4-metal cone, 5-capillary for argon injection.

To study the possibilities of the proposed source, it was installed on the ICP mass spectrometer ELEMENT 2 instead of the ICP source. The source was cooled with water using a refrigerator.

The maximum rate of water entry into the capillary is determined by the pumping rate of the discharge chamber, the vacuum in which should be low enough to provide a high-voltage discharge in the hollow cathode. I.e., the range of water entry rates into the capillary when analyzing

liquids on a mass spectrometer with a medium–capacity vacuum pump for pumping an ion source is narrow enough - the maximum water entry rate is not should exceed 1-2 mm^3/s.

The study of the analytical capabilities of the developed source was carried out on the ELEMENT 2 mass spectrometer, on which a new source was installed instead of an ICP source. Glow discharge sources can only be coupled with high-resolution dual-focus mass analyzers, because glow discharge mass spectra always contain multiplets on almost every mass spectral line at the level of 10^{-3} -10^{-5}%. In the vast majority of cases, these are hydrocarbons and gas impurities desorbed from the inner surfaces of the discharge chamber. The ELEMENT 2 mass analyzer has a resolution of up to 10 000 with a sufficiently high sensitivity, quite sufficient to separate the lines of the analyzed elements and hydrocarbons. The source was cooled with water using a refrigerator.

The source used a hollow cathode with a lid on the top [19]. At the same time, a "plasma bubble" in water vapor is formed in the inner cavity of the cathode. The "bubble" inhibits the flow of water vapor into the discharge chamber. The use of such a cathode makes it possible to increase the diameter of the hole for pulling ions in the discharge chamber to 1.5-2 mm, and increase the intensity of the pulled ion beam by almost an order of magnitude. Figure 5 shows the mass spectrum of a distilled water sample with a low sensitivity of the mass spectrum registration system. In steady-state mode, the rate of water supply to the discharge chamber did not exceed 1 mm^3. The main lines in the glow discharge mass spectrum at up to 1% of the intensity scale with m/e = 18 and 16 correspond to molecular water, oxygen, and other components of water, and the intensity of the oxygen line is an order of magnitude less than water (H_2O and H_3O). Naturally, there are almost no argon lines in the mass spectrum. Argon, its compounds and impurities contained in argon interfere with the determination of Si, K, Cr, Mn, Fe in the liquid and the exclusion of argon from the analysis cannot but have a positive effect on the results of the analysis.

Naturally, the most intense lines relate to water and its components, including molecular ions. But the lines of gas impurities present in the water are also clearly visible. The resolution of the 4000 analyzer is often quite sufficient to separate these ions from the lines of the elements. The copper lines in the spectrum are associated with the capillary material — it was a copper tube with an inner diameter of 0.7 mm and a length of 70 mm, into which about 40 tungsten wires with a diameter of 0.05 mm were inserted. The cone for cooling the capillary was also made of copper.

First of all, the process of establishing a stable mode of spraying impurities in a water solution was studied. For this purpose, water was injected into the hollow cathode, into which silver was injected at the level of 10-4% (1 ppm). The rate of water supply to the hollow cathode is about 1 mm^3/min. The mass spectrum of water was taken every 2 minutes. The silver content in the mass spectrum increased over time from spectrum to spectrum. After 10-15 minutes, the intensity of the silver line changed within ~ 30%. That is, a fairly stable mode of water entering into vacuum, its evaporation, cathodic sputtering of the liquid and its components was established. This process of achieving a steady state can be observed in Figure 5.
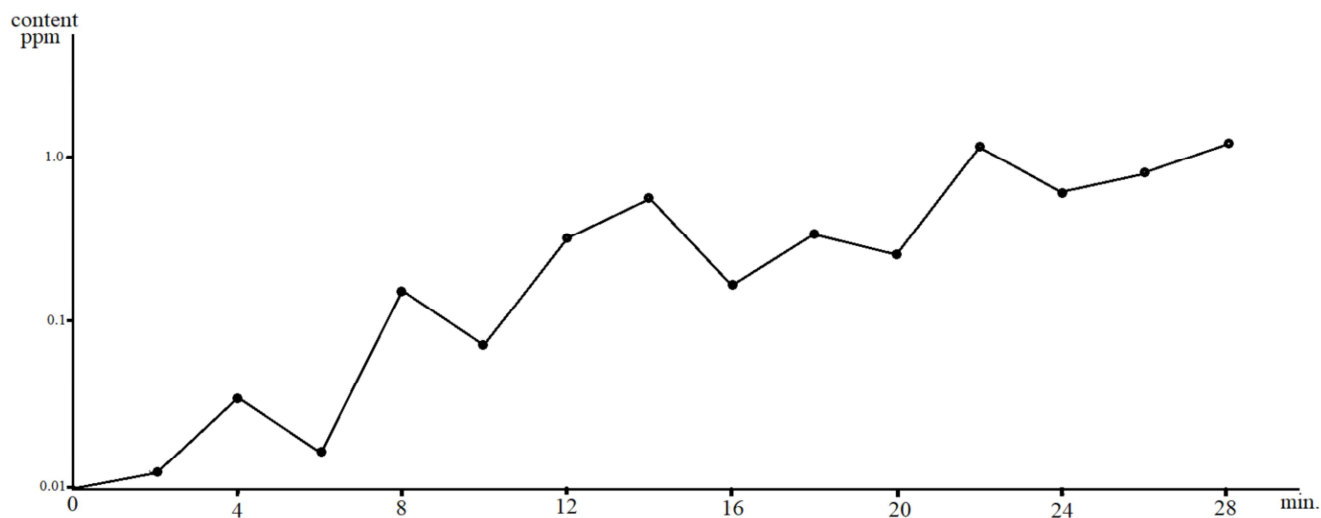

Figure 5. Achieving a steady state of spraying of a liquid with an admixture of silver.

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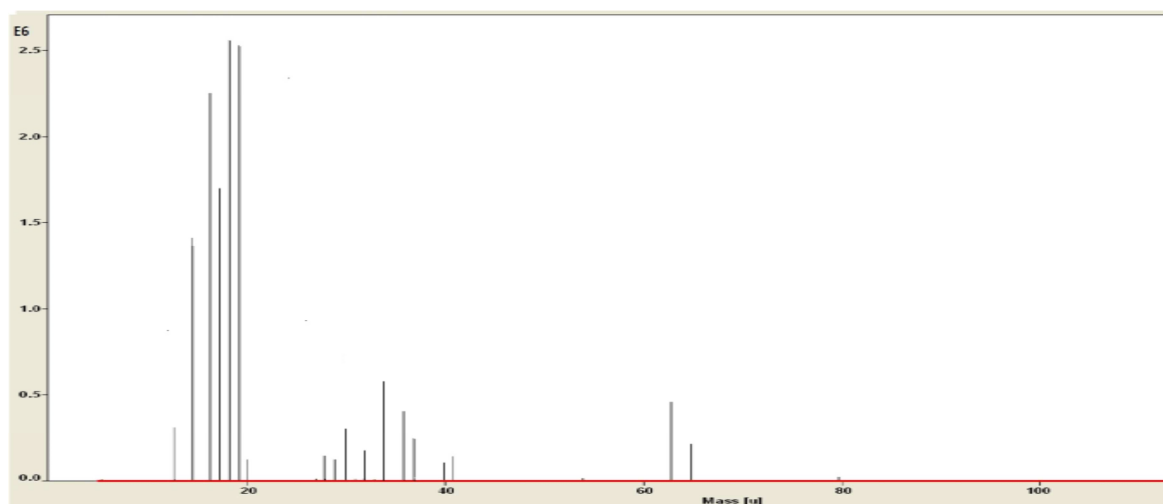
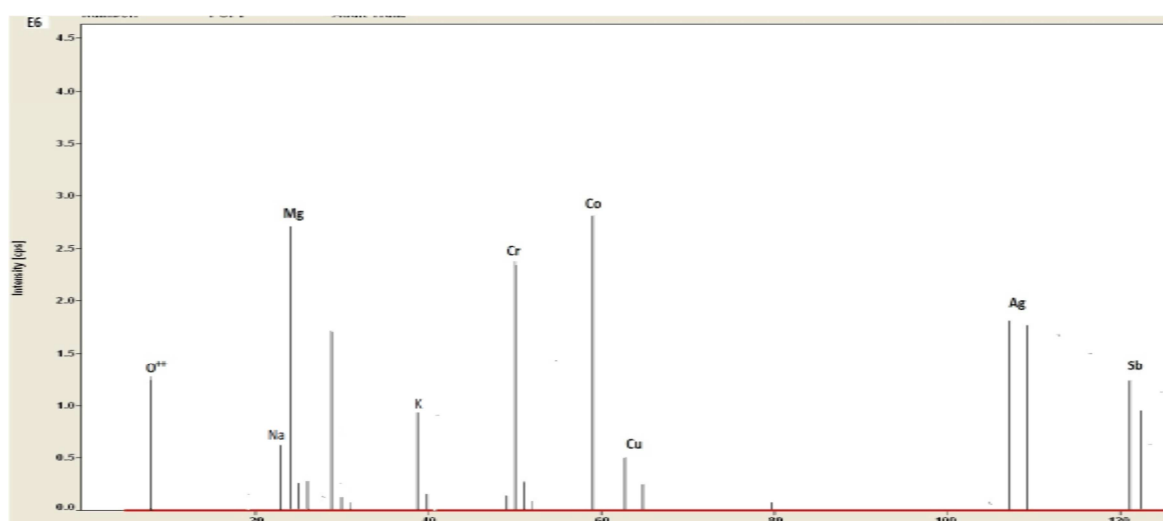**Figure 6.** *Mass spectrum of distilled water.*

Figure 7. *The mass spectrum of distilled water with elements introduced into it.*

Figure 6 shows the mass spectrum of distilled water, in which the standards of some elements used in ICP mass spectrometry were introduced. The content of the introduced elements is at the level of 3-10 ppm. All the introduced elements have All the introduced elements are present in the mass spectrum and sufficiently high intensity in the spectrum. The achieved sensitivity is at the level of ppb units. The lines of water and its components were cut out of the mass spectrum. During the analysis (20-25 spectra), no more than 1 mm^3 of water is consumed.

It can be summarized to smooth out the instability of the discharge. This means that the absolute sensitivity of the proposed method is at least three to four orders of magnitude higher than the absolute sensitivity of the ICP mass spectrometry method.

Calculations show that when the concentration of impurities in the solution is at the level of 100 ppm, the protruding capillary and cone are covered every second with a monomolecular layer of impurities. These impurities are sprayed in the discharge. The discharge has the form of a plasma torch.

The coefficients of relative sensitivity of the introduced elements are within the same order, they are easy to determine with the help of standards. If necessary, you can use an internal standard.

The efficiency of spraying the liquid and its components in a glow discharge can be tested experimentally if salt solutions are fed into the ionization region through the capillary. Experiments have shown that the glow discharge functions stably for a long time, even when saturated (up to 25%) solutions of KCl, NaCl, etc. are injected into the capillary. At the same time, the color of the plasma changes in full accordance with the injected components of the salts. I.e., in the cavity of the capillary, the spraying of liquids and its components really takes place.

This paper is the first to present a new method for analyzing water in glow discharge mass spectrometry. The method is based on well-known physical phenomena of adsorption of water with impurities on a metal surface and its desorption (ion sputtering) in a glow discharge, i.e. the work demonstrates the possibility of direct elemental analysis of water (and, apparently, other liquids) in glow discharge mass spectrometry. An ion source based on a hollow cathode

allows for multi-element analysis of solids and liquids with high sensitivity. Naturally, work with this source should be continued in order to fully and in more detail reveal its capabilities in analytical practice. It is necessary to conduct elemental and possibly molecular analysis with other liquids, solutions, including organic substances.

Thus, summing up the above, it can be stated that direct multi-element analysis of water in glow discharge mass spectrometry is quite possible. To carry out the analysis, water with components is injected into the ion source using a capillary at a rate of ~ 1 mm^3/min. Getting into the ion source, water spreads in a thin layer along the top of the capillary and cone, is adsorbed and evaporates into a vacuum. A smoldering discharge is ignited in the water vapor. The tip of the cone and capillary are bombarded with ions that spray the adsorbed water and its components. The atomized atoms and molecules diffuse into the negative glow region and are ionized and analyzed in a double-focusing mass analyzer.

3. Conclusions

An ion source has been developed for direct multi-element analysis of liquids in glow discharge mass spectrometry. The analyzed liquid (water with components) is fed directly into the ion source of the glow discharge through the capillary, spreads over the metal surface of the cone and is adsorbed. The glow discharge is ignited exclusively in the vapors of the injected liquid. And desorb water molecules and adsorbed impurities. There was no need for additional argon injection. In a glow discharge, ions bombard the surface covered with water, the adsorbed liquid and impurities are sprayed with ions, ionized and analyzed in a mass spectrometer.

Relative elemental sensitivity at the ppb level and high absolute sensitivity have been achieved. Currently, it is too early to talk about all the advantages and disadvantages of an ion source with a glow discharge for liquid analysis. It should be investigated in detail, as a result of which its potential capabilities and limitations will be revealed.

It is impossible to give a complete description of the new method of analysis and all its analytical characteristics in the volume of one article. This work only shows that elemental analysis of liquids in a glow discharge at the level of ppb fractions is fundamentally possible and promising. The cathode plasma of a glow discharge has been studied quite well and is used quite successfully in the analysis of solids. Differences in the characteristics of cathode plasmas formed during sputtering of solids and liquids can hardly be an obstacle in the elemental analysis of liquids. However, the analytical characteristics of the method can be more clearly defined after additional research.

Acknowledgements

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