

MASS SPECTROMETER FOR ANALYSIS OF SOLIDS

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Abstract- Despite a number of benefits of Secondary Ion Mass-Spectrometry (SIMS), the studies of solids by this method involves disadvantage associated with a spread of energies of ions ejected from the sample surface. This leads to a limitation of analytical characteristics of the SIMS. This paper presents the results of development and testing time of flight mass spectrometer with axial symmetric electric field, with the ability to triple focus of ion (by angle, energy, and coordinates) with the high specifications of the developed instrument were obtained.

Keywords: Time of Flight, Mass Spectrometry, Axial Symmetric Mass Analyzer, Secondary Ion, Relative Sensitivity Factor (RSF).

I. INTRODUCTION

For mass spectrometry of solids (laser, spark or secondary ion emission) is the problem of obtaining reliable quantitative data. Despite a number of advantages of mass-spectrometric method, the composition of the mass spectrum does not always match the true composition of the sample. For accounting of this discrepancy using the coefficients of the relative sensitivity (CRS) determined the element with respect to the internal standard.

In this work devoted determination the coefficient of relative sensitivity and note its value to unity for the different elements by selecting the experimental conditions under which this equation is satisfied. In the work performed the results of experimental work carried out by laser, spark by ionization and secondary ion emission (SIE). Considering the dynamics of the laser plasma bunch conditions for influence the parameters of experimental (q and d) on the processes of ionization, acceleration and recombination of ions. It is shown that the initial size of the bunch d is an important condition for the impurity ions of specified charge. This allows predicting conditions under which detected ions of elements impurity of different charging if similar charges matrix.

On the basis of data on the degree of ionization of a number of simple substances under the influence of a spark in a vacuum, it is shown that the sensitivity of detection of impurities (i.e. CRS) to sensitivity check of the matrix is the ratio of ionized simple substances. The formula for calculating the CRS is considered without the use of internal standards.

In this case the lower limit of detection for most impurities is 5×10^{-4} atomic percent which shows that the quantitative measurement by mass spectrometry of secondary ions (SI) are associated with some difficulties that are associated primarily large difference of coefficients of secondary ion emission (SIE). In addition, the absolute values of these coefficients are highly dependent on the experimental conditions. Numerous experiments show that the relative yield of ions of different elements of impurity depends on the first and second potentials of ionization (φ_i) and has a quadratic form. Dependence K_i^+ on the binding energy shows the influence of the process of the atomization, i.e. the impact speeds and energy of the evaporated atoms on the relative yield of the SI. The largest K_i^+ observed for elements with smaller, but with more energy of atomization (φ_a).

The value λ_1 is only the coefficient characterizes the broadening ion packet $T_1^{(1)}$ due to the initial angular divergence in the radial direction α and in the sum $\lambda_1 + \lambda_2$ in $T_5^{(1)}$ and $T_6^{(1)}$.

For investigations the trace elements and the distribution of impurities in solids the physical methods are increasingly being used. One of the most important methods among them is mass spectrometry. The advantages of mass spectrometric methods of elemental and isotopic compositions are: the lack of constraints on the physical form of the sample (compact or powder sample), complete analysis is determination of 60 elements in materials, a wide dynamic range of masses, the relative high (10^{-5} - $10^{-8}\%$) and absolute (10^{-10} - 10^{-16} g) sensitivity, etc.

These advantages of mass-spectrometric method contribute to its widespread use for the analysis of environmental samples and industrial materials. Recently, in connection with the specifics of natural objects and a number of technical materials for the ionization of the samples used secondary ion emission. However, using the phenomenon of secondary ion emission (SIE) for elemental and isotopic analysis requires the use of mass spectrometers with a double (triple) focus due to the fact that the secondary ions ejected by the primary ions from the sample surface, have a large energy spread [1, 2].

Studies show that the variation of the initial energy of secondary ions is in a fairly wide range (0-100 eV). Attempts have been made to use of quadruple mass spectrometers, allowing the analysis of ion beams with large energy spread [3]. However, calculations show that the possibility of Time of Flight (TOF) mass spectrometers is far from exhausted.

New opportunities are opened for use for these purpose devices that provide the technical implementation of the principle of energy focusing. One such device is a mass analyzer with an axially symmetric electric field. This article is devoted to the development and testing of axially symmetric TOF mass spectrometer with a secondary ion emission for elemental and isotopic analysis of solids and natural objects.

II. THEORETICAL PART

It is known that the main advantage of the TOF mass analyzer over other types of such devices are the quickness of registration of the mass spectrometer, reaching tens of microseconds, unlimited mass range of studied ions, a panoramic view, as most of the mass spectrum, as well as its individual parts. A significant disadvantage of limiting the area of application of the TOF mass analyzers has long been their low resolution, associated with the spread of initial velocities of the investigated ions formed in the same equipotential plane source.

Currently, there are a number of devices that provide the technical implementation of the principle of focusing the energy of the ions. More promising is the use of TOF mass analyzers elements representing sectorial axisymmetric field. We have calculated TOF mass analyzer with inhomogeneous energy fields, taking into account the impact on the transit time of ions in the analyzer of six small parameters characterizing the ion packet α , β , S/r_0 , h/r_0 , their divergence of energy $\Delta V/V_0$, the mass $\Delta M/M_0$ and the analyzer $\Delta U/V_0$, where α and β are angles of divergence of the ions in the radial and axial directions; S/r_0 , h/r_0 are dimensionless width and height of the package, r_0 is average radius of the trajectory of the ions; V_0 , ΔV are the average energy of the ions and their spread; U_0 is deflecting potential, M_0 , ΔM are the average mass of ions and their spread.

There were determined the trajectories of ions in an axially symmetric field, depending on the above seven parameters by the method described in [4]. The expressions for determining the transit time of ions in the mass analyzer in the linear approximation.

$$t = \frac{r_0}{v_0} (T^{(0)} + \sum_{i=1}^7 T^{(1)} a_i) \quad (1)$$

$$T_1^{(1)} = \frac{1-k}{\omega^2} [1 + a_1 \lambda_1 (1-k)] + \frac{\lambda_1}{\omega} (1-k) \sin \omega \psi -$$

$$- \frac{1-k}{\omega^2} [1 + a_1 \lambda_1 (1-k)] \cos \omega \psi$$

$$T_2^{(1)} = 0$$

$$T_3^{(1)} = \frac{a_1}{\omega^2} (1-k^2) + \frac{1-k}{\omega} \sin \omega \psi - \frac{a_1}{\omega^2} (1-k^2) \cos \omega \psi$$

$$T_4^{(1)} = 0$$

$$T_5^{(1)} = \left[\frac{(1-k)^2}{2\omega^2} - \frac{1}{2} \right] \psi - \frac{(1-k)^2}{2\omega^3} \sin \omega \psi - \frac{\lambda_1 + \lambda_2}{2}$$

$$T_6^{(1)} = \left[\frac{(1-k)^2}{2\omega^2} + \frac{1}{2} \right] \psi - \frac{(1-k)^2}{2\omega^3} \sin \omega \psi - \frac{\lambda_1 + \lambda_2}{2}$$

$$T_7^{(1)} = \frac{1}{2} \left[\frac{a_2(1-k)}{\omega^2} + \psi \right] - \frac{a_1(1-k)}{2\omega^2} \cos \omega \psi$$

where,

$T^{(0)} = \lambda_1 + \lambda_2 + \psi$ is unperturbed transit time of ions in the first (λ_1) and second (λ_2) field free part of analyzer; ψ is angle of rotation of the ions in the radial field; $T_1^{(1)} - T_7^{(1)}$ are changes the flight time in a linear approximation, due to the seven parameters.

So, the time span t is determined by: the ratio of electric and magnetic forces of the field k quantity ω_1 to characterizes the distribution of the field in the analyzer tilt input border a_1 angle ions in the field. The expressions were obtained for all $T_i^{(1)}$ [5]. Having solved these equations, we obtained the condition for focusing the ion transit time

$$\frac{1-k}{\omega^2} (1 - \cos \omega \varphi) = 0 \quad (2)$$

where,

$$k = k - \frac{r_0 E_0}{2V_0} \left(1 - \frac{U_0}{V_0} \right), \quad eV_0 \text{ is ion energy, } U_0 \text{ is potential}$$

for average trajectory, ω^2 is radial distribution function of the electric field, $\omega \psi = 2n\pi$ ($n=0,1,2$). Studies have shown that the root of the Equation (2) is

$$\omega \varphi = 2n\pi, \quad n = 1, 2, \dots \quad (3)$$

The analysis of the trajectories of ions passing through the electrodes, in which Equation (3) comply with, shows that this condition is due to the symmetry of motion with respect to the average trajectory, that is, the path traversed on one side of the average trajectory of the ions is equal to the path traversed by the other side. This means that the ions having different divergence angles (α , β), the initial energy spread (ΔV) and enter the coordinates (S and h) will be focused at an angle of rotation, satisfying

$$\varphi = \frac{2\pi}{\omega} = 254^\circ 17' \quad (4)$$

The dispersion of the mass analyzer, which is defined as the difference between the times of the passage of a package consisting of ions of different masses is given by

$$D_\gamma = \frac{r_0}{v_0} \cdot \frac{\psi^3 (1-k)}{2\pi^2} \quad (5)$$

On the basis of these expressions have been calculated and the structural elements made TOF analyzer ions with axially symmetric electric field, which has a resolution of more than 500, the relative sensitivity of $10^{-6}\%$.

III. RESULTS AND DISCUSSIONS

The experiments were performed on the setup is shown in Figure 1. As a source of primary ions it is used arc discharge in argon. Argon ions have reached the cathode passing through a hole in the middle of its stretched and accelerated to energy of 4-5 keV, formed in a narrow beam and directed onto the target at an angle of 45 degrees.

The collection, pre-acceleration and focusing of the secondary ions ejected from the sample, was carried out by immersion lens 5. Optimal conditions for secondary ions collection, highly differing masses, chosen by varying the distance between the sample and the first electrode of the lens.

The energy of ion entering mass analyzer was 1200 eV. The secondary ions are separated by mass in the analyzer detected by secondary electron multiplier (SEM-7) and recorded by two-beam oscilloscope C1-64. The studies were conducted at 22, more or less pure metals with different physical properties. Figure 2 shows typical oscillograms of the mass spectra of several metals and impurities, at a current of argon 8×10^{-5} A. These waveforms are selected from multiple images. Not a very high reproducibility (50%) led to the repeated bombardment of the surface of the sample.

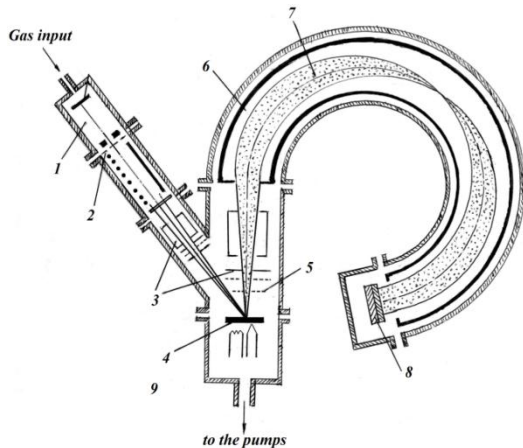


Figure 1. Experimental facility of secondary ion mass-spectrometer:
 1- gas discharge; 2,3- primary ions' ion-optic system; 4- sample;
 5- secondary ions' ion-optic system; 6- axial symmetric;
 7- mass-analyzer; 8- Ion detector

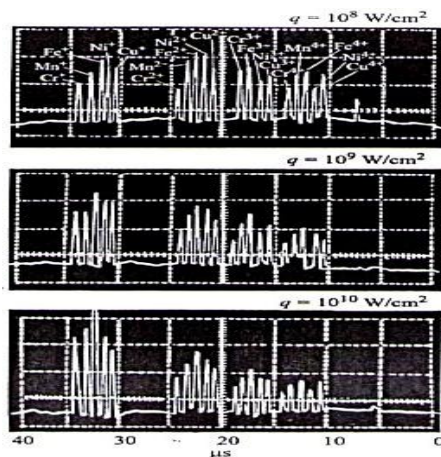


Figure 2. Mass-spectra of single and multi-charged ions of stainless steel

Analysis of the relative ion yield of the matrix and impurity elements on the basis of the obtained mass spectra suggest that is of interest, both from a practical point of view and to understand some features of the mechanism of secondary ions' formation.

For example, depending on the nature of the target, ion emission intensity can vary by three orders of magnitude (Mg, and Au). This is natural and leads to a differential sensitivity analysis of the $5.5 \times 10^{-7}\%$ for magnesium, up to $5 \times 10^{-3}\%$ for gold. Note that this sensitivity is not limiting.

In [6] conducted a theoretical analysis of a large number of factors that determine the sensitivity threshold of Secondary Ion Mass-spectrometry (SIMS). The principal possibility of obtaining the mass spectra with the current of secondary ions of 10^{-8} A that when using the secondary electron multiplier (SEM) with a low level of noise in the detector dynamic range of the ion corresponds to the nine orders of magnitude. Under ideal conditions (no overlap of the peaks; the absence of harmful effects of the primary ions; big differences of atomic masses under investigation) can be detected impurity concentrations less than $10^{-8}\%$ depending on the type of element.

Results of the study the correlation between the relative yield of ions of different elements with their ionization potentials and energy analysis are shown in Figure 3. As the figure shows the highest yield is observed for elements with lower ϕ_i , but with great energy of atomization ϕ_a .

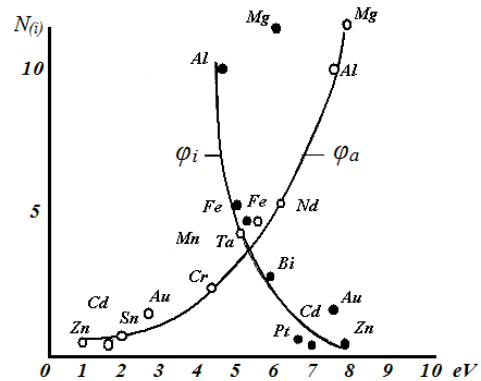


Figure 3. Relative yield of ions different metals depended on their ionization potential (ϕ_i) and energy of atomization (ϕ_a)

The data were compared of relative yield as a function of the elements in the periodic table. Studies have shown that for the most metals are in the same row in the periodic table of elements, the relative yield K_i^+ decreases with increasing atomic number z , or the principal quantum number n , which characterizes the number of electrons orbiting an isolated atom (Figure 4). As one might be seen from the figure, for each series, K_i^+ decreases linearly with the number z . Furthermore straight line function $K_i^+(z)$ for different groups is parallel.

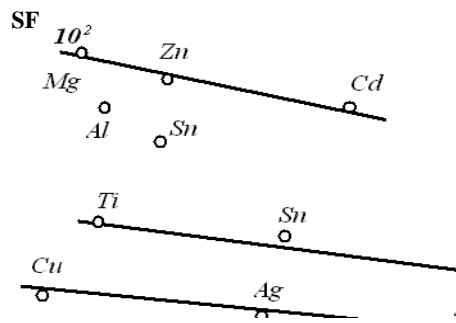


Figure 4. Dependence relative sensitivity factor (RSF) on serial number on periodic table

Such behavior of the curves $K_i^+(z)$ can be explained as follows. Since the elements of one row in the periodic system are isoelectronic, i.e. number of outer electrons from them the same, a significant decrease in intensity of secondary ions with increasing z , apparently due to the influence of inner electron shells in the process of emission.

Such formulation of the problem in a priori excludes several approaches to explaining the energy exchange between the primary particle and the metal atoms. Among the mechanisms include, radiation theory, the theoretical and pulse theory.

IV. CONCLUSIONS

Theoretical and experimental studies demonstrated the possibility of investigations of secondary ions with an energy spread by *TOF* mass analyzer with a high relative sensitivity of 10^{-6} mass %. It revealed a huge opportunity for the SIMS analysis of both the chemical composition and molecular structure, in the case of organic compounds. Experimentally, the dependence of the relative yield of secondary ions from the atomization energy φ_a and ionization potential φ_i , has been established.

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BIOGRAPHIES



Zulfuqar Kamil Nurubeyli was born in Azerbaijan on 06.05.1976. He graduated in Master degree in Honours from Azerbaijan State Oil Academy, Baku, Azerbaijan in 2001. Since 2006, he is Candidate of Physics-Mathematical Sciences (Ph.D.). His research interests are in

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Kamil Zulfuqar Nuriyev was born in Azerbaijan on 03.09.1939. He is Candidate of Physical-Mathematical Sciences, Chief Researcher of Laboratory "Physics and Techniques of High Voltages". His research interests are in development, production and investigation of time

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Tarana Kamil Nurubeyli was born in Azerbaijan on 17.02.1979. She graduated in Master degree in Honours from Baku State University, Baku, Azerbaijan in 2001. Since 2004 she is Research Assistant in Institute of Physics, Azerbaijan National Academy of Sciences, Baku,

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