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Mass-spectrometric Analysis of Solids Using Laser Ion Sources

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The development of lasers has permitted their application in the evaporation and ionisation of comparatively small sections of the solids to be investigated with subsequent mass-spectrometric analysis of the vapours and ions formed. Mass-spectrometric analysis using lasers has many advantages compared with the traditional procedures (spark, thermal emission) for the ionisation of solids. In the review, attention is concentrated on the analytical characteristics of the method of the laser evaporation and ionisation of solids in the ion sources of mass-spectrometers.
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I. INTRODUCTION

The development of radioelectronics, the physics of superconductors, nuclear energetics, and other fields of science and engineering has led to a need for methods of analysis of high-purity solids. The optical, emission, radioactivation, and X-ray fluorescence analytical methods were developed first, and followed in recent years by mass-spectrometric analysis using a spark ion source[1].

The development of laser techniques[2,3] permitted the application of lasers in the evaporation and ionisation of comparatively small sections of test solids with subsequent mass-spectrometric analysis of the ions formed. Mass-spectrometric analysis employing lasers has many advantages, which include the comparatively simple design of the mass-spectrometer having a laser ion source, rapidity of analysis, the possibility of layer-by-layer studies and local analysis of the surface of solids, the simplicity of the mass spectra obtained, and the possibility of analysing not only metals and semiconductors, but also dielectrics. All these factors make mass spectrometry with a laser ion source very promising for the investigation of the content and distribution of impurities in solids. In the first studies on the interaction of laser radiation with solids, use was made of mass spectrometers of the Mattauch–Herzog type[4] as well as time-of-flight instruments[5,6].

Two fundamental operating modes of pulsed lasers are distinguished: the free running mode and the use of a Q-switched resonator[2] ("giant" pulses). In the first case, the radiation pulse has a lifetime $\tau \simeq 10^{-3}$–10^{-4} s and a power $P \simeq 10^{3}$–10^{6} W. For giant radiation pulses, $\tau \simeq 10^{-7}$–10^{-9} s and $P \simeq 10^{6}$–10^{8} W. The interaction of the laser radiation pulse with the substance depends significantly[2,3] on the time τ and P. In this review, we shall therefore consider separately the application in mass-spectrometric analysis of lasers operating in different modes. Attention will be concentrated on the analytical characteristics of the method of laser evaporation and ionisation of solids in the ion sources of mass-spectrometers.

II. ANALYSIS USING A LASER OPERATING UNDER FREE RUNNING CONDITIONS

Under the influence of the laser pulse with a lifetime $\tau \simeq 10^{-3}$ s and a power density of the focussed radiation $q \simeq 10^{5}$–10^{7} W cm^{-2}, a given section of the test specimen undergoes intense evaporation. The diameter of the resulting crater is determined by the conditions of focussing of the radiation and its depth[3] can vary from 10 μm to 10^{3} μm, depending on the type of substance, the duration of the pulse, and the energy density in the beam.

The vapour of the substance formed in the laser flash is partly ionised. The ratio of the neutral and ionised vapour components is described satisfactorily by the Sacha–Langmuir equation[4]. The neutral vapour component has a kinetic energy spread $\Delta T \simeq 1$ eV and, after its ionisation (for example by an electron beam), can be analysed with respect to mass in a time-of-flight mass-spectrometer with single space-time focussing. The ionic component of the vapour[2,3] is characterised by the quantity $\Delta T \leqslant 10$ eV. In order to achieve adequate mass resolution, one therefore employs a double focussing instrument or a time-of-flight instrument in which the ionic component is accelerated to energies T such that $\Delta T/T \ll 1$ (the condition for a monoenergetic ion beam).

The problems of the mass-spectrometric applications of lasers operating in the free running mode for the determination of the composition of solids and the investigation of the distribution of impurities in the specimens have been discussed in a number of cases[7-29]. A large group of investigations[7-13,18] have been devoted to the analysis of gases in solids. A typical experimental arrangement[7-9] is illustrated in Fig. 1. The gas evolved from the specimen under the influence of the radiation enters the ion source of a MSKh-3 Chronotron (or MSKh-3A) time-of-flight instrument, where it is partly ionised by the electron beam and, after passing through the drift tube, is recorded by the electron multiplier. In order to eliminate the single-pulse nature of the recording of the spectra and accumulate the evolved gases, the effusion method[17] has been used[13].

A number of investigators[10-12,18] placed the test specimen between the electrodes of the ion source of the MSKh-3A instrument to improve the sensitivity of the analysis. The working pressure in the measuring chamber of the mass-spectrometer was maintained at a level of 5×10^{-9}–5×10^{-8} mmHg and the mass resolution did not exceed 20.

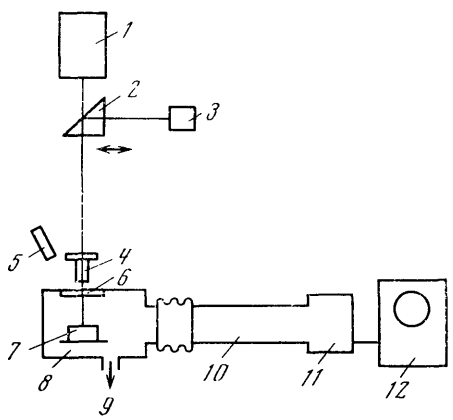


Figure 1. Schematic representation of the instrument with a time-of-flight analyser: 1) laser; 2) prism; 3) eye-piece; 4) object lens; 5) illuminator; 6) inlet window; 7) specimen; 8) vacuum chamber; 9) outlet to vacuum point; 10) "Chronotron" sensor; 11) electronic component; 12) secondary electron multiplier.

By applying the method of calibration graphs, procedures were developed for the quantitative analysis of hydrogen, oxygen, and nitrogen, in titanium, silicon, and zirconium specimens[8,9] as well as in aluminium, titanium, and niobium alloys[11,12]. Reference specimens would apparently extend the range of substances susceptible to analysis by the above method. The experiments carried out with silicon of different origins[8] yielded identical dimensions of the craters formed by the laser pulse regardless of the impurity concentration. Consequently the volume of the sample taken for analysis is independent of the content of the alloying impurities, which leads to a linear relation between the height of the mass-spectrometric peak for the impurity and its concentration in the specimen. Over a wide range of impurity concentrations, the calibration graph consists of a straight line with a slope determined by the type of impurity and the matrix in which it is contained.

In estimating the sensitivity of the method, investigators[9,11,12] used specimens saturated by the given gas to a specified concentration. The lower limit of the observation was[12] 1×10^{-4} wt.% for oxygen and nitrogen, and 5×10^{-5} wt.% for hydrogen with 95% confidence limits. A decrease of the pressure of the residual gases by evacuating the system led to a further improvement of sensitivity[9].

It was shown that the degree of localisation of the analysis is determined by the type of test substance and the conditions governing the focussing of the radiation. For example, the diameter of the focussed spot was 30 μm in one investigation[11], while other workers[7] investigated the distribution of hydrogen in the grains and in the intergranular boundaries of aluminium by interposing a diaphragm in the laser beam. The errors in the determination of the concentration of gases ranged from 5 to 25%, depending on their content and the nature of specimen. The scatter of the analytical results is apparently determined by the variations in the size of the sample evaporated per laser flash and can also be a consequence of the inhomogeneous distribution of the impurities in the specimens analysed.

Gaseous impurities in the bulk phase, in a surface layer approximately 50 μm thick, and on the surface of nickel have been studied[10] with a time-of-flight MSKh-3A mass-spectrometer using a laser to evaporate the sample material (radiation energy $E \simeq 2$ J, $\tau \simeq 0.5$ ms). The authors noted that, bearing in mind that the binding energy of the sorbed gases is approximately 10 kcal mole^{-1}, in a study of the surface desorption of gases one must employ a defocussed laser beam with $q \simeq 10^3$ W cm^{-2}. In this case, the surface gases are fully desorbed for only slight heating of the surface, which does not therefore entail the desorption of gases from the bulk phase. In an experimental test of the distribution of oxygen in the surface layer and in the bulk phase, nickel specimens were employed. The results of laser probing were compared with data obtained on etched plates by a dynamic method at 900°C. The comparison demonstrated a satisfactory agreement of the results obtained by the local and integral methods. The amount of gases (H_2, H_2O, $CO + N_2$, O_2, and CO_2) present in the surface layer exceeded by a factor of 2–3 their concentration in the bulk of the material. However, one should note that the application of a laser operating in the non-Q-switched mode has led[10] to unduly thick layers (~ 20 μm) removed per laser flash and the distribution of gases with respect to depth in the material could be investigated only very approximately. According to the authors' estimates, the sensitivity of the layer-by-layer analysis of gases was in the range 5×10^{-5}–1×10^{-4} wt.% and the reproducibility of the results was within approximately 50%.

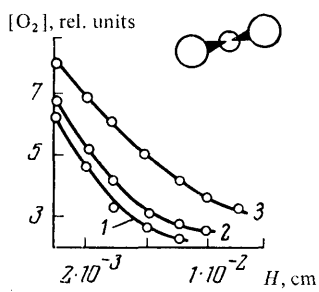


Figure 2. Curves for the distribution of oxygen with respect to the depth of the crystals after oxidation for 20 h at different temperatures (0°C): 1) 400; 2) 500; 3) 650.

The distribution of gases at different depths in the specimens has also been investigated in a study[13] where the distribution of oxygen in a cadmium telluride crystal was determined. These data (Fig. 2) are apparently of the same kind as obtained in another study[10], but similar

curves are not quoted. Fig. 2 shows that the probing of the depth of specimens using a free running laser is restricted to a 20 μm region.

A novel problem, involving the study of the composition and partial pressures of the gases within the cavities of the 22KhS ceramic and also the study of its gas content due to its natural porosity, has been solved[18]. The authors note that the laser ($E \simeq 2$ J, $\tau \simeq 0.5$ ms) makes it possible to "open" cavities (0.5–1.2 mm in size) and pores in the ceramic material and cause the complete evolution of the gas contained therein, followed by its analysis on a time-of-flight mass-spectrometer. The experimental data obtained for the gas content in the cavities and pores led to the conclusion that the composition of the gases in the cavities differs somewhat from that in the pores in containing a higher proportion of carbon-containing gases. It was also established that the gas pressure varies linearly with the reciprocal of the radius of the defect.

Thus methods for local, rapid, and quantitative mass-spectrometric analysis of gases in elements[8,9], alloys[10,12], and chemical compounds[13,16] have been developed using a free running laser. The laser has been used in these studies to evaporate small (20–100 μm) sections of the specimen with subsequent ionisation of the evolved gas by an electron beam and the analysis of the ions on a time-of-flight mass-spectrometer of type MSKh-3A. Analysis based on the plotting of calibration curves makes it possible to investigate the distribution of gaseous impurities in the specimen.

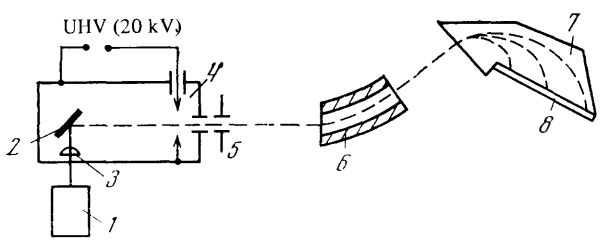


Figure 3. Schematic representation of the instrument with an analyser of the Mattach–Herzog type: 1) laser; 2) specimen; 3) focussing lens; 4) electrodes of the spark generator; 5) mass-spectrometer slit; 6) electrostatic analyser; 7) magnetic analyser; 8) recording plate.

The laser has been used[19–28] both for the evaporation and ionisation of chemical compounds. In this case, the resolving power of the mass-spectrometer (R) should be higher than in the analysis of light gases. Furthermore, in selecting the mass-spectrometric apparatus, it is necessary to take into account the considerable (~ 10 eV) scatter of the kinetic energies of the ionic component of the laser plasma and the complexity of the mass-spectra obtained[20,22–28]. Mass-spectrometers with an analyser of the Mattauch–Herzog type[19,25–28] (Fig. 3) having $R \geqslant 1000$ or with a time-of-flight analyser[20,22–24] having a resolution of approximately 100 have been used for the analysis. In order to obtain such resolution, the authors[20,22–24] achieved a monoenergetic ($\Delta T/T \ll 1$) ionic component of the laser plasma by accelerating it specifically using the electrodes of the ion source (Fig. 4). The detector could record both the ionic and neutral components of the plasma generated by the laser radiation. The spectra of neutral vapours have been obtained[20,22–24] following their ionisation by an electron beam with an energy of 15 eV, while other investigators[25–28] ionised the neutral component in a high-frequency spark discharge.

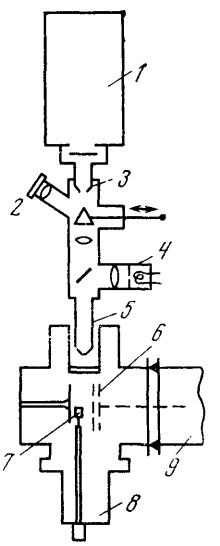


Figure 4. Schematic representation of the ion source: 1) ruby laser; 2) eye-piece; 3) diaphragm; 4) illuminator; 5) object lens; 6) accelerating grid; 7) specimen; 8) vacuum manipulator; 9) flight tube.

Studies have been made[20,22–24] on the products of the evaporation by the laser beam ($q \simeq 10^7$ W cm^{-2}) of Group VA and VIA elements, their intermetallic compounds[22–24], and also certain solid organic polymers[20]. It has been noted that the spectrum contains a large number of polyatomic ions of the elements and their compounds and that the number of polyatomic compounds in the mass-spectrum of the neutral component is greater than in the spectrum of the ionic component of the vapour. The results presented in these studies indicate a considerable difference between the laser and the usual (for example Knudsen) thermal evaporation. This difference is reflected in the type of polyatomic fragments constituting the vapour, the relative intensities, and the maximum number of atoms entering into the compound. The correlation between the type of polyatomic formations in the vapour and the structure of the condensed phase has been discussed[23,24]. It has been shown[24] that the structural difference between the polymorphic modifications of As_2O_3 is reflected in the type of polyatomic compounds present in the vapour. However, this relation has not been observed in all cases[22]. The relative intensities of the peaks of the polyatomic formations are in some instances unexpected. For example, Te_5, Sb_3, and Bi are the strongest ionic components in the vapours of tellurium, antimony, and bismuth respectively. In the experiments[30] on the usual thermal evaporation, these components are present in small amounts or are altogether absent. Fragmentation may occur in the vapour as a result of the high (close to critical) temperatures and

pressures obtained in the zone where the laser radiation operates. The analytical characteristics of the apparatus are not indicated[20,22-24], but the Tables of the mass-spectra presented[20] show that the resolving power was approximately 100.

Mass-spectrometric studies of the plasma produced on evaporation of ferrites and semiconductor compounds of the type A(III)B(V) by a laser have been carried out[25,27]. When nickel ferrite ($NiO.Fe_2O_3$) is atomised, the ionic part of the vapour consists of products of the complete dissociation of its constituent oxides. Additional ionisation by a high-frequency spark does not affect the quantitative and qualitative compositions of the mass spectrum. The ratio of the intensities of the isotopic iron and nickel ions corresponds approximately to the stoichiometric formula of this ferrite. A study of yttrium ferrite (Y_2O_3). .(Fe_2O_3) showed[25] that, together with the dissociation products (Fe,Y,O), oxygen-containing groups of atoms, in the first place YO and FeYO, are present in the mass spectrum. The ratio of the Y^+ and Fe^+ ionic currents deviates appreciably from that required by the stoichiometric formula. Additional ionisation by high-frequency sparks leads in this case to an appreciable redistribution of the ionic currents of the elements and compounds. It is believed[25] that the difference between the degrees of ionisation of iron and yttrium in the laser plasma can be accounted for by the difference between their ionisation potentials.

Analysis of intermetallic compounds of the type A(III)B(V) showed[27] that the Ga^+, As^+, and As_2^+ ions derived from gallium arsenide specimens and the Ga^+, P^+, and P_2^+ ions derived from gallium phosphide specimens predominate in the mass spectrum of the ionic component of the vapour. Ionisation of the neutral vapour causes an increase of the relative content of ions of the type As_n^+ and P_n^+, which the authors believe indicates the predominance of these species in the neutral part of the vapour. Comparison of the results of the laser and the usual thermal evaporation of compounds of the type A(III)B(V) leads to the conclusion that the degree of ionisation of gallium vapour following evaporation by laser radiation is much higher than in thermal evaporation. Lasers operating under specific conditions are preferable for the analysis of impurity concentrations averaged with respect to the volume of the specimen on a static mass-spectrometer of the Mattauch–Herzog type. For example, a laser with a radiation pulse frequency of 6.25 Hz has been used to analyse geological specimens[19]. Each pulse had $\tau \simeq 2.5 \times 10^{-4}$ s and $E \simeq 0.15$ J. The specimen analysed was moved automatically at a rate of 1 mm min^{-1}. The ion current generated by the laser radiation was 10^{-11} A, which, according to the authors, permitted analysis with a fairly short exposure time. The shape of the mass-spectrometric lines on the photographic plate was much more distinct than in the mass spectra obtained using a spark ion source. It was shown[19] that the presence of 5 wt.% of graphite increases the sensitivity of the method for certain elements (Si, Ti, and Fe), probably because the presence of carbon in the laser plasma promotes the dissociation of the metal–oxygen bonds. The concentrations of the majority of the impurities detected in the above study[19] (with the exception of alkali metals) were in the range 10^{-2}–10^{-3} at.%.

It is seen from the results quoted above that the published reports of investigations do not contain data on the coefficients of relative sensitivity for various (non-gaseous) impurities. There are no estimates of the lower limit at which impurities can be detected and of the accuracy of the results. Thus methods for quantitative mass-spectrometric analysis of non-gaseous impurities in solids using lasers operating under free running conditions have not so far been developed.

III. ANALYSIS USING A LASER OPERATING WITH A Q-SWITCHED RESONATOR (GIANT PULSE CONDITIONS)

When a giant laser pulse ($\tau \simeq 10^{-7}$–10^{-9} s, $q \geqslant 5 \times 10^8$ W cm^{-2}) acts on a solid, a highly ionised plasma is produced[2,3]. The diameter of the resulting crater is determined by the focussing conditions and its depth $H < 1$ μm depends on the type of substance and the power density in the laser beam.

The appreciable spread (0.5–2 k eV) of the initial energies of the ions formed when giant laser pulses act on a solid[3] makes many instruments with ordinary focussing unsuitable for mass-spectrometric analysis in this case. For example, the design of a time-of-flight mass-spectrometer with a laser ion source has been described[31], but its low resolving power (< 10), caused by the appreciable spread of the initial ion energies, apparently precludes its use for analytical mass-spectrometry. Calculations[32] for a time-of-flight mass-spectrometer with a laser source, designed for the analysis of gaseous mixtures in metals, showed that the high initial spread of the kinetic ion energies ($\Delta T \simeq 1000$ eV) requires an additional acceleration of the ion beam in order to achieve adequate mass resolution. The authors quote data for the time and amplitude characteristics of the accelerating potential pulses necessary to achieve a mass resolution of approximately 15. Theoretical estimates of the sensitivity of this instrument yield approximately 10^{-7}–10^{-8} at.% in the determination of gaseous impurities. However, allowance for the influence of the space charge of the ion beam apparently leads to an impairment of the analytical characteristics of the instrument compared with the calculated characteristics.

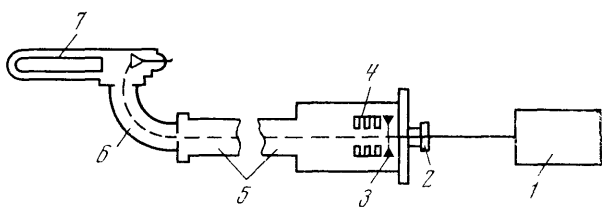


Figure 5. Schematic representation of the instrument with an energy analyser: 1) Q-switched laser; 2) object lens; 3) foil specimen; 4) single-potential lens; 5) flight space; 6) energy analyser; 7) scintillation detector.

In order to improve the resolution of the mass-spectrometer, an electrostatic analyser with a 90° deflection of the ion beam was placed[33] at the end of the flight tube (Fig. 5). Nevertheless, the resolving power of the instrument did not exceed 30. This is probably due to the high space charge in the ion beam. In order to improve the

resolving power of the instrument (up to 90), some investigators[35-39] placed at the end of the flight tube (approximately 3 m long) an analyser with crossed electrostatic and magnetic fields (Fig. 6). The design of the instrument also made it possible to employ the electrostatic and magnetic analysers separately. A characteristic feature of the time-of-flight instrument used in some investigations[41-47] (Fig. 7) involves the use of the analytical component of a commercial MKh 1303 mass-spectrometer as the analyser. A resolution of 100 was obtained at the 5% level of the peak height. The fundamental analytical characteristics of the instrument employed[41-47] are as follows: lower limit of detection approximately 1×10^{-4} at.%, error of analysis 15% for an impurity concentration of approximately 10^{-2}%, information capacity[48] of the mass-spectrometer approximately 5×10^3 bits. The parameters of the laser radiation were $E \simeq 1$ J, $\tau \simeq 40$ ns, and $q \simeq 2 \times 10^9$ W cm^{-2}. The high density of the laser plasma[2,3] and the large scatter of the ion energies forced the investigators[35-39,41-47] to reject any ion-optical systems in the laser source. The ions spread throughout the flight tube with the energies which they acquired at the initial stage of the fragmentation of the condensed portion of the plasma. The lack of ion focussing and the considerable length of the flight space lead to an appreciable impairment of the transmission coefficient and hence to a decrease of sensitivity to approximately 10^{-5}–10^{-4} at.%.

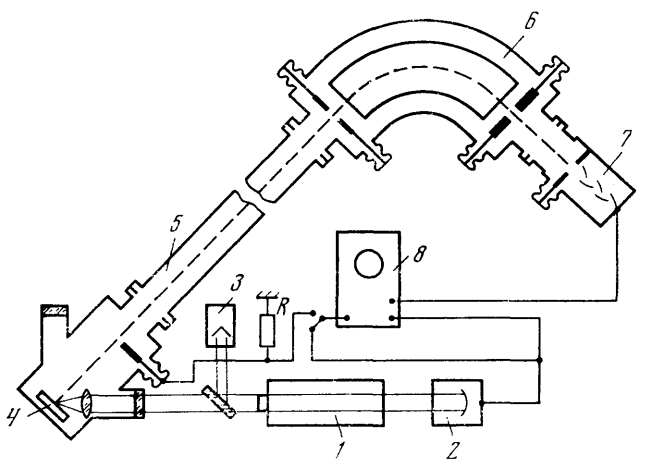


Figure 6. Schematic representation of the instrument with an analyser comprising cross electrostatic and magnetic fields: 1) laser; 2) photoelectric cell; 3) energy measuring device; 4) specimen; 5) time-of-flight analyser; 6) analyser with crossed electrostatic and magnetic fields; 7) secondary electron multiplier; 8) recording oscillograph.

When Q-switched lasers were used, several interesting analytical problems were solved. A Q-switched ruby laser ($\tau \simeq 30$ ns, $q \simeq 10^{10}$ W cm^{-2}) was used to evaporate and ionise thin specimens of a solid[33]. According to the authors' estimates, the efficiency of the ionisation of copper was 10^{-2} ions per atom. The ionisability of certain other thin metallic foils (Al, Fe, Ag, Au, and Li) was approximately the same with the exception of sodium and potassium films, the ionisability of which was higher. Apart from these substances, specimens of solutions of various substances, particularly metal nitrates, hydroxides, and chlorides, were also investigated. Copper and aluminium foils served as supports for these solutions. Peaks corresponding to singly charged and multicharged atomic ions only were observed in the resulting mass spectra. The ionisation efficiencies of various metals in such specimens were approximately the same, but for other components of the specimen, for example H, N, O and Cl, the differences between ionisabilities reached two orders of magnitude.

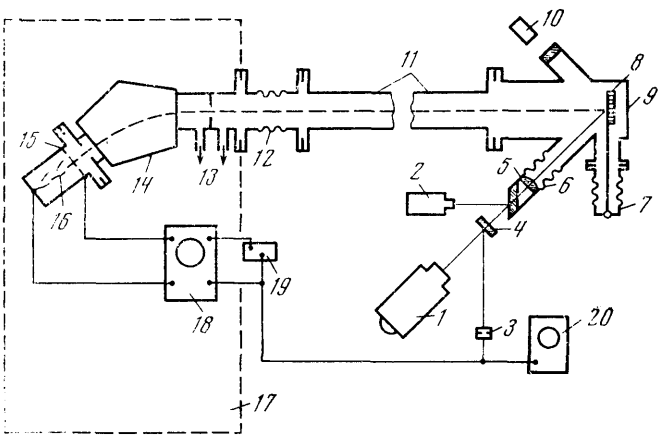


Figure 7. Schematic representation of the instrument with a magnetic analyser; 1) laser; 2) device measuring radiation energy; 3) photoelectric cell; 4) plane-parallel plate; 5) lens; 6) bellows; 7) vacuum manipulator; 8) cassette with specimens; 9) cover of ion source; 10) telescope; 11) flight tube; 12) mechanical compensator; 13) outlet to diffusion pumps; 14) magnetic analyser; 15) retarding potential grid; 16) secondary electron multiplier; 17) analytical section of the MKh-1303 instrument; 18) "Chronotron"; 19) G5-15 generator; 20) time interval measuring device.

The abundances of the isotopes of elements atomised by laser pulses ($\tau \simeq 40$ ns, $E \simeq 0.5$ J) have been measured[36]. The authors note that the accuracy of the determination of the isotope ratios (approximately 3% of the measured quantity) is lower than in measurements on instruments of the static type, because of the relatively low accuracy of the measurements which is in general characteristic of dynamic instruments. It was concluded that fast measurements of the isotopic abundances, restricted to a region limited mainly by the aberrations of the optical system and the divergence of the laser beam, may be made by the proposed method.

Analysis of lead, indium, and niobium specimens led to the detection of impurities[39] whose content in the lead specimen was approximately 10^{-4} at.%. The authors believe that the sensitivity of the instrument is sufficient to detect impurities at concentrations of approximately 10^{-5} at.%.

The possibility of investigating the elemental composition of multicomponent geological rocks has been reported[37]. The ion source used to evaporate and ionise the sample was a neodymium laser ($\tau \simeq 40$ ns, $q \simeq 4 \times 10^{10}$ W cm^{-2}). Comparison of the results with data from emission spectroscopic analysis showed that elements with low atomic weights can be more effectively determined on a laser mass-spectrometer. In order to determine the concentrations of the elements in geological rocks, the energy distributions of the detected ions were found from the experimental results. Integration of the distributions makes it possible, according to the authors, to obtain the average atomic concentrations of the elements present in the sample. However, this method of determining the concentrations of the elements is extremely laborious and unsuitable for local or layer-by-layer analysis of the impurities present in the specimen. It should also be noted that, in order to employ this method, it is necessary to make sure initially that the ionisations of the atoms of various substances under the influence of laser radiation with flux density $q \simeq 4 \times 10^{10}$ W cm^{-2} are equally probable.

The experimental determinations of the stoichiometric compositions of ionic crystals of the type $A_nB_mC_p$ have been published[38]. The power density of the laser emission was $q \simeq 2 \times 10^9$ W cm^{-2} in the analysis. The stoichiometry of the selected crystals was determined from the ratio of the peak heights for singly charged ions of the elements A, B, and C having an energy of 100 eV. This method for the determination of stoichiometry conflicts with other data[33], which, however, may be accounted for by the differences between the objects analysed in the two investigations[33,38] and also by the differences between the energies of the ions used for analysis†.

Using a time-of-flight mass spectrometer (with an electrostatic analyser to improve mass resolution) in combination with an "Arzni" laser, Kholodar' et al.[40] studied the distribution of carbon in silicon specimens. By scanning the surface of the specimen with a laser beam, they established that carbon may be present in the form of inclusions consisting (according to electron diffraction data) of the β-phase of silicon carbide. The size of the inclusions, determined by electron microscopy, is between 0.1 and 20 μm. The analytical characteristics of the mass-spectrometer are not quoted.

It is seen from the above results that the problem of the consistency between the composition of the substance in the solid phase and the composition of the ions formed from the solid under the influence of giant pulses of laser radiation was not studied in the above investigations[31-40]. The relevant reports do not therefore describe methods for the quantitative analysis of impurities in the elements and in the compounds, stating merely the possibility of the qualitative analysis of solids using laser ion sources. For a quantitative determination of impurities, it is necessary to know the coefficients of the relative sensitivity to impurities in different matrices, or the instrument must be calibrated against standards with known impurity contents, or analytical methods without standards must be developed‡.

In view of the foregoing considerations, the authors[41-46] concentrated attention on the justification of methods for the quantitative mass-spectrometric analysis of the elements using calibration graphs[42,43] and an internal standard[46] as well as the method of the layer-by-layer analysis[44,45,47] of solids with ionisation of the sample by giant laser pulses.

For the purpose of mass-spectrometric analysis using a laser ion source, it was necessary to elucidate the dependence of the ejected mass of the irradiated specimen (the sample size) on the concentration of its impurities. The upper limit of the impurity concentrations for which the mass ejected from specimens with a matrix of the given type changes under the influence of irradiation by giant laser pulses was studied using silicon, iron, and aluminium specimens with significantly different types of chemical bonds between the atoms in the lattice. The form and concentration of the impurities in these specimens were known. It was found[46] that the ejected mass is independent (within the limits of a 12% experimental error) of the content of impurities if the concentration of the latter does not exceed 9, 6, and 0.9 at.% for aluminium, iron, and silicon specimens respectively.

In the development of the method for the quantitative analysis of steel for carbon, manganese, and chromium, spectroscopic standards were used[43]. It was established that the dependence of the height of the mass-spectrometric peak of the impurity element on its concentration is linear. The sensitivity of the instrument to the impurity depends on its nature and can vary severalfold. The data used to plot calibration graphs for each impurity were reproduced several times and the slope (sensitivity) for each impurity did not vary with time. It was concluded that the sensitivity of the instrument to carbon in silicon is twice as high as the sensitivity to carbon in steel and approximately equal to the sensitivity to vanadium in steel. Consequently the sensitivity depends not only on the nature of the impurity element but also on the nature of the main substance. Thus, quantitative mass-spectrometric analysis of solids requires at least one standard of the same type as the specimen analysed.

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†The energy spectrum of the ions formed under the influence of giant laser pulses is complex (see, for example, Bykovskii et al.[60]) and the form of the spectrum has still not been fully explained. Unfortunately, the authors of the analytical studies do not by any means always state the energies of the ions used for analysis. The problems of the determination of the stoichiometric compositions of solid binary compounds have been investigated in greatest detail by I.D.Kovalev, N.V.Larin, and G.A.Maksimov [Letters to Zhur.Tekh.Fiz., 1, 798 (1975)] and by G.G.Devyatykh, I.D.Kovalev, N.V.Larin, and G.A.Maksimov [Dokl.Akad.Nauk SSSR, **226**, 109 (1976)], whose papers were published after this review had been written.

‡The problems of the development of methods without standards are dealt with in the reports by I.D.Kovalev, G.A.Maksimov, and N.V.Larin ["XI Mendeleevskii S'ezd po Obshchei i Prikladnoi Khimii; Analiticheskaya Khimiya, Referaty Dokladov" (The XIth Mendeleev Congress of General and Applied Chemistry. Analytical Chemistry. Abstracts of Reports), Izd.Nauka, Moscow, 1975, p.110] and Yu.A.Bykovskii, G.I.Zhuravlev, L.M.Babenkov, T.A.Basova, X.I.Belousov, V.M.Gladskoi, V.V.Gorshkov, V.G.Degtyarev, and V.N.Nevolin [V Vsesoyuznaya Konferentsiya po Polucheniyu i Analizu Veshchestv Osoboi Chistoty, Gor'kii, Tezisy Dokladov" (The Vth All-Union Conference on the Preparation and Analysis of Specially Pure Substances, Gorky. Abstracts of Reports), Izd.Nauka, Moscow, 1976, p.125], which were published after this review had been written. The second communication reports the attainment of a detection limit of 10^{-7} at.%.

Despite its satisfactory accuracy (to within approximately 8%), the method of quantitative analysis using calibration graphs plotted from the determinations of impurities in standard specimens suffers from a number of disadvantages associated with the lack of standard specimens for different impurities in matrices of various types. For this reason, a method has been developed for quantitative mass-spectrometric analysis without standards[46]. In a study of the effect of giant laser pulses on the elements, the authors established that, for these substances, the number of ejected atoms (N), the yield of ions (n^+), and the ionisability ($\epsilon = n^+/N$) have a periodic relation to the atomic number of the element. The absolute ionisability of iron, for example, is 1.4%§, which is close to the value of Fenner and Daly[33]. It has been shown that the ratio of the ionisability of the impurity to the ionisability of the matrix is equal to the coefficient of relative sensitivity[49] in mass-spectrometric analysis¶. Depending on the nature of the material of the matrix and the impurity, the above coefficient can vary by a factor of ten[46]. A method for the quantitative analysis of the elements using an internal standard, which is the substance of the matrix of the given specimen, has been developed on the basis of these data.

Since the coefficient of relative sensitivity K for many pairs of elements is unknown, a formula has been proposed[46] for the estimation of this quantity:

$$K = \frac{\Delta Q_i \varphi_i \sigma_0^2}{\Delta Q_0 \varphi_0 \sigma_i^2}, \qquad (1)$$

where ΔQ is the heat of sublimation, φ the ionisation potential, σ the cross-section for the ionisation of the atoms by electrons, and the subscripts i and 0 refer to the corresponding impurity element and the matrix. For the majority of the elements, the calculated and experimental data are in satisfactory agreement.

The results of the analysis of the impurities in various standard steels, specimens of silicon, chromium, germanium, copper, and aluminium indicate the possibility of employing the method with an internal standard. The accuracy of the analysis is to within approximately 15% for an impurity concentration of approximately 10^{-2} at.% and the lower limit of the detection of impurities is 10^{-4}–10^{-3} at.%, depending on the nature of the impurity and the main substance.

The effect of the giant laser radiation pulse on the solid leads to the appearance of a crater at the point of the interaction of the laser beam with the surface of the specimen[3]. The average thickness (H) of the layer of substance removed by one laser pulse has been determined[45] from the results of Devyatykh et al.[41] The results of the calculation of H are presented in the Table with a relative error not exceeding 20%. The thicknesses of the layers removed from the majority of elements are not quoted in the literature, but the values of H for silicon agree satisfactorily with the data of Grevtsev et al.[50] The determination of H for different energy densities of the laser beam showed that an increase of the energy density from 0.35×10^2 to 1.6×10^2 J cm^{-2} leads to an increase of the thickness of the layer removed by a factor of 2–4.

The average thicknesses (H) of the layer removed for a radiation energy of 1 J, area exposed to radiation $S = 1 \times 10^{-2}$ cm^2, and a pulse duration of 40 ns.

Element	H, μm	Element	H, μm
C(graphite)	3.22	Zn	0.53
Al	0.7	Ge	1.92
Si	1.49	Zr	0.37
Mg	1.08	Nb	0.16
V	0.29	Mo	0.17
Cr	0.25	Ag	0.51
Fe	0.42	Cd	0.64
Ni	0.45	Sn	2.19
Cu	0.21		

The concentrations of the impurities detected in the layer of substance can be determined from the mass spectrum. The lower limit of the detection of impurities in the layer-by-layer analysis is at the level of 10^{-4} at.% and can vary over a factor of ten depending on the ionisability of the matrix and the impurity; the error of the measurements is approximately 25%. The spatial resolution with respect to depth in the method involving the laser probing of solids is at least 0.5 μm for the majority of the substances investigated (see Table). For iron, niobium, molybdenum, and many other transition metals, the resolution with respect to the depth of the layers removed reaches 0.05 μm for an energy density of the giant laser pulse of approximately 0.35×10^2 J cm^{-2}. The layer-by-layer analytical method has been used[47] to investigate the distribution of carbon in chromium films. It is seen from the results that the employment of giant laser pulses to evaporate and ionise a sample in the ion source of the mass spectrometer makes it possible to take into account the distribution of impurities in thin layers of solids.

Taking into account the above features, the use in mass spectrometry of lasers working under giant pulse conditions may be regarded as promising for the determination of the average content of impurities and for the elucidation of their distribution with respect to depth and on the surface of solids†.

§The dense plasma formed under the influence of giant laser pulses is almost fully ionised ($\epsilon \simeq 100\%$). However, at the end of the laser pulse, there is sufficient time for the dispersal of only a small part (n^+) of the peripheral ions. The so called "quenching" of the degree of ionisation is observed for ions of this kind[60]. These ions can in fact be recorded in mass-spectrometric analysis. The remaining ions on the inner part of the concentrated region of the plasma recombine almost completely to neutral atoms within distances of the order of the initial size of the plasma[61]. Attempts to remove all the ions from the concentrated part of the plasma have not so far been described in the literature.

¶Ions corresponding to the high-energy maximum[60] in the energy distribution for the given element have been used for analysis[41–47].

†The report by S.V.Gaponov, I.D.Kovalev, V.I.Luchin, G.A.Maksimov, L.I.Pontus, and A.I.Suchkov in "V Vsesoyuznaya Konferentsiya po Polucheniyu i Analizu Veshchestv Osoboi Chistoty, Gor'kii, Tezisy Dokladov" (The Vth All-Union Conference on the Preparation and Analysis of Specially Pure Substances, Gorky. Abstracts of Reports), Izd.Nauka, Moscow, 1976, p.132, was published after this review had been written. The authors obtained a focussed spot 15 μm in diameter, which enabled them to investigate the distribution of microinclusions in solids.

IV. COMPARATIVE CHARACTERISTICS OF LASER, SPARK, AND THERMIONIC ION SOURCES USED IN THE MASS-SPECTROMETRIC ANALYSIS OF SOLIDS

An ion source with surface ionisation (a thermionic source) was proposed for mass-spectrometers by Dempster in 1918. In 1936, he developed methods for obtaining ions based on the electrical breakdown of the interelectrode gap *in vacuo* (spark ion source). The first publications[4-6] on the use of lasers in the ion sources of mass-spectrometers appeared in 1963. A monograph dealing with the mass-spectrometric methods using ion sources with electric discharges[53] states that the authors included in the book a chapter on a laser source which successfully supplements the technique employing a spark source. It is also noted in this monograph that the available information about laser sources is at present inadequate. The comparative characteristics of the thermionic, spark, and laser mass-spectrometric methods are described below. The source with secondary ion–ion emission has been excluded from consideration, because quantitative analytical methods have not so far been developed for this method of obtaining ions from a solid.

When the surface of a metal with the electron work function φ and the first ionisation potential I is heated to a certain temperature, there is a definite probability of evaporation of positive and negative ions together with neutral species. The relative intensities of the fluxes of positive ions n^+ and neutral atoms n^0 are defined by the Sacha–Langmuir equation (see, for example, Kaminsky[54]). The ionisation efficiency varies exponentially with the difference between the electron work function and the ionisation potential. For alkali metals on the surface of tungsten, $\varphi - I > 0$ and the ionisation efficiency in evaporation is approximately unity. If the difference $\varphi - I < 0$, which occurs with the majority of elements, the ratio n^+/n^0 decreases[1] to 10^{-6}. In order to employ the thermionic emission effect in mass-spectrometry, ion sources with one or three tungsten filaments[1,54] and a crucible ion source[55] are used. The mass-spectrometers of types MI 1305, MI 1308, MI 1309, MI 1310, and MI 1311 produced in the USSR are nowadays equipped with three-filament ion sources with surface ionisation.

Three types of sources can be distinguished in accordance with the method used to achieve the electrical breakdown of the vacuum gap[1,49]: the high-frequency spark source, the source of the "vacuum vibrator" type, and the low-voltage source. The high-frequency spark source has been used most frequently in analytical mass-spectrometry. It has been shown in a report by Gorman[56] and in many subsequent publications that the efficiencies of the ionisation of the atoms of various elements are different in the high-frequency spark source. The quantity characterising this difference is the coefficient of relative sensitivity K which is determined empirically using standard specimens. Extensive data on the determination of relative sensitivity coefficients have been compiled in a monograph[49]; it has been noted that K remains constant for a wide range of impurity concentrations in the matrix investigated. The same applies to a laser ion source[43,46]. In the spark source, the differences between the relative sensitivity coefficients for a given impurity in different matrices can reach an order of magnitude. For example K for indium[49] is 1.1 in iron and 9.2 in zinc. The differences between the values of K for a laser source[46] are of the same order of magnitude‡. Consequently, when no account is taken of the corrections introduced by the coefficient of relative sensitivity, the error in the determination of the concentration (for both spark and laser sources) may reach 1000%. Since the values of K for all impurities in different substances cannot be obtained experimentally, attempts have been made in spark mass-spectrometry to determine them from certain physical parameters characterising the substance. The best agreement with experiment is given by the calculation of K from the formula[49] $K = \sigma/\Delta Q\varphi^4$, where σ is the effective ionisation cross-section of the atom, ΔQ the heat of sublimation, and φ the ionisation potential. Comparison of the above relation with Eqn. (1) demonstrates some similarity between the evaporation and ionisation processes when the substance is acted upon by the laser radiation and the "spark".

Thus the differences between the ionisabilities of the atoms of various elements in spark and laser sources are an order of magnitude. A much higher selectivity in the ionisation of the substance is characteristic of the thermionic source, the difference between the ionisation efficiencies reaching in this case six orders of magnitude. However, in view of the limitations of the thermionic emission method associated with the difficulty of preparing the samples for analysis, the possibility of their contamination, and the effect of the "memory" of the thermionic source[57], the authors of a monograph[52] note that the method is not universally applicable in mass-spectrometry.

The sensitivity of the analysis by spark mass-spectrometry is 10^{-5}–10^{-7} at.%.[1,49,53] The sensitivity of the determination of impurities when a laser ion source is used amounts to 10^{-4}–10^{-5} at.%, but the comparatively low sensitivity of the laser method can be explained by the inadequacy of the ion-optical systems of the mass spectrometers§ which have been used in combination with this ion source; there was no ion-optical arrangement directly in the source[33-46]. In the thermionic emission method, the sensitivity of detection is 10^{-5}–10^{-7} at.% only for alkali metals, while for the majority of other elements it is less satisfactory by several orders of magnitude[1,57].

The formation of ions in the laser source is probably more efficient than in the spark source. Thus it has been stated[49] that, in order to detect an impurity at the level 10^{-3} at.% in substances with a high atomic weight, the volume of the specimen which must be atomised in the ion source is approximately 3×10^{-5} cm^3. This corresponds (for average densities of the substance $\rho \simeq 5$–6 g cm^{-3}) to the atomisation of a mass of approximately 2×10^{-4} g. The ejection of such a mass may be achieved only for comparatively long exposures to the spark. In a laser ion source, impurities at a concentration of 10^{-3} at.% can be detected after a single exposure to a giant laser pulse. The ejected mass does not then exceed 10^{-6} g for the majority of substances. The integral ion current generated under the influence of a single laser radiation pulse is then > 1 A. The coefficient of the ionisation efficiency is $n^+/n^0 \simeq 10^{-2}$. The corresponding currents for spark ion sources are not quoted in the literature.

The comparatively long exposures to the spark required to detect an impurity at a level $\geqslant 10^{-3}$ at.% hinder to a large extent local layer-by-layer analysis of solids. The scope of the laser ion source for local layer-by-layer analysis is characterised by average thicknesses of the layer removed by a single layer pulse (see Table). The size of the spot in analysis using a laser reaches 10^{-5} cm^2

‡ See the second footnote to Russ. p. 2131.

§ See the first footnote to Russ. p. 2130.

and the ease with which a given section of the surface to be irradiated is selected makes it possible to investigate, for example, the distribution of gases in the grains and along the intergranular boundaries of metals. For the above reasons, the method of layer-by-layer analysis using a laser[45] is simpler than the corresponding method using a spark ion source[58]. There are no methods of layer-by-layer analysis using a thermionic source.

The spark ion source does not apparently allow experiments designed to investigate the surface sorption of gases. The application of a laser makes it possible to investigate the composition of the gases sorbed on the surface, since giant laser pulses with $q \simeq 10^7$ W cm^{-2} do not disrupt the specimen but do eliminate the gases present on the surface of the sample[45,59].

The employment of a laser in the ion source permits a rapid determination of the composition of the substance. The time consumed in obtaining the complete mass-spectrum of the impurities in the substances analysed does not exceed 2–5 min. When the spark source is used, the time is several hours. The simple structure of laser mass spectra (giant pulses), consisting of the lines corresponding to singly and multiply charged atomic ions[35,46], permits a rapid interpretation of the spectrogram, while the structure of the spark mass-spectra is very complex[1,49,53]. The lines recorded in the spectrum correspond to a wide variety of multiply charged and polyatomic ions. The number of lines depends on the number of isotopes of the element, its physical properties, and the parameters of the spark discharge. The mass-spectrum always contains lines due to the ionisation of the residual gases. In order to take into account the organic impurities and to make sure that the lines of the multiply charged and polyatomic ions detected in the mass-spectrum do not overlap, the analytical lines of the impurities, the resolving power of the mass-spectrometer must be fairly high ($\geq$ 1000).

In analysis using a laser ion source, it is in fact immaterial whether the test specimen is a conductor, a dielectric, or a semiconductor. Analysis of dielectric materials and geological rocks on a mass-spectrometer with a spark ion source requires fairly complex preliminary operations owing to the impossibility of the direct analysis of non-conducting solids in a spark source. Analysis of dielectrics is based on the application of special "igniting" electrodes (probes) made of conducting high-purity materials. The electrodes for the analysis of non-conducting powders are made by packing the samples into metallic tubes, by pressing them with added graphite powder, or by sputtering films of the dielectric investigated onto metallic electrodes[49]. The complexity of the spark mass-spectra is in this case aggravated by lines due to the conducting additives introduced into the substance analysed.

The error in the determination of the concentration of impurities using a laser ion source is 12–15%, which corresponds approximately to the errors in spark mass-spectrometry[49]. Such non-reproducibility of the results is caused mainly by the scatter in the parameters of the laser radiation pulses. The rapid development of laser techniques gives rise to the hope that in the immediate future the characteristics of the lasers will be improved and that this will increase the accuracy of the results obtained on mass-spectrometers with laser ion sources.

The characteristics of laser ion sources described above indicate the possibility of extending the range of problems soluble by the mass-spectrometric analysis of solids as well as good prospects for the development of the mass-spectrometric analytical method using laser ion sources.

REFERENCES

1. I. P. Alimarin (Editor), "Fizicheskie Metody Analiza Sledov Elementov" (Physical Methods for the Determination of Trace Elements) (Translated into Russian from English), Izd. Mir, Moscow, 1967.
2. J. F. Ready, "Effects of High-Power Laser Radiation" (Translated into Russian), Izd. Mir, Moscow, 1974.
3. A. M. Bonch-Bruevich and M. A. El'yashevich (Editors), "Deistvie Izlucheniya Bol'shoi Moshchnosti na Metally" (The Effect of High-Energy Radiation on Metals), Izd. Nauka, Moscow, 1970.
4. R. E. Honig and F. P. Wolston, Appl. Phys. Letters, 2, 138 (1963).
5. R. W. Linlor, Appl. Phys. Letters, 3, 210 (1963).
6. N. R. Isenor, Canad. J. Phys., 42, 1413 (1964).
7. L. A. Arbuzov, V. A. Danilkin, Ya. A. Imas, V. A. Molchanov, and A. G. Mileshkina, Zavod. Lab., 34, 1199 (1968).
8. G. F. Ivanovskii, L. M. Blyumkin, S. V. Varnakov, and L. P. Lisovskii, Zavod. Lab., 34, 1263 (1968).
9. G. F. Ivanovskii and S. V. Varnakov, Zavod. Lab., 35, 956 (1969).
10. G. D. Glebov, N. A. Iofis, and M. S. Chupina, Izv. Akad. Nauk SSSR, Ser. Fiz., 35, 644 (1971).
11. V. S. Talaev and V. A. Danilkin, Zhur. Anal. Khim., 29, 773 (1974).
12. R. A. Savinkov, A. A. Kiselev, and O. P. Obukhov, Zhur. Anal. Khim., 29, 779 (1974).
13. F. F. Vodovatov, G. V. Indenbaum, and A. V. Vanyukov, Fiz. Tverd. Tela, 12, 22 (1970).
14. K. A. Lincoln, Int. J. Mass-Spectrom. Ion Phys., 2, 75 (1969).
15. B. E. Paton and N. R. Isenor, Canad. J. Phys., 46, 1237 (1968).
16. P. D. Zavitsanos, Carbon, 6, 731 (1968).
17. "Lokal'nye Metody Analiza Materialov" (Local Methods for the Analysis of Materials), Izd. Metallurgiya, Moscow, 1973.
18. A. M. Morozov and M. S. Chupina, "Elektronnaya Tekhnika" (Electronic Engineering), Series 6, "Materialy" (Materials), 1972, No. 6, p. 105.
19. R. H. Scott, P. F. S. Jacson, and A. Straghaim, Nature, 232, 623 (1971).
20. F. T. Vastola and A. T. Pirone, in "Advances of Mass-Spectrometry", Berlin, 1968, Vol. 4, p. 107.
21. T. Bercowits and W. A. Chupka, J. Chem. Phys., 40, 2735 (1964).
22. V. S. Ban and B. E. Knox, Int. J. Mass-Spectrom. Ion Phys., 3, 131 (1969).
23. V. S. Ban and B. E. Knox, J. Chem. Phys., 52, 243 (1970).
24. V. S. Ban and B. E. Knox, J. Chem. Phys., 52, 248 (1970).
25. V. P. Zakharov, I. M. Protas, and V. N. Nechuev, Zhur. Tekh. Fiz., 41, 1296 (1971).
26. H. E. Winter and E. Kay, "Proceedings of the 18th Annual Conference on Mass Spectrometry and Allied Topics, San Francisco, California, 1970", p. B277.
27. V. P. Zakharov and I. M. Protas, Zhur. Tekh. Fiz., 42, 670 (1972).
28. V. P. Zakharov and I. M. Protas, Dokl. Akad. Nauk SSSR, 215, 562 (1974).
29. H.-I. Dietze and H. Zanh, Exp. Tech. Phys., 20, 389 (1972).
30. H. B. Gutbier, Z. Naturforsch., **14a**, 32 (1959).
31. L. C. Bernal, L. P. Levine, and J. F. Reedy, Rev. Sci. Instr., 37, 938 (1966).

32. G.V.Mikhailova, N.P.Pergament, Yu.A.Kulakov, and A.S.Semenov, Symposium, "Metody Opredeleniya i Issledovaniya Soderzhaniya Gazov v Metallakh" (Methods for the Determination and Investigation of the Gases Present in Metals), Izd.Nauka, Moscow, 1968, p.164.
33. N.C.Fenner and N.R.Daly, Rev.Sci.Instr., 37, 1068 (1966).
34. K.Board and W.G.Townsend, Microelectron Reliab., 5, 251 (1966).
35. Yu.A.Bykovskii, V.N.Dorofeev, V.I.Dymovich, B.I.Nikolaev, and S.M.Sil'nov, Zhur.Tekh.Fiz., 38, 1194 (1968).
36. Yu.A.Bykovskii, V.I.Dymovich, Yu.P.Kozyrev, V.N.Nevolin, and S.M.Sil'nov, Zhur.Tekh.Fiz., 40, 2401 (1970).
37. Yu.A.Bykovskii, B.A.Grigin, V.I.Dymovich, Z.N.Matveeva, and V.N.Nevolin, Zhur.Tekh.Fiz., 41, 442 (1971).
38. Yu.A.Bykovskii, N.M.Vasil'ev, N.N.Degtyarenko, and V.N.Nevolin, Zhur.Tekh.Fiz., 42, 1749 (1972).
39. Yu.A.Bykovskii, V.I.Dorofeev, V.I.Dymovich, B.I.Nikolaev, S.V.Ryzhikh, and S.M.Sil'nov, Zhur. Tekh.Fiz., 39, 1272 (1969).
40. G.A.Kholodar', Yu.V.Dankovskii, G.A.Dobrokhotov, G.A.Zykov, V.V.Konoplyannyi, and V.L.Vinetskii, Ukrain.Fiz.Zhur., 18, 1452 (1973).
41. G.G.Devyatykh, N.V.Larin, G.A.Maksimov, and A.I.Suchkov, Zhur.Fiz.Khim., 47, 2917 (1973) [Russ.J.Phys.Chem., No.11 (1973)].
42. N.V.Larin and G.A.Maksimov, Trudy po Khim.i Khim.Tekhnol., No.4, 133 (1973).
43. N.V.Larin and G.A.Maksimov, Symposium, "Polu-chenie i Analiz Veshchestv Osoboi Chistoty" (The Preparation and Analysis of Specially Pure Substances), Izd.IREA, Gorky, 1974, p.167.
44. G.A.Maksimov, N.V.Larin, and A.I.Suchkov, Trudy po Khim.i Khim.Tekhnol., No.4, 139 (1973).
45. G.G.Devyatykh, G.A.Maksimov, A.I.Suchkov, and N.V.Larin, Zhur.Anal.Khim., 30, 664 (1975).
46. V.G.Devyatykh, N.V.Larin, G.A.Maksimov, and A.I.Suchkov, Zhur.Anal.Khim., 29, 1516 (1974).
47. V.I.Mel'nikov, B.S.Kaverin, G.A.Maksimov, G.A.Domrachev, N.V.Larin, and G.G.Devyatykh, Dokl.Akad.Nauk SSSR, 219, 929 (1974).
48. H.Kaiser, Anal.Chem., 42, 24A (1970).
49. M.S.Chupakhin, G.I.Ramendik, and O.I.Kryuchkova, "Analiticheskie Vozmozhnosti Iskrovoi Mass-Spektrometrii" (The Analytical Scope of Spark Mass-Spectrometry), Atomizdat, Moscow, 1972.
50. M.V.Grevtsev, V.G.Karbutov, A.S.Skripchenko, and A.A.Uglov, Fiz.i Khim.Obrabotki Materialov, No.3, 8 (1970).
51. G.A.Maksimov, Candidate's Thesis, Gorky State University, 1974.
52. G.P.Barnard, "Modern Mass-Spectrometry" (Translated into Russian), Inostr.Lit., Moscow, 1953.
53. M.S.Chupakhin (Editor), "Mass-Spektrometricheskii Metod Opredeleniya Sledov" (Mass-Spectrometric Method for the Determination of Traces) (Translated into Russian from English), Izd.Mir, Moscow, 1975.
54. M.Kaminsky, "Atomic and Ionic Impact Phenomena on Metal Surfaces" (Translated into Russian), Izd. Mir, Moscow, 1967.
55. V.Voshaae and H.Hinterberger, Z.Naturforsch., 14a, 216 (1958).
56. I.G.Gorman, Anal.Chem., 23, 483 (1951).
57. G.H.Palmer, in "Uspekhi Mass-Spektrometrii" (Advances in Mass Spectrometry) (Translated into Russian), Inostr.Lit., Moscow, 1963.
58. M.S.Chupakhin and G.I.Ramendik, Zhur.Anal.Khim., 25, 1301 (1970).
59. S.M.Bedais, J.Appl.Phys., 40, 4776 (1969).
60. Yu.A.Bykovskii, N.N.Degtyarenko, V.F.Elesin, Yu.P.Kozyrev, and S.M.Sil'nov, Zhur.Eksper. Teor.Fiz., 60, 1307 (1971).
61. M.Mottioli, Plasma Physics, 13, 19 (1971).

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