Magnetic resonance mass spectrometer with resolution 350 000

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A procedure is considered for calculating the optimal parameters of the analyzer of a magnetic resonance mass spectrometer, such as to ensure maximum sensitivity of the instrument at a given resolution. The theoretical conclusions are experimentally confirmed and the possibility of attaining a resolution of 350 000 at half-maximum of the mass line at sufficiently small dimensions of the analyzer is demonstrated (maximum ion trajectory 160 mm). The sensitivity of the mass spectrometer is in this case 7.5×10^{-8} A/Torr. A mass spectrogram of the $^3He^+$–$^3H^+$ doublet is obtained.

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1. INTRODUCTION

The need for developing mass spectrometers with resolution of several hundred thousand is connected with the solution of a number of problems in nuclear physics, geochemistry, analytic chemistry, as well as with the problem of exact measurements of the masses of atoms. During the last 10–15 years there were produced in the world several instruments with resolutions from 100 000 to a million.[1-3] An examination of the characteristics of these instruments shows that they do not combine simultaneously the parameters necessary for the solution of complicated analytic problems connected with the separation of close multiplet lines and with the measurement of large ratios of the components in the analyzed mixture of substances.

The principal analytic parameters of a mass spectrometer are the dispersion, the resolution, and the absolute and the relative sensitivities. The dispersion (the displacement of the ion beam in the plane of the exit slit of the instrument when the ion mass is changed) predetermines in essence both the resolution and the absolute sensitivity, and influences also the mass-spectrum line shape, i.e., it determines also the relative sensitivity. Unfortunately, in static magnetic mass spectrometers the dispersion is determined by the radius of the ion trajectory in the magnetic field, and consequently to increase it is necessary to increase the dimensions of the instrument. Therefore a dispersion amounting to several dozen, and all the more hundreds of mm, for 1% of change in the ion mass in static mass spectrometers is unattainable in practice if the apparatus is to have reasonable dimensions.

When ions are separated by time of flight (as is done in dynamic mass spectrometers), there is no longer a rigid connection between the analyzer dimensions and the dispersion. In such instruments the dispersion can be greatly increased by choosing the parameters of the alternating electric field that controls the motion of the ion packets. Thus, in the magnetic resonance mass spectrometers (MRMS) developed at our Institute, the dispersion at an ion trajectory radius ~100 mm reaches 100 mm and more for 1% change of the ion mass.

It is convenient to characterize the analytic properties of various mass spectrometers by the complex dimensionless parameter

$$K=R\frac{P_{max}}{P_{min}}=R\frac{I_{max}}{I_{min}},$$

where R is the resolution of the instrument at the level of 10% height of the peak; I_{max} is the maximum ion output current of the instrument, corresponding to the maximum attainable partial pressure of the gas in the source ($P_{max}\approx5\times10^{-5}$ Torr); I_{min} is the minimum measured ion current at the output of the instrument ($\sim10^{-18}$ A), corresponding to the minimum recordable partial pressure of the gas in the source P_{min}.

Obviously, the larger the parameter K the better the analytic properties of the separating system. The values of K for the better static instruments without vertical focusing of the ion beam lie in the range 1×10^9–5×10^{10}, while for the magnetic-resonance mass spectrometers they range from 2.5×10^{12} to 5×10^{13}. So large a difference between the values of the parameter K of static and magnetic resonance mass spectrometers gives grounds for hoping to be able to develop MRMS with an ultrahigh resolution and high sensitivity at low values of the ion-trajectory radius in the magnetic field.

2. OPERATING PRINCIPLE OF THE INSTRUMENT

The operating principle of an MRMS with the modulator fed with a sinusoidal voltage has been described quite fully in Refs. 4 and 5. A schematic diagram of the analyzer is shown in Fig. 1. The analyzer is in a uniform magnetic field. Preliminary separation of the ion beam that emerges from the source is carried out in the first static 180° stage. Ions with close values of M/q enter the slit of the modulator and are separated by time of flight in the high-resolution stage. A high-frequency voltage with frequency much higher than the cyclotron frequency of the ions in the given magnetic field is applied to the central electrode of the modulator, while the two lateral electrodes are at zero potential. When passing through the gaps of the modulator, the ion beam is modulated in energy and consequently also in the trajectory radius. The figure shows the instantaneous position of the ion beam. The drift slit S_2 cuts out of the beam short packets that acquire, if the frequency of the modulating voltage is properly set, a second energy increment needed for the ions to land in

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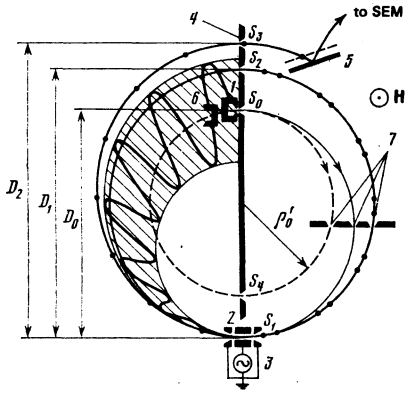

FIG. 1. Schematic representation of the MRMS analyzer: *1*—ion source, *2*—modulator, *3*—high-frequency generator, *4*—ion packets, *5*—reflecting gap, *6*—360° collector, *7*—aperture slits, S_0—exit slit of source, S_1—modulator slit, S_2—drift slit, S_3—exit slit of analyzer, S_4—control slit, D_0, D_1, D_2—orbit diameters.

the exit slit S_2. A reflecting system extracts the beam from the region of the magnetic field and causes it to strike a secondary electron multiplier (VÉU-6), whose current is registered with an electrometric amplifier.

With changing ion mass, the cyclotron period T_c (the time of flight of the ions over a closed circle in the magnetic field) changes, the resonance relations needed for the ions to land in the exit slit are violated, and the ions therefore strike the screen on one side of the slit S_3 or the other. Even at a large dispersion, to obtain a high resolution it is necessary that the dimension of the ion packet (in the direction of the trajectories radius) be small as it approaches the slit S_3, and determined mainly by the width of the ion-source slit S_0. To this end one can use a small slit S_2, but then the useful current of the source is very small and accordingly the overall sensitivity of the instrument is small. There exist, however, an operating regime in which narrow ion packets are obtained with a wide slit S_2. This is the so-called compensation regime, wherein the ions of the packet cut out by the slit S_2, accelerated first in the modulator by the rising part of the sinusoidal voltage curve, land in the modulator a second time during the decrease of the voltage.[6] As a result of such a relation between T_c and the period T of the high-frequency generator voltage, the ions of the packet, acquiring a maximum acceleration during the first pass through the modulator, are minimally accelerated in the second pass through the modulator. As a result, all the ions of the packet have after the two passes practically equal total accelerations, and the packet arrives at the exit slit S_3 in the form of a slightly bent arc. The total width of the packet in the radial direction is then small.

3. PRINCIPLES OF CALCULATION AND CHOICE OF OPTIMAL PARAMETERS OF THE ANALYZER

Prior to this paper, no exact theory was developed for the motion of ions in the compensation regime of an MRMS analyzer, and the structural parameters of the instruments were determined semi-empirically. The possibility of taking exact account of the dispersion

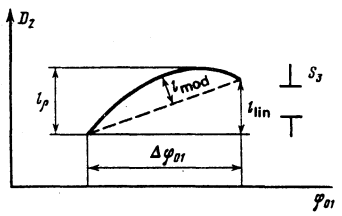

FIG. 2.

and of the form of the ion packets ahead of the exit slit S_3 (see Fig. 1) has made it possible to determine the optimal parameters an analyzer with given dimensions. In analogy with the preceding paper,[7] where exact equations were obtained for the motion of the ion in resonant operation of an MRMS with a three-grid modulator, for the compensation regime of the MRMS we obtained a system of nine transcendental equations, which connect the phases and angles of the ion flight over the gaps between the electrodes of the three-chamber modulator. The coefficients of this equation are the geometric, electric, and frequency parameters of the analyzer. By specifying the phase for the first entry of the ions into the modulator φ_{01}, and by solving the system of obtained equations, it is possible to determine the increment of the ion-orbit diameter after two passes through the modulator. The position of these ions (ion packet) ahead of the slit S_3, calculated with a computer, is represented by the curve of Fig. 2. The shape of the packet, its length, and orientation relative to the slit S_3 are determined by the width of the drift slit S_2, by the parameters of the modulator, and by the character of the nonlinear dependence of the increment of the ion-orbit radius on their phase of entry in the first and second accelerations in the first and second accelerations in the modulator.

The compensation regime is realized at a packet orientation relative to the exit slit S_3 (Fig. 2) such that

$$l_{lin}=0. \tag{1}$$

In this case the packet has a minimal dimension l_{mod} in the radial direction. The task of the optimization is to find, under the conditions of the compensation regime, a ratio of the analyzer parameters such that the analyzer has maximum sensitivity at a given resolution.

An examination of the operating principle of the analyzer shows that the expression for the resolution over the base of the mass line is of the form

$$R_{\text{base}}=\frac{M}{\Delta M}=\frac{2\pi n\, dD_2}{\Sigma\, dq}, \tag{2}$$

where n is the number of the harmonic and is equal to the integer closest to the ratio of the frequency f of the voltage that feeds the modulator to the cyclotron frequency f_c of the ions in the given magnetic field:

$$q=2\pi(f/f_c-n); \tag{3}$$

Σ is the sum of the widths of the ion packet at the exit slit of the analyzer and the slit S_3 itself.

The value of Σ is determined by the expression

$$\Sigma=S_0+\frac{D_0}{2}\left(1-\frac{D_0}{D_2}\right)\left(\gamma^2+\frac{\Delta U_0}{U_0}\right)+l_{magn}+l_{mod}+S_3, \tag{4}$$

in which D_0 and D_2 are the diameters of the orbits (see

Fig. 1); γ is half the divergence angle of the ion beam emerging from the source; ΔU_0 is the width of the ion energy distribution in the beam emerging from the source; U_0 is the potential difference that accelerates the ions in the source; l_{magn} is the integral broadening of the ion packet at the slit S_3, and is connected with the presence of spatial inhomogeneities of the magnetic field; l_{mod} is the nonlinear component of the dimension of the ion packet. At a given distribution of the inhomogeneities of the magnetic field, the value of l_{magn} is determined by the procedure considered in Ref. 8.

An expression was obtained also, characterizing the absolute sensitivity of the analyzer:

$$\eta=(k-l_{mod})(2r_c l_{mod}-l_{mod}^2)^{1/2}/\pi D_0. \quad (5)$$

This quantity has the dimension of length and indicates the part of the source slit S_0 from which the current goes directly to the exit of the analyzer. In Eq. (5), k is determined from (4) and is equal to

$$k=\Sigma-\frac{D_0}{2}\left(1-\frac{D_0}{D_2}\right)\left(\gamma^2+\frac{\Delta U_0}{U_0}\right)-l_{magn}-S_3, \quad (6)$$

and r_c is the ion-packet curvature radius. A test of the extremum of Eq. (5) shows that η has a maximum if

$$S_0=2l_{mod}. \quad (7)$$

Thus, from the condition of maximum sensitivity at a given resolution we obtain the condition for choosing the width of the slit S_0 of the ion source and of the drift slit S_2 with aid of expressions (4) and (7), inasmuch as at a given shape of the ion packet the width S_2 is uniquely connected with l_{mod}. The choice of the optimal values of the entire set of parameters of the MRMS analyzer was made with the aid of a computer. A program was written for the solution of the system, using nine transcendental equations, as well as of Eqs. (2), (4), and (5) and conditions (1) and (7). The program made it possible to calculate η for each set of initial parameters and for the specified resolution, as well as the values of those parameters which were not specified initially. By varying the sets of the initial values of the parameters we obtained the optimal parameters corresponding to our technical capabilities. At the given values $R_{base}=1.5\times10^5$, $B=0.12$ T, and $n=100$ we obtain the following parameters: $d_1=1$ mm, $d_2=2.4$ mm, $d_3=1$ mm, $D_0=186$ mm, $D_1=214$ mm, $D_2=232$ mm, $U/U_0=0.27$, $\Sigma=109$ μm, $S_0=27$ μm, $S_2=1.2$ mm, $S_3=55$ μm, $\eta=0.23$ μm. (Here d_1 and d_3 are the widths of the first and second accelerating gaps, and d_2 is the width of the field-free drift chamber in the modulator.) With these parameters, the dispersion of the instrument is 160 mm for 1% change in the ion mass.

The developed exact theory has made it possible to calculate the maximum permissible (for a 10% decrease of the resolution) instabilities of the principal units of the mass spectrometers. These amount to the following: for the frequency of the modulating voltage $\Delta f/f=1.7\times10^{-7}$; for the amplitude of the modulating voltage $\Delta U/U=1.0\times10^{-4}$; for the accelerating voltage $\Delta U_0/U_0=1.3\times10^{-4}$; for the induction of the magnetic field when the spectrum is recorded $\Delta B/B=1.7\times10^{-7}$.

4. RESULTS OF EXPERIMENT

On the basis of the calculated data we constructed a laboratory mockup of the MRMS. Principal attention was paid to ensuring the necessary operating stability of the supply sources. To study the influence of the inhomogeneities of the magnetic field on the resolution, we were able to vary the height of the ion beam with the aid of a movable wedge-shaped slit located in the modulator region.

The ion-optical system of the ion source with electron impact was simulated with a rubber-membrane installation analogous to that considered in Ref. 9, and was constructed in accordance with the optimal variant obtained in the simulation. The ion source of the instrument has the following characteristics: width of exit slit S_0—27 μm, height—3.8 mm; when the investigated gas is admitted in the analyzer chamber to a pressure $(1-2)\times10^{-6}$ Torr, the output ion current is $\sim1\times10^{-9}$ A; the horizontal angle divergence of the ion beam does not exceed $\pm1.5°$ and the vertical $\pm1°$.

To check on the resolution of the static stage of the MRMS, an ion beam from the source was passed through an auxiliary slit S_4 of width 18 μm and was received by collector 6 (see Fig. 1). At the maximum permissible aberration values assumed in the calculations, the resolution at 10% of the height of the mass peak should be 1500. In our instrument it turned out to be 1900, i.e., the operations were much less than the maximum permissible values.

Since we used a permanent magnet with $B\approx0.12$ T, light masses were tested. The instrument was tuned by varying the accelerating voltage in the ion source from ~1.5 to ~3 kV, and by correspondingly changing the generator frequency. The instrument was tuned to the maximum of the resolution by shifting, within small limits, the draft slit S_2 and rotating the exit slit S_3 relative to the direction of the magnetic field. When accurately tuned, the resolution at half-height of the mass line is ~350 000. The peak has the good shape traditionally obtained with MRMS. At the 1% peak-height level, the resolution is ~110 000 (Fig. 3). The output current of the instrument (the current at the input to the multiplier), at a pressure in the analyzer $(2-3)\times10^{-6}$ Torr, amounts to $\sim2.5\times10^{-13}$ A. The sensitivity of the static stage is $\sim2.5\times10^{-4}$ A/Torr, and the sensitivity of the instrument in

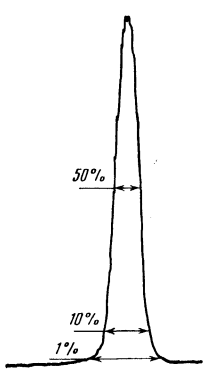

FIG. 3. Mass-spectrum line shape.

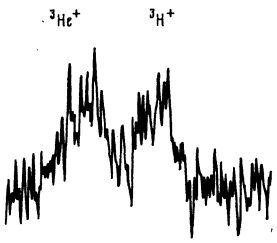

FIG. 4. Mass spectrum of $^3He^+$—$^3H^+$ doublet.

the dynamic regime at maximum resolution is $\sim 7.5 \times 10^{-8}$ A/Torr. The results of the calculations were well confirmed in the investigations of the instrument.

To illustrate the resolution of the mass spectrometer, we plotted the $^3He^+$–$^3H^+$ doublet. The value of $M/\Delta M$ of this doublet is ~150000. To our knowledge, there is no published report of its direct recording. The main difficulty when recording the $^3H^+$–$^3H^+$ doublet is the large dark current due to the β activity of the tritium. The dc component of the dark current exceeded by approximately one order of magnitude the current of the mass line of the tritium. The fluctuations of the dark current resulted in a strong jaggedness of the lines, not connected with the intrinsic shot noise of the ion beam at the input to the secondary electron multiplier. Despite the interfering background of the β electrons, the peaks of $^3He^+$ and $^3H^+$ are well resolved (Fig. 4). We are now taking measures to eliminate the influence of the background β-electron current.

5. CONCLUSION

The considered procedure of calculating the optimal parameters of the MRMS can be successfully used when a MRMS is constructed, and is experimentally confirmed up to a resolution of hundreds of thousands. Experience with the instrument has shown that the development of a mass spectrometer in accordance with the MRMS principle, with a resolution of 500 000–1 000 000 is difficult but technically feasible task. We have in mind here an instrument with a sensitivity sufficient to measure line intensity ratios of the order of 10^5–10^6.

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