

Determination of Rare Earth Elements and Some Toxic Elements in Mine Waters of Donetsk Region by GD-MS

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The paper discusses influence of the molecular ions on the detection limit at determination of Rare Earth Elements and some toxic elements in mine waters of the Donetsk region using glow discharge mass-spectrometry (GD-MS). High resolution mass spectrometer was used to study impact of individual molecular ions formed from components of the sample and discharge gas Ar. Mass spectra were calculated in the area of masses of isotope studied and the most suitable isotopes were selected. It is shown that the sensitivity of analysis depends on the overall composition and isotope and is within 0.1-20 ppb at resolving power of the instrument of the order of 5000. Simulation of mass-spectra allows avoiding erroneous interpretation of mass spectra and correctly estimate detection limit of analysis.

В роботі розглядається вплив молекулярних іонів на межу визначення РЗЕ та деяких токсичних елементів в шахтних водах Донецького регіону з використанням мас-спектрометрії жевріючого розряду. За допомогою спектрометра високої роздільної здатності вивчався вплив окремих молекулярних іонів, які утворюються з компонентів зразка та розрядного газу аргону. Були розраховані мас-спектри в ділянках мас досліджуваних ізотопів та визначено найбільш придатні для аналізу ізотопи. Показано, що чутливість аналізу залежить від загального складу та ізотопу і при роздільній здатності порядку 5000 знаходиться в межах 0.1–20 ррб. Моделювання мас-спектрів дозволяє уникнути помилкової інтерпретації мас-спектрів та правильно визначити межу визначення.

Keywords: glow discharge mass-spectrometry, molecular ions, simulation of mass-spectra, mine waters, detection limit

Ключові слова: мас-спектрометрія жевріючого розряду, молекулярні іони, моделювання маспектру, шахтні води, межа визначення

In the Donetsk region annually is pumped out about 900 million m³ of mine waters, what fall in the surface horizons and significantly worsen the environmental situation. Mine water coming from deep, heavily mineralized and contains virtually all elements of the periodic table of elements. Average salinity of Zaslavko's shaft water is about 6 g/l and it contains about 0.5 g/l of mineral particles in suspension [1]. The waters contain toxic elements that could be involved in the biosphere exchange, which requires the development of methods for neutralizing them. Mine waters contain also certain elements, particularly Rare Earth Elements (REE), silver, at the concentrations at which it becomes economically feasible to extract them. Thus can be solved two problems at once – cleaning the water from toxic elements and extract useful elements. For analysis of geological samples are widely used atomic absorption, emission spectral

methods and mass spectrometry with inductively coupled plasma (ICP-MS) [2-4]. Mass-spectrometry, in contrast to emission spectral analysis, has a higher sensitivity and the ability to measure isotopic ratios. GD-MS is successfully used for highly sensitive and accurate analysis of metals and alloys, as well as non-conductive samples [5, 6]. The goal of this paper is to analyze the mass spectra of samples of dry deposits of mine water in mass areas of rare earth elements and some toxic elements (Be, As, Cd, Hg, Tl, Pb, Th, U), determine detection limit and required resolution of the instrument to achieve it.

Method of molecular interferences calculation

Results of the GD-MS analysis of complex matrices to a great extent is influenced by molecular ions. They are formed as a result of ion-molecular reactions between isotopes of the sample components,

components and discharge gas. For multicomponent geological samples or alloys the number of possible combinations is significant and for correct interpretation of mass spectra it is necessary to consider their impact. Even on devices with high resolution, this problem is urgent. For quadrupole mass spectrometers their effect significantly reduces detection limit of analysis. A large number of molecular interferences requires the development of a method allowing calculation of their concentration for simulation of mass spectra in the mass area of isotopes studied. Implementation of this approach requires the knowledge of the concentration of reacting particles in discharge plasma, but the mass-spectrometric method allows measuring concentration of ions only. Concentrations of neutral particles participating in reactions remain unknown. Much more reliable are data on concentrations of the components in the solid phase. The concept of effective equilibrium constant (EEC) was proposed for calculation of concentration of molecular ions [7]. The concept is based on the assumption of proportionality of concentration of atoms and ions in the plasma to their concentration in the sample. Effective equilibrium constant by definition is the proportionality factor in the equation:

$$[XY^+] = EEC(XY^+)[X]_s[Y]_s \quad (1)$$

where $[X]_s$ and $[Y]_s$ are isotopic concentrations of components in the solid phase, $[XY^+]$ is "concentration" of molecular ions.

EECs introduced by analogy with the common equilibrium constants of chemical reactions with the exception of concentrations of reagents that are the concentration in the solid phase. To compare the concentrations of the components of the sample with "concentration" of molecular ions they are found by the same algorithm that is used to determine their amount in the solid phase, i.e., by normalization of ion current of molecular ions by matrix current. "Concentration" of argon ions and material of secondary cathode were also determined by the same normalization procedure. This approach allows avoid the difficult and unreliable determination of concentrations in plasma discharge and so was very convenient for practical purposes. Effective equilibrium constants are functions of the state and depend on the parameters of the discharge – current, voltage, pressure of argon in the cell, and its temperature. In cryo-cooled cell concentration of molecular ions is several times higher than that for the cell without cooling. The study of these relationships revealed the mechanism of reactions of ionic dimers formation in glow discharge plasma and methods of reducing their amount [8, 9]. It should be noted that the EECs also depend on the substrate material, if technique of secondary cathode is used for non-conducting samples. This is due to the fact that the overall composition of the plasma is determined by the equilibrium concentration of all components - atoms and ions of the sample, substrate and the discharge gas. When using tantalum as secondary cathode

much of the oxygen goes into its compound and stored in plasma (mainly in the form of ion TaO^+ , intense peak of which is always present in the spectra), and in the form of oxides deposited on the walls of the cell. Therefore EECs values were found experimentally with samples of known composition, similar to the samples analyzed using areas of mass spectrum where interferences are well resolved. Accuracy of EECs with regard to the above is of the order of 30 % with samples of similar composition. For samples of different composition or by using a different material of substrate concentration of molecular ions can be determined only approximately, to within an order of magnitude. On the basis of measurements database of EECs was created for reactions of dimers types of ArX^{+1} , XZ^{+1} (X, Z – isotopes of gases, the sample components and of the substrate). Effect of triatomic molecular ions (ArX_2^{+1} , Ar_2X^{+1} , X_2Z^{+1} , XZT^{+1}) can also be significant, so the model takes into account their presence and the presence of doubly charged ions. The value of EECs for bimolecular reactions ranges from 10^{-11} ppm $^{-1}$ for compounds with argon ions to 10^{-8} ppm $^{-1}$ for the intermetallic compounds and metal oxides. The exception is ion ArH^+ , for which the EEC is about 10^{-4} ppm $^{-1}$. This value correlates with the dissociation energy of ArH^+ (3 – 4 eV) [10], which allows us to consider this molecular ion as a true chemical compound, not just solvated dimer. This also explains why the ArH^+ concentration in the discharge plasma is higher than the concentration of ions H^+ , i.e., the equilibrium is shifted toward the formation of ArH^+ .

Experimental method and instrumentation

Analysis was performed using mass spectrometer VG9000 (VG-Elemental, UK). The spectrometer has a dual focus – magnetic sector and electrostatic analyzer, which provides a resolution of the order of 5000 at 5 % above the background or 7,000 – 9,000 at half peak height. The later figures are more convenient for mathematical simulation of mass-spectra because the line shape was approximated by Gauss curve.

Non-conductive samples were analyzed using technique of secondary cathode. Secondary cathode material must meet a number of requirements – to be sufficiently pure for analyte components, the molecular ions formed should not create spectral interferences, react with gases to reduce the gas concentration in the cell, and it is desirable – to be monoisotopic. These requirements mainly meet tantalum. Tantalum substrate, besides, are easily cleaned by treatment in "aqua regia", which does not dissolve tantalum. To determine REEs and other impurities with masses less than the weight of tantalum as secondary cathode was used tantalum of purity 5N. For the analysis of platinum group metals and gold tantalum is not suitable because it formed strong interferences for isotopes of these elements ($^{181}Ta^{16}O$ – ^{197}Au , $^{181}Ta^{13}C$ – ^{194}Pt , $^{181}Ta^{14}N$ – ^{195}Pt and others). To determine these elements high purity aluminum may be used as a

secondary cathode.

The dry residue after evaporation and drying in a drying oven at 200 °C was applied as thin layer on tantalum substrate using a tool from high purity sapphire. The flat cell assembly was used for analysis. The surface of the sample was subjected to preliminary purification by argon ions in the glow discharge at a current of 2 mA during 10 – 15 min. to establish stable discharge parameters (voltage – 850 – 900 V, current – 2 mA).

Quantitative analysis was performed with relative sensitivity factors (RSFs) that were found using standard samples. To understand the potential impact of lighter REEs and other elements on the following elements in the periodic table calculations were performed gradually. Using prior tested isotopes, the interferences were calculated for each isotope of the next element. Composition of samples from different mines and horizons, of course, varies. This paper provides examples for typical sample concentration. Main components are presented in Table 1.

Table 1. Composition of the sample for which experimental mass spectra and calculations are presented.

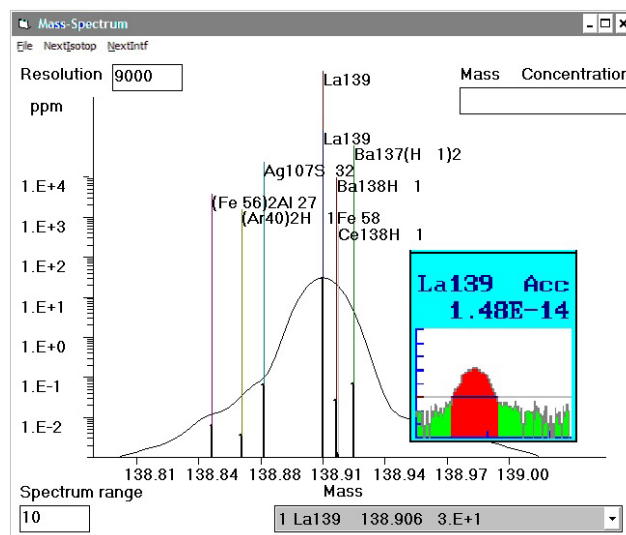
Element	Concentration, ppm	Element	Concentration, ppm
H	1.0E+04	Fe	1.6E+05
C	5.0E+03	Zn	1.9E+03
N	8.0E+03	Ag	5.8E+02
O	1.0E+05	Ba	2.3E+03
Na	6.0E+05	La	3.0E+01
Mg	5.2E+03	Ce	1.2E+02
Al	6.0E+04	Pr	2.0E+02
Si	1.4E+04	Nd	1.1E+02
P	2.4E+02	Sm	2.4E+02
S	1.4E+05	Gd	7.0E+02
Cl	1.4E+03	Dy	2.4E+02
Ca	1.6E+04	Er	1.0E+01
Ti	1.0E+03	(Ta)	3.0E+06*
Mn	1.0E+03		

*Effective value (ion current of Ta-substrate is greater than the matrix current).

Results and discussion

Results of mathematical modeling of mass spectra in the areas of mass of isotopes ^{139}La and ^{140}Ce are given in the Fig. 1.

It is seen that the contribution of ion clusters can be neglected because their concentration is smaller on 3 orders of magnitude than the lanthanum content. A similar situation is for ^{140}Ce , which is insufficiently resolved with molecular ions $^{139}\text{LaH}^+$ and $^{138}\text{BaH}^{2+}$, but their impact is less than 200 ppb.



(a)

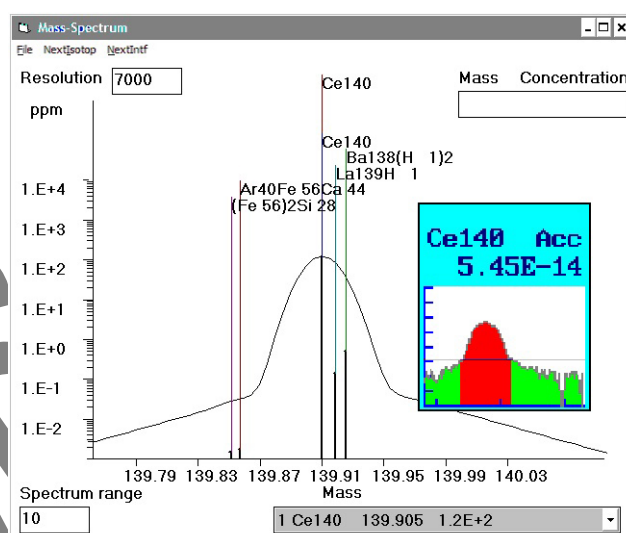


Fig. 1. Experimental and calculated mass-spectra for isotopes of ^{139}La (a) and ^{140}Ce (b) at analysis of mine waters.

The same remarks are valid for isotopes of ^{147}Sm and ^{169}Tm (Fig. 2). The calculations and experiment show, that there are polyatomic clusters $^{40}\text{Ar}^{107}\text{Ag}^+$ and $^{137}\text{Ba}^{32}\text{S}^+$ close to them. There is good agreement between calculated and measured mass-spectra. Geological samples usually contain high concentration of Ba. Its oxides, compounds with carbon and other components may form interferences for some isotopes of REEs. However, calculations show that their contribution at given concentration of Ba significantly lower, than the measured concentrations (Table 2.). This table shows the most suitable isotopes for this system and detection limit at $R_{0.5} = 9000$.

Detection limit is calculated for composition of sample shown in Table 1. For different concentration approximate correction should be done according to the Eq. 1.

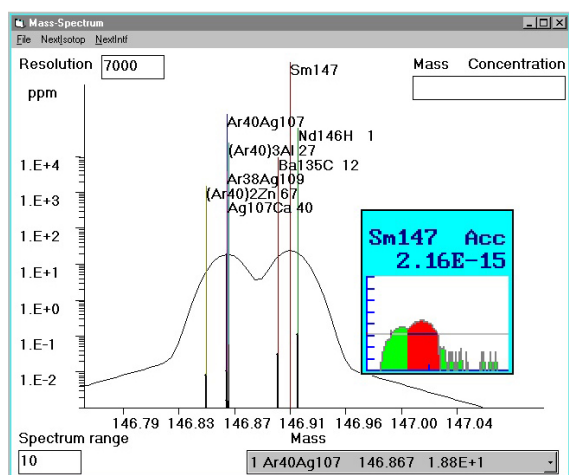
Table 2. Polyatomic clusters and detection limit for REEs determination in dry sediments of mine waters (secondary cathode – Ta).

Isotope	Mass (m/q)	"Concentration" in maximum, ppb	Detection limit in dry sediment at $R_{0.5} = 9000$, ppb*
^{139}La	138.9064	-	
$^{137}\text{Ba}^1\text{H}_2^+$	138.9215	70	>200
$^{107}\text{Ag}^{32}\text{S}^+$	138.8772	60	
$^{138}\text{Ba}^1\text{H}^+$	138.9131	30	
^{140}Ce	139.9054	-	
$^{138}\text{Ba}^1\text{H}_2^+$	139.9209	500	>900
$^{139}\text{La}^1\text{H}^+$	139.9142	150	
^{141}Pr	140.9077	-	
$^{140}\text{Ce}^1\text{H}^+$	140.9133	500	>800
$^{109}\text{Ag}^{32}\text{S}^+$	140.8768	70	
^{143}Nd	142.9098	-	
$^{141}\text{Pr}^1\text{H}_2^+$	142.9230	40	>70
^{147}Sm	146.9149	-	
$^{146}\text{Nd}^1\text{H}^+$	146.9210	520	>2000
$^{40}\text{Ar}^{107}\text{Ag}^+$	146.8675	380	
$^{145}\text{Nd}^1\text{H}_2^+$	146.9282	16	
^{153}Eu	152.9212	-	
$^{137}\text{Ba}^{16}\text{O}^+$	152.9007	60	>100
$^{152}\text{Sm}^1\text{H}_2^+$	152.9276	20	
^{157}Gd	156.9240	-	
$^{141}\text{Pr}^{16}\text{O}^+$	156.9026	150	>100
^{158}Gd	157.92410	-	
$^{142}\text{Nd}^{16}\text{O}^+$	157.9026	110	>100
$^{142}\text{Ce}^{16}\text{O}^+$	157.9042	85	
^{159}Tb	158.9254	-	
$^{158}\text{Gd}^1\text{H}^+$	158.9319	30	>100
^{163}Dy	162.9287	-	
$^{140}\text{Ce}^{23}\text{Na}^+$	162.8952	15	>10
$^{147}\text{Sm}^{16}\text{O}^+$	162.9099	4	
^{165}Ho	164.9303	-	
$^{164}\text{Dy}^1\text{H}^+$	164.9370	10	>50
^{166}Er	165.9303	-	
$^{150}\text{Nd}^{16}\text{O}^+$	165.9158	14	>30
$^{134}\text{Ba}^{32}\text{S}^+$	165.8766	360	
^{169}Tm	168.9342	-	
$^{137}\text{Ba}^{32}\text{S}^+$	168.8779	640	>50
^{172}Yb	171.9364	-	
$^{156}\text{Gd}^{16}\text{O}^+$	171.9171	70	>50
$^{138}\text{Ba}^{34}\text{S}^+$	171.8731	900	
^{175}Lu	174.9408	-	
$^{40}\text{Ar}^{135}\text{Ba}^+$	174.8681	30	>20

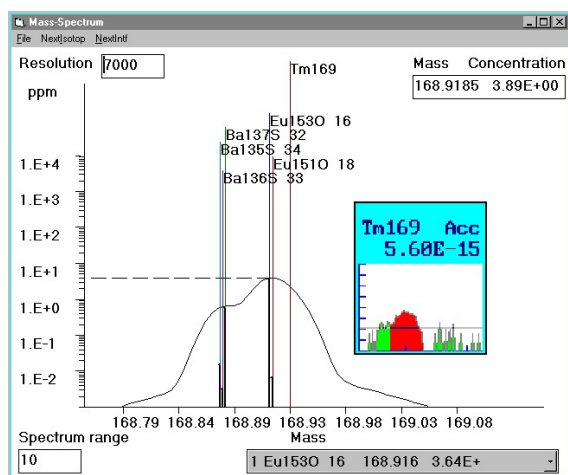
Toxic elements are discussed in sequence of increasing masses. Close to Be there is two-charged ion of oxygen O^{+2} , but with high resolution mass-spectrometers it is well resolved. Its influence becomes significant at resolving power $R_{0.5} < 500$. Polyatomic clusters form close to isotope ^{75}As signal equivalent to approximately 0.1 ppm for above mentioned sample composition (Table 3). In determination of Hg, Th and

U molecular ions do not create problem. As show Fig. 3 and Fig. 4, molecular interferences are well resolved at $R_{0.5} > 7000$. The isotope ^{200}Hg cannot be used with Ta-cathode because of intense peak $^{181}\text{Ta}^{18}\text{O}^1\text{H}^+$.

Detection limit of analysis of water taking into account concentration is better approximately in two orders of magnitude and ranging from 0.1 to 20 ppb.

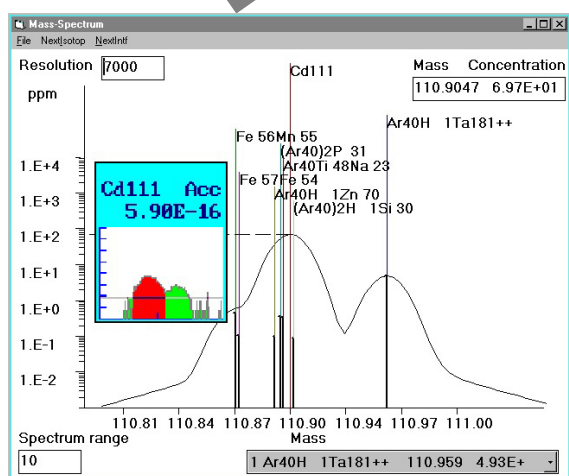


(a)

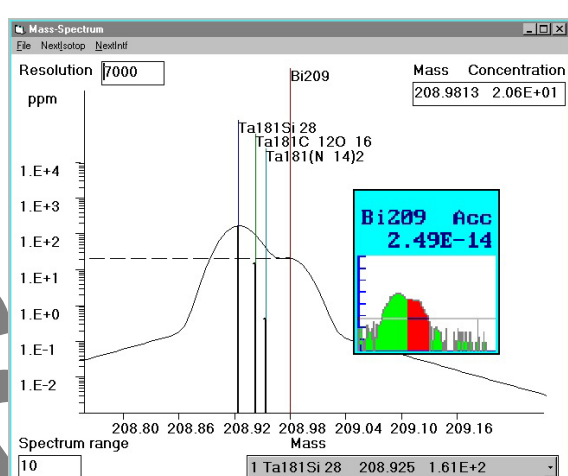


(b)

Fig. 2. Experimental and calculated mass-spectra for isotopes of ^{147}Sm (a) and ^{169}Tm (b) at analysis of mine waters.

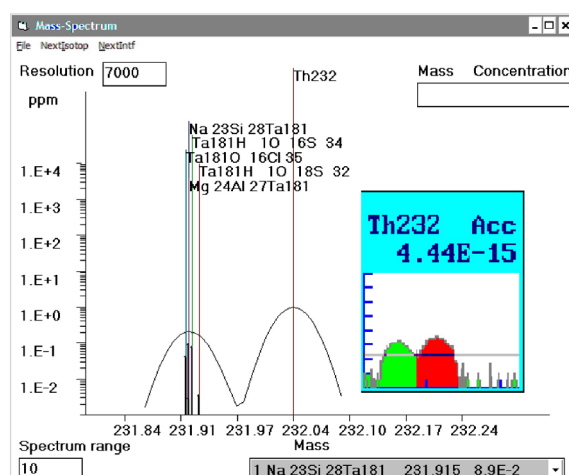


(a)

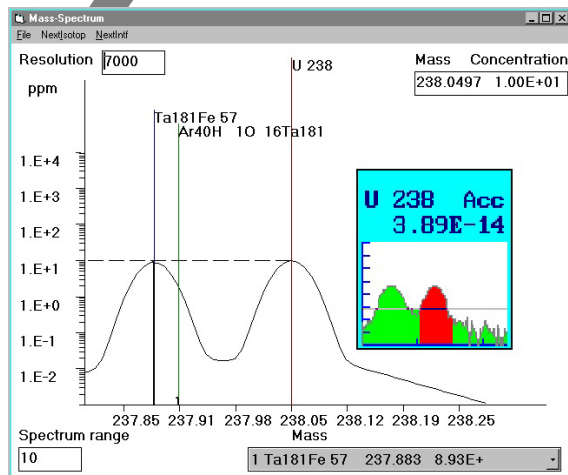


(b)

Fig. 3. Experimental and calculated mass-spectra for isotopes of ^{111}Cd (a) and ^{209}Bi (b) at analysis of mine waters.



(a)



(b)

Fig. 4. Experimental and calculated mass-spectra for isotopes of ^{232}Th (a) and ^{238}U (b) at analysis of mine waters.

Conclusions

GD-MS analysis of REE and other elements in such systems requires a critical attitude to the measured intensities. Example analysis of these objects shows that the presence of other rare earth elements, oxygen,

hydrogen, sulfur and other elements can significantly affect the accuracy of results. The result depends on the concentrations of these elements, and developed method allows carry out calculations for each ratio of concentrations. The calculations show, that the proposed approach allows correctly interpret complex

Table 3. Polyatomic clusters and detection limit at analysis of some toxic elements in dry sediments of mine waters (secondary cathode – Ta).

Isotope, molecular ion	Mass (m/q)	Maximal "concentration", ppb	Detection limit in dry sediment at $R_{0.5} = 9000$, ppb*
1	2	3	5
^9Be	9.012182	-	>10
O^{+2}	8.9996	<1000	
^{75}As	74.92159	-	>100
$^{43}\text{Ca}^{32}\text{S}^+$	74.93085	500	
$^{40}\text{Ar}^{35}\text{Cl}^+$	74.93124	120	
$^{36}\text{Ar}^{38}\text{Ar}^1\text{H}^+$	74.9381	110	
$^{58}\text{Fe}^{16}\text{O}^1\text{H}^+$	74.93602	40	
^{110}Cd	109.9030	4000	>2000
$^{56}\text{Fe}^{54}\text{Fe}^+$	109.8746		
$^{40}\text{Ar}_2^1\text{H}^{29}\text{Si}^+$	109.9091		
$^{40}\text{Ar}^{14}\text{N}^{56}\text{Fe}^+$	109.9004		
$^{40}\text{Ar}^{70}\text{Zn}^+$	109.8877		
^{112}Cd	111.9028	-	>1000
$^{56}\text{Fe}_2^+$	111.8699	4000	
$^{40}\text{Ar}_2^{32}\text{S}^+$	111.8968	700	
$^{40}\text{Ca}_2^{32}\text{S}^+$	111.8972	100	
$^{40}\text{Ar}^{16}\text{O}^{56}\text{Fe}^+$	111.8922	70	
^{202}Hg	201.9706	-	>10
$^{40}\text{Ar}^{139}\text{La}^{23}\text{Na}^+$	201.8585	40	
$^{40}\text{Ar}^{135}\text{Ba}^{27}\text{Al}^+$	201.8496	20	
$^{138}\text{Ba}^{32}\text{S}_2^+$	201.8494	3	
^{203}Tl	202.9723	-	>10
$^{180}\text{Ta}^{23}\text{Na}^+$	202.9373	50	
^{205}Tl	204.9744	-	>50
$^{181}\text{Ta}^{24}\text{Mg}^+$	204.9331	1300	
^{207}Pb	206.9759	-	>100
$^{181}\text{Ta}^{26}\text{Mg}^+$	206.9306	900	
$^{181}\text{Ta}^{12}\text{C}^{14}\text{N}^+$	206.9511	200	
^{208}Pb	207.9766	-	
$^{181}\text{Ta}^{27}\text{Al}^+$	207.9296	3.8E4	>100

* See note for Table 1.

mass spectra, which is important in the case of thermal drift of the peaks position. Calculations allow also enter adjusting for the impact of molecular ions in the measurements of isotopic ratios (in the case of artificially enriched isotopes) and determine the necessary resolution at which influence of polyatomic ions can be neglected.

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