INVESTIGATION OF ANALYTIC CHARACTERISTICS OF MASS-SPECTROMETER WITH INDUCTIVELY COUPLED PLASMA "AGILENT-TECHNOLOGIES 7700 ICP-MS"

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The main characteristics of mass-spectrometer with inductively coupled plasma of "Agilent-Technologies 7700 İCP-MS" (USA) firm are investigated. It is shown that device has enough wide range of calibration linearity (up to 5 orders of concentration changes of investigated elements). The ion composition of inductively coupled plasma mainly consists of singly ionized ions as distinct from laser and spark mass-spectrometers that gives the possibility of etalon-free analysis of solid substances. The measured sensitivity of mass-analyzer isn't worse than 100 ppb. The measuring accuracy of several metals doesn't exceed S=0,003 at right choice of devise mode.

INTRODUCTION

The mass-spectrometry with inductively coupled plasma (ICP-MS) is widely adopted for analysis of both inorganic and organic substances. The water solutions are analysis objects in ICP-MS in many cases. The solid samples are solved in nitric or hydrochloric acids (2-5%) and later they are analyzed.

Such popularity PCP-MS method has gained by the fact that here these processes are divided from each other by time and space as distinct from ionization process by laser and spark methods where laser impulse energy (or vacuum spark discharge) is given to dissociation and ionization of sample elements that leads to energy variation of analyzed ions. That's why the energies of different ions differ. Indeed, the ions of different elements having the different dissociation energies (W_a) and potentials of single and double ionizations lose the different energies $\varphi_a+\varphi_i$ in spite of the fact that they gain the similar energy during laser impulse.

The quite opposite situation is in ICP-MS. The sample long before measurements is dissolved in 2% nitric acid (or hydrochloric one in dependence on sample chemical composition) where the substance divides into atoms of substance elements, further the solution is put into sprayer and there it transforms into aerosol with the help of argon. The aerosol being in argon plasma ionizes under influence of high temperature of inductive plasma. Thus, processes of dissociation and ionization of elements almost separated from each other in ICP-MS and ions leaving the plasma have the energy variation ($\Delta W<10eV$) not exceeding the ionization energy of different element atoms.

The more detail investigation of main parameters of both mass-spectrometer with inductively coupled plasma and their comparison with analogous parameters of laser and spark spectroscopy is the aim of present paper.

EXPERIMENTAL PART

Experiment condition: *Ion source*: ICP-MS type; inductor, consisting of three turns to which the voltage of high frequency 27,12*MHz* by power 1,2*kW* in standard mode is applied; the average temperature of plasma is 8000-7000K. The so-called interface is used at constant evacuation for transition of ion flux from plasma being under the pressure near 0,1*bar* in vacuum part of mass-spectrometer in which the pressure is 10^{-5}-10^{-7} *mbar*.

Investigated samples. The samples are chosen so that one can cover the major number of parameters on the base of limited quantity of experiments, in particular, such as consistency (compact samples, thin layers); melting point (easy-evaporating and refractory materials).

It is known that the definition of chemical composition of solid substances by mass-spectrometry method is based on division of ions of investigated substance in electric or magnetic fields. For ionization of these substances the energy is applied by different ways (laser and spark ions with high energy and etc). This energy consumes on dissociation and ionization of atoms of investigated substance.

The general scheme of mass-spectrometer with inductively coupled plasma is shown in fig.1. It consists of the system of sample introduction consisting of peristaltic pump **1** and sputtering chamber **2** supplied by pneumatic sprayer **3**; plasma burner block **4**, which is connected to extraction ventilation for ozone elimination forming from the atmospheric oxygen under ultraviolet influence, products of sample decomposition and released heat; interface part **5,** extractor **6**, serving for ion taking from plasma and their transportation into high-vacuum part of mass-spectrometer ; deflection system **7**, ion optics system **8**, quadrupole mass-analyzer **9**, ion detector (SEM) **10**.

Moreover, ionization mode is chosen so that ion charge doesn't exceed the one-and two-multiplicity. The formed positive charged ions goes through ion optics system into mass-analyzer where the ion division by mass and detection takes place.

The quadrupole (fig.2) presents itself the parallel and symmetrically posited four rods to which the combination of constant and high-frequency voltage is applied in pairs. Moreover, the ion division by mass takes place in dependence on alternating voltage frequency.

$$M_i = \frac{a(U_0)}{\omega^2}$$

where U_0 is constant voltage amplitude, ω is high-frequency voltage, a is instrument constant.

The experimental investigations show that the output in one-, two- and more multiply charged ions depends on laser radiation parameters (wave length, pulse duration, power and etc) in laser mass-spectrometers.

The majority of ions in inductively coupled plasma is singly charged as distinct from laser and spark plasmas. The high temperature of argon plasma in such devices allows ionizing the atoms of all elements of periodic system with first ionization potential up to 15,76 eV (the potential of single ionization of Ar atoms). However, the formation of double charged ions and elements having the low second ionization potentials is possible in ICP-MS. The experiments show that series of (Be, Ca, Sr, Ac, Sc, Ga) elements have the least secondary potentials and the appearance of M^{++} is very often observed especially for these elements. Bur such ions as Pb ($\varphi_i^{++} = 15,03\ eV$), Mg ($\varphi_i^{++} = 15,13\ eV$) and Mn ($\varphi_i^{++} = 15,64\ eV$) have the small intensity in mass-spectra.

Consequently, the almost third part of periodic table elements is the potentially dangerous by formation of double charged ions. The presence of M^{++} in ICP-MS leads to intensity decrease of M^+ ion signals though it is considered that if $M^{++}/M^+ < 5\%$ so the decrease of intensity peak of M^+ is insignificant one [1,2]. That's why the definition of ratio M^{++}/M^+ of separate elements plays the essential role in calculations of concentration of these elements by measured mass-spectrum.

If we suppose that the thermo-dynamic equilibrium takes place in ICP-MS plasma, then the formation efficiency of double-charged ions (M^{++}) which depends on ion ionization second potential (φ_i^{++}) one can obtain by Sakha equation [3]:

$$\frac{M^+}{M^0} = \left(\frac{2\pi m T}{h^3}\right)^{3/2} \cdot \frac{2Z_i^+(T)}{Z_i^0(T)} \cdot \frac{1}{n} exp\left(-\frac{e\varphi_i^+}{kT}\right) \quad (1)$$

$$\frac{M^{++}}{M^+} = \left(\frac{2\pi m T}{h^3}\right)^{3/2} \cdot \frac{2Z_i^{++}(T)}{Z^+(T)} \cdot \frac{1}{n} exp\left(-\frac{e\varphi_i^{++}}{kT}\right) \quad (2)$$

where m, n are mass and concentration of electron; h is Planck constant; k is Boltzman constant; $Z_i^0(T)$, $Z_i^+(T)$ and $Z_i^{++}(T)$ are sums over states of atom, single and double charged ions at T temperature correspondingly.
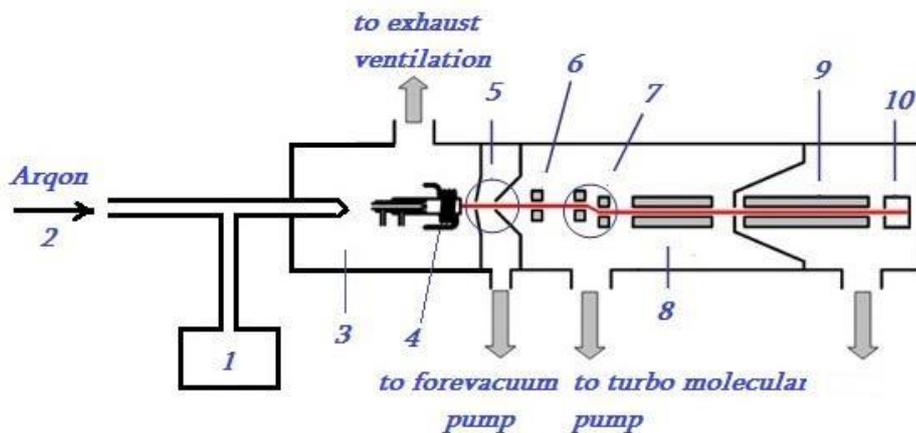

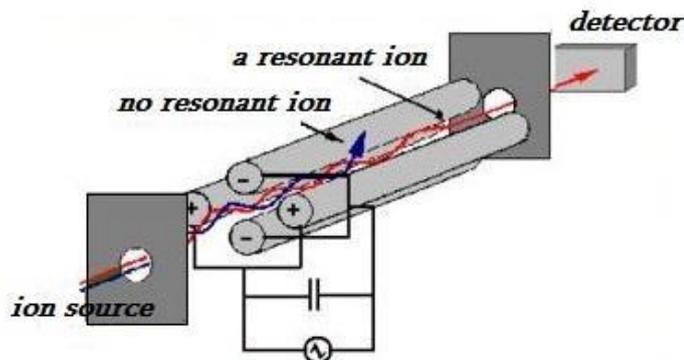*Fig.1*. The general scheme of mass-spectrometer with inductively coupled plasma.

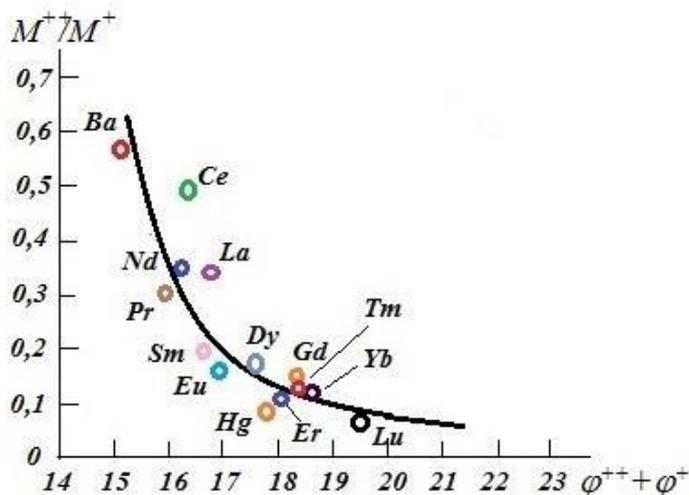*Fig.2*. The scheme of quadrupole mass-analyzer.

Fig 3. The experimental relation of M^{++}/M^+ ion concentrations in dependence on sum of first and second potentials of atom ionization.

THE RESULTS AND DISCUSSION

As it is above mentioned the presence of M^{++} ions in ICP-MS of defined elements decreases the analytical signal of M^+ of given elements (M^+) and, therefore, makes worse their detection limit. Simultaneously, the presence of M^{++} ions of corresponding elements (especially, if their concentrations are high ones) leads to disturbance appearance [4].

That's why in modern devices ICP-MS the index M^{++}/M^+ is the main to characterize of technical feasibilities of devices and it is established by $Ce^{++}/Ce^+=1\%$ or $Ba^{++}/Ba^+=3\%$, especially by this relation of analytical signals on output of the given elements(Ce^{++}, Ba^{++}) the device tuning of working mode is carried out.

At development of concrete analysis method with ICP-MS help, it is necessary to take into consideration the possibility of M^{++} mass-spectrum appearance and moreover, one can orientate on regularities of their formation in inductive plasma. About 20 pure elements having the different energies of dissociation and first ionization potential are investigated by us. The coincidences of experimentally obtained relations of concentrations of double-charged ions to one-charged ones on sum of first and second ionization potentials ($\varphi_i^+ + \varphi_i^{++}$) are given in fig.3. φ_i^+ and φ_i^{++} are taken from [5].

From the figure it seen that the type of functional dependence $M^{++}/M^+=f(\varphi_i^+ + \varphi_i^{++})$ is observed enough definitely. The study of reference [5-7] on M^{++} ion formation where the significant scatter of readings shows that the observable high relations of M^{++}/M^+ are connected with the appearance of second discharge (breakdown) between plasma having the definite high potential and grounded construction elements. The many experiments show that plasma potential depend on such parameters as argon flow rate [6], discharge power and inductor connection method.

M^{++}/M^+ relation is defined by ion energy, increases with plasma potential increasing, argon central flow rate increasing and discharge power decreasing.

The measurements are carried out in ICP-MS of firm "Agilent-Technologies 7700" (USA). Note that the calibration wide range is the distinctive characteristics of the given type of mass-spectrometer. That's why the device calivration is carried out up to 5 orders of concentration change ($n \cdot 10^5$ cm^{-3}) in dependence on chosen condition. *Cu, Ag, Ni, Al, Zn, Mo, W* and etc are used as samples. These samples are solved in 2% nitric acid, further they are injected in plasma. The internal standards are used at element analysis of solid substances. In ideal case the internal standard on physicochemical properties (atomic mass, ionization potential and etc) should be close to analyte. The following elements: ^6Li, ^{45}Sc, ^{72}Ge, ^{103}Rh, ^{115}In, ^{175}Lu are used as internal standards.

The soil taken from the parts adjacent to oil fields is examined for the revealing the heavy metals in their compositions.

The device calibration with the help of following elements with participation of above mentioned internal standards: *Mg, Al, Cr, Mn, Fe, Co, Cu, Ni, As, Zn, Mo, Pb* is carried by us at preparation of analysis sample of soil composition polluted by petroleum products. The calibration is carried out from *1 ppb, 5 ppb, 10 ppb, 20 ppb* and *40 ppb*. The 4 calibration curves for *Cu, Cr, Co* and *Ni* are given for example in fig.4. The straight lines in fig.4 show on the calibration regularity.

The samples taken from the different soil depths polluted by petroleum products before the analysis on mass-spectrometer are treated by the following way. The soil taken from each depth, is divided into 4 parts. The first part is solved in 60% nitric acid (sample 1), the second part is treated by constant voltage $U=8kV$ and $14kV$ after pure water washing and ozonized water purification.
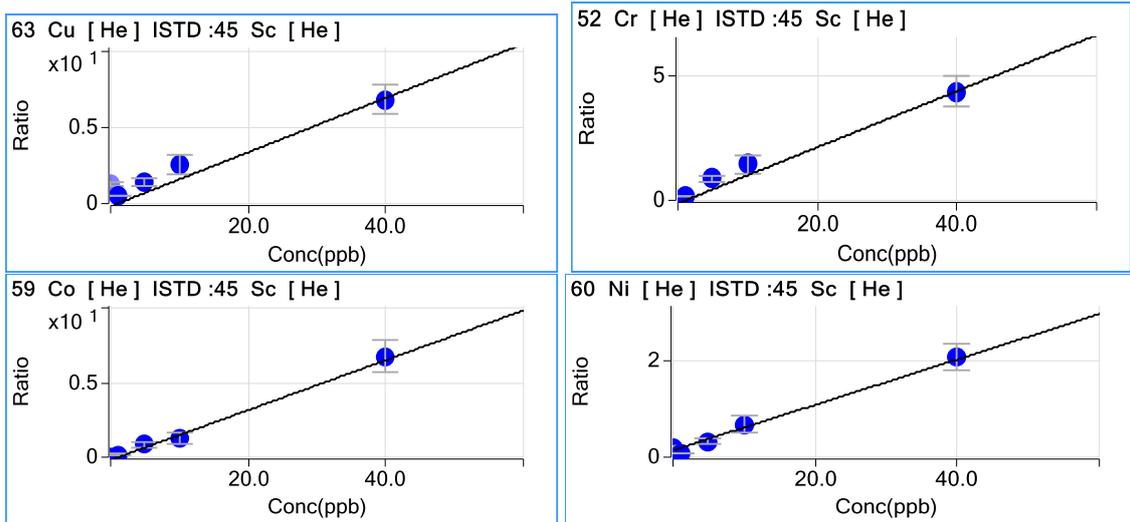
Fig.4. The element calibration in internal standard.

Table 1.

The concentrations of several elements consisting in soil after treatment.

Metal	The analysis of initial sample, ppb	The purifica-tion by water, ppb	The purification by ozonized water, U = 8kV		The purification by ozonized water, U =14кV		The purification by water, U = 14кV
			ppb, t=15min	ppb, t=30min	ppb, t=15min	ppb, t=30min	ppb, t=30min
Pb(0-10cm)	4,927	1,290	0,703	1,099	3,140	4,576	
Pb(10-20cm)	4,536	5,738	-	6,534	3,068	1,434	1,594
Ni(0-1cm)	7,112	2,520	2,580	1,985	1,231	1,630	
Ni(10-20cm)	6,070	3,710	-	3,196	1,349	1,200	1,344
Cu(0-10cm)		3,427	3,830	2,395	3,697	3,113	
Cu(10-20cm)		8,407	-	13,364	3,405	4,085	3,867
Mo(0-10cm)	164,178	35,766	42,224	6,584	19,564	20,521	
Mo(10-20cm)	331,694	30,364	-	25,395	22,536	22,662	20,521
Al(0-10cm)	528,248	72,757	149,119	215,68	222,047	258,435	
Al(10-20cm)	583,065	276,400	-	185,920	246,153	148,102	118,889

Further, the soils treated by electric field (samples №2 and samples №3) are separately solved in 60% nitric acid and their mass-spectrometric analysis is carried out.

The analysis results, i.e. the ion concentrations of several metals being in the soil composition, are given in table. The depths, from which the soils are taken for the analysis, are given in brackets after metal names.

The element concentrations are measured in ppb, i.e. the device sensitivity is from 10-100 *ppb* with accurate within 10^{-3} *ppb*. This shows the high sensitivity and resolution of device.

Result regularity. It is known that the one- (M^+) and double-charged (M^{++}) ions dominate in laser and spark mass-spectrometers [7,8]. That's why this fact presents the interest of definition of relative sensitivity factor (RSF) on lines of both one- (RSF_i^+) and double-charged ions by mass spectrum obtained in ICP-MS. The experiments on definition of M^{++}/M^+ relation are carried

out for the several pure metals. Moreover, the plasma composition corresponds to experiment requirements and is $Ar^+ + M^+ + H_2O$. The argon consumption through pneumatic sprayer doesn't exceed 1l/min. The sample solution feed rate is 1l/min, the spray-type system efficiency is 0,02, the analyte composition is 10mg/l. *Cu, Ni, Zn, Al, Cr, Mn, Fe, Mg* are used as analyte.

RSF calculated by experimentally measured lines of above mentioned pure metals by following formula [7]:

$$RSF_{in.st.}^x = \frac{J_x}{J_{in.st}} \cdot \frac{n_{in.st.}}{n_x}$$

are given in table 2.

From the table it is seen that the calculation by cuprum lines gives RSF value close to 1 for both one-and double-charged ions.

Table 2.

The relative sensitivity factor calculated by results of measured concentrations of pure metals.

Elements	$n_x^+ \cdot 10^8 cm^{-3}$	$n_x^{++} \cdot 10^6 cm^{-3}$	RSF_i^+	RSF_i^{++}
Al	159	42	1,68	3,57
Cu	345	125	1,41	2,61
Ni	2415	512	1,16	4,73
Zn	450	315	1,43	0,95
Cr	178	2140	2,12	1,21
Mn	367	164	1,71	2,7
Fe	213	95	2,07	0,63
Mg	47	161	6,95	0,38

For one-charged ions the relation of maximum RSF_i^+ to minimum one is 2,5, i.e. the value range is approximately better on order than in laser and spark mass-spectrometry (RSF_{max}^+/RSF_{min}^+=17,5). The value range of this relation for two-charged ions is equal to 12,5. Therefore, the lines of these ions are less suitable for etalon-free analysis than lines of one-charged ions. Note that sometimes one should use the double-charged ions at analysis with application of internal standards.

Thus, the regularity of etalon-free analysis carried out on CP-MS, changes from matrix to another one and in general, it is comparable with regularity of laser and spark mass-spectrometry. Probably, changing the influence conditions on sample (frequency and power of high-frequency voltage) one can chose the conditions for which $RSF_{in.st.}^x$ values are more close ones for the definite matrix class.

CONCLUSION

1. The enormously wide range of linear calibration is the distinctive characteristics of mass-spectrometry with inductively coupled plasma. The calibration linearity is saved up to 5 orders of concentration change.
2. The regularity is about 2,5 (i.e. the relation RSF_{max}^+/RSF_{min}^+=2,5) at analysis on mass-spectrometer with inductively coupled plasma by lines of one-charged ions as at analysis by method of spark and laser mass-spectroscopy.
3. The device sensitivity ICP-MS for soil analysis is not less than 100 ppb.
4. The division of process of atomization and ionization by both the space and time in ICP-MS device allows us to use it for carrying out of etalon-free analysis of solid substances [9].

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