VILNIUS UNIVERSITY

Žilvinas Ežerinskis

STUDY AND REDUCTION OF THE MATRIX EFFECTS IN ANALYTICAL ICP MASS SPECTROMETRIC MEASUREMENTS

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VILNIAUS UNIVERSITETAS

Žilvinas Ežerinskis

**BANDINIO SUDĖTIES ĮTAKOS
ELEMENTŲ KONCENTRACIJŲ NUSTATYMUI INDUKCINĖS PLAZMOS
MASIŲ SPEKTROMETRIJOJE TYRIMAS**

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1. Introduction

Elemental composition of materials is needed for most modern research techniques and technology, environment and health fields. Therefore, analysts have to investigate a wide variety of the samples. At the same time requirements to the accuracy of analysis are increasing nanograms per gram mass fractions and significantly lower concentrations must be measured, the study of the refractive and insoluble materials. Most often adequate detection limits are available by physical methods, including spectrometry. However, particularly in these methods, analytical signal and the measurement result depend not only on the analyte concentration, but on the overall sample composition and structure also. Matrix influence may be eliminated by the dissolution of the sample, but the overall sample composition effect on the analytical signal is one of the largest problems in chemical analysis. In most cases it is dealt by calibration of the analytical measurement, with reference materials of the very similar and known composition. Ever expanding applications of the chemical analysis, the number of reference materials is uprising fast, but cannot meet the needs of the accelerated growth of the variety of substances.

On the other hand, even a similar composition to the reference material is never identical to the test sample. Therefore, application of the reference material only cannot solve the problem of the accuracy of the analytical results. Own methods tests, more comprehensive understanding of the physical and chemical contents of the methods used and the nature of the inherent phenomena is no less important way to improve performance, ensure the reliability and accuracy of the analytical assessment.

The main aim of doctoral dissertation

The aim of this work is to study the effect of a single concomitant element or the overall sample composition on the analytical result of the inductively coupled plasma mass spectrometric measurement, understand and reduce those effects, aid to elaboration of the means for analysis of the complex samples, evaluation of the uncertainty and feasibility of the analytical results.

The work focuses on the several subjects. First of all, it can be expected that the problem of the influence of the sample composition will be less severe if the work is restricted to a narrow class of samples. One of the objectives of this work was to check

how effectively the variation of the sample composition can be reduced by narrowing the class of the samples, prepare a method for classification of sample and identification of their origin from the data of the multi-elemental mass spectrometric analysis and methodology to estimate the level of confidence of such a classification, to check how much the composition of the samples influence the analytical measurement results and the classification quality.

Influence of the sample composition can be reduced by dilution of the samples. In practice it works almost exclusively with liquid samples, and the concentration must be much higher than the limit of detection to enable the diluted sample to be analyzed. Therefore, often the method of addition is applied, where the small amount of the pure analyte is added to the samples in order to calibrate the signals. The most advanced version of this method is the isotope dilution. The best metrological characteristics are achieved by this method so far. However, the method is suitable only when the analyte or any of its elements is in the form of at least two stable isotopes. But many chemical elements have only one stable isotope. Therefore, one of the goals of the study was to reduce the uncertainties of the method and test what accuracy of this method is accessible for analysis of the mono-isotopic elements.

As interest in direct analysis of solids remains in analytical practice, it is not possible or sample is lacking for realization of the method of addition interest in reduction or, at least estimation of the role of the overall sample composition or the particular concomitants, or uncertainty of analysis also remain. Therefore, one of the tasks was to understand what general conclusions on the matrix effect on the analytical signal follow from simple, close to thermodynamic equilibrium, models, how they correlate with the experimental results, what are the reasons for the differences.

The method of external calibration and method of additions with internal standards were used to solve these problems. Inductively coupled atmospheric pressure argon plasma was used as the plasma source Electric and magnetic sector high resolution mass spectrometer was used for measurement of the ionic signals. Plasma state was modeled in partial thermodynamic equilibrium accounting for the elements at relative mass fractions exceeding one part per million.

Novelty

Method of calibration of the dependence of the sensitivity of the mass spectrometer on the ion masses and methods to determine the electron density and temperature from the mass spectrometric measurement data were proposed. It enables calibration of the relative signals for semi quantitative chemical analysis.

It is shown that impurities in argon plasma, depending on the structure of the excited atomic energy levels the chemical elements with low first and second ionization potentials differ in possibilities to take part in charge transfer reaction between doubly ionized ions and argon atoms. Phenomenon is important for the balance of ionization in the argon plasma with impurities.

Practical importance

It was shown that if the number of the data and their classes is large, it is appropriate to perform the classification by steps to more detailed classes. At each classification step only the most specific for the particular step parameters should be selected in order to minimize the noise impact. The classification to sub-classes is not an effective way to reduce the variation of the sample composition and the matrix effect in the analytical results.

Proper application of the method of additions allows linear relationship between the measured signal and the analyte concentration. Adequate selection of internal standard and methodology of measurements enable the accuracy of the method of addition comparable to that of isotope dilution.

It is shown that in order to reduce the influence of the overall sample composition on the chemical analysis results in ICP plasma measurements of the ion signals as compared to the atomic ones ought to be preferred usually. For complex samples, where no acceptable standards are available, calibration of the relative sensitivity of the analytical system and the plasma diagnostic data enable the relative semiquantitative analysis of samples and aid estimation of the uncertainty of the results. Effect of elements with low first and second ionization potentials on the analytical results can be effectively reduced by application of the internal standards.

Statements presented for defense

Classification of the samples to sub-classes is not an effective way to reduce the matrix effect in chemical analysis.

Application of the higher accuracy linear relationships of the method of addition, selection of the appropriate internal standard and full integration of the analytical signal enable accuracy of the method of addition, including analysis of the monoisotopic elements, comparable to the accuracy of the isotope dilution method.

In the close to equilibrium ICP argon plasma at atmospheric pressure the low ionization potential atoms of the chemical elements are ionized. The matrix effect on the ion signals of those elements is relatively small, while the atomic signals are reciprocal to the electron concentration. The sample composition effect on signals of atoms and ions of elements with high ionization potentials depends on the degree of ionization. The proposed techniques for calibration of the sensitivity of mass spectrometer and determination of the electron temperature and concentration from mass spectrometric measurements can be effective for relative semiquantitative chemical analysis.

Relatively large effect of the elements with low first and second ionization potentials to analytical signals can be due to the charge transfer between argon atom and the doubly ionized ions and ambipolar diffusion. The effect can be essentially reduced by application of the internal standards.

2. EXPERIMENTAL

An Element2 (Thermo Finnigan MAT, Bremen, Germany) double focusing sector field mass spectrometer and argon inductively coupled plasma source were used for the measurements. The main operating characteristics of the mass spectrometer and sample introduction system are presented in Table 1. Those are characteristic for nonrobust plasma and have been selected to ensure an acceptable accuracy of the measurement of the signals, including the doubly ionized ions up to second ionization potentials about 16 eV of interest in the matrix effect and plasma diagnostic studies.

Table 1 Element 2 instrument and operating conditions

RF frequency		27.12 MHz
RF power		1100 W
Reflected power		<5 W
Resolution		Medium, 4000; low 300
Gas flows: Plasma gas		$14 \, l \, min^{-1}$
	Auxiliary gas	$0.75 \, l \, min^{-1}$
	Aerosol carrier gas	$1\text{-}1.3 \, l \, min^{-1}$
Torch		Fassel type
Nebuliser		Meinhard C
Spray chamber		Cyclonic
Cones		Nickel
Injector diameter		1.75 mm
Sample uptake rate		$0.7 \, ml \, min^{-1}$
Nebulizer efficiency		6%
Sampling depth		12 mm from the load coil
Instrument tuning		Maximum signal, multielement solution
Scan type		E scan over small mass range
Mass window		150%
No acquisition points per mass segment		15
Settling time		1 ms
Dwell time		10 ns
Detector mode		Counting, both counting and analog

A stock ICP Multi Element Standard Solution VI CertiPUR (Merck, Darmstadt, Germany) was used as a CRM sample for analytes B, Na, Mg, Al, K, Ca, V, Cr, Mn, Fe,

Co, Ni, Cu, Zn, Ga, As, Se, Rb, Sr, Ag, Cd, Sn, Ba, Tl, Pb, Bi, U while mono elemental Na, Sr or Sm solutions (Spex CertiPrep Ltd., UK) in addition were used in some special experiments (section 3.4). Ultra pure water prepared by a NANOpure Barnstead/Thermolyne Co. (Dubuque, USA) water purification system was used for all sample dilutions. Up to 2% of nitric acid (Suprapur®, 65.3%, Merck) was added to the diluent for stabilization of the subsamples.

3. RESULTS

3.1. Study of the variation of the elemental composition within one class of samples. Application to the sample classification.

The absolute concentrations of 23 elements, namely Li, Be, B, Na, Mg, Al, K, Ca, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, As, Rb, Sr, Ba, Tl, U in 103 wines from seven countries were measured. The results of measurements in different resolutions, for different isotopes, in the samples of different dilution coincide within precision of 5 %, in most cases within 2 %. Possible inputs from different uncertainty sources in preparation of the test samples and reference materials, sample introduction, measurement and data analysis including dilution, purity of diluent, weighing, clean-up, signal instability in time, matrix effects, uncertainty of the reference material and blank were accounted for in the uncertainty estimates. Total uncertainty essentially depend on element and concentration range. Mainly it does not exceeded 7% (k=2) while for some elements, *e.g*., Tl (mainly due to irreproducibility of the signals and blank) Cu and Zn (because of the matrix effects) the measurement uncertainty was up to 10%, or even 15% (Tl). In particular, because of the large concentrations of K in the samples adequate rinsing of the apparatus needed a long time. The ranges of variation of the measured concentrations in absolute and relative units are presented in Table 2.

Discrimination between regions of origin was based on the variations of the measured concentrations of elements. As the number of elements was large the pattern recognition techniques should be applied to classify the data. The Principal Component Analysis (PCA) was used in the present work. It is a convenient tool for the reduction of data dimension to some principal components and visualization of the similarities.

Table 2. Intervals of variation of the concentrations of elements (ng g^{-1}) in the measured wines

Element	min	max	max/min	Element	min	max	max/min
Al	264.74	$5.62 \cdot 10^3$	21.24	Mg	$2.93 \cdot 10^4$	$1.53 \cdot 10^5$	5.22
As	5.20	105.61	20.31	Mn	308.85	$3.60 \cdot 10^3$	11.67
B	$3.39 \cdot 10^3$	$1.49 \cdot 10^4$	4.41	Na	940.23	$7.06 \cdot 10^4$	75.12
Ba	41.90	443.02	10.57	Ni	12.54	54.80	4.37
Be	0.16	6.23	40.08	Pb	6.42	165.50	25.77
Ca	$5.37 \cdot 10^4$	$1.34 \cdot 10^5$	2.49	Rb	184.92	$4.85 \cdot 10^3$	26.24
Co	1.32	9.79	7.40	Se	0.89	16.58	18.60
Cr	9.02	77.31	8.57	Sr	330.67	$2.23 \cdot 10^3$	6.75
Cu	10.67	520.20	48.77	Tl	0.04	1.10	26.29
Fe	730.95	$8.78 \cdot 10^3$	12.01	U	0.20	3.11	15.93
Ga	0.08	0.97	12.35	V	5.01	377.22	75.30
K	$1.35 \cdot 10^4$	$6.87 \cdot 10^5$	51.08	Zn	125.37	$2.18 \cdot 10^3$	17.39
Li	3.79	286.72	75.70				

It provides a new set of variables obtained as the best linear combination of the original parameters which accounts for more of the variance than any other combination. At the same time this chemometric tool enables to find out in what respects the samples are different and which variables contribute most to the difference.

The variations between batches larger than those within batches are expected for the successful classification. The real situation is different for every element and countries of interest. Application of as wide set of elements as possible seems most straightforward. Data from five to nine wines from seven countries were tested for the preliminary screening. Poor classification possibilities were found. One can expect that rejection of the nonspecific information and inherent noise can be helpful. Anova software was used for the purpose.
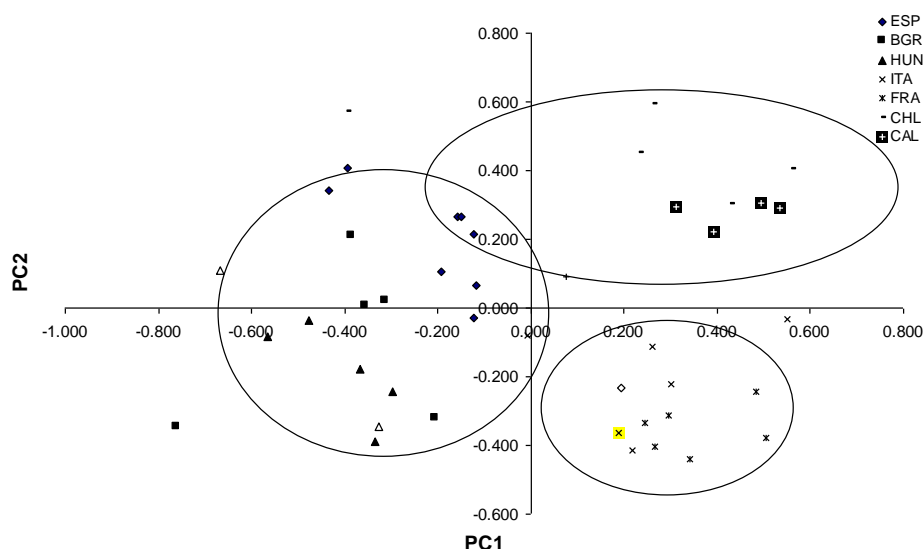
Fig 1. Classification of wines from seven countries based on concentrations of Rb, Sr, and Zn. Explained variance: 53% (PC1) and 34% (PC2). Absolute loadings of Rb and Zn to the principal components were from 0.5 to 0.8, those for Sr 0.04 and 0.26

In Fig. 1 the classification pattern as obtained according to concentrations of Sr, Rb and Zn is presented. For those elements F test parameter was the largest for the batch including all countries, namely $F > 8\ F_{crit}$. Three groups of the samples could be clearly distinguished: wines from Bulgaria, Hungary and Spain, samples from France and Italy, and those from Chile and California. In a similar way other sets of the most specific elements were to be selected for each further classification step, including individual countries or the geographical regions within those.

Table 3. Dispersion of K, Ca and Na concentrations in wide range of sample classes.

Element	Average conc., ng ml^{-1}	Relative standard deviation, %			
		All data	CHL, ESP, FRA	FRA	Bordeux
K	163 000	97	34	38	37
Ca	90 500	20	19	11	8
Na	8 800	110	43	26	18

The multicomponent Gauss distributions were successfully applied for evaluation of the level of the confidence of the classification. The accuracy of the measurements as mentioned above usually was enough for classification at the level of confidence about 0.9 in the studied cases. However, as presented in Table 3 further classification of

samples was not effective to reduce the variations of the composition of the samples and could not enable proper selection of the certified reference materials to eliminate the matrix effects in analysis. Other means for the more detailed understanding and reduction of the matrix effects are discussed below.

3.2. Method of addition. Application to the accurate measurement of the concentration of the monoisotopic element.

It followed from the mathematical analysis that an internal standard was to be preferred in the method of addition measurements. Fast measurements are needed to enable good correlation between the signals of the standard and the analyte. According to the technical specifications of the spectrometer Element 2 fast intensity ratio measurements are possible if the masses of the isotopes differ by less than 30%. Because of this limitation as the possible internal standards for As measurements were tested Zn, Se and Mo. Only concentrations of Zn and Mo in the test sample were high enough for such application. Unfortunately, the chemical characteristics and the ionization potentials of those elements are different from the characteristics of arsenic. Se (ionization potential 9,75 eV as compared to 9.79 eV for As) was present in the test sample but at small concentrations. For application as the internal standard, corresponding amount of pure Se solution was added to the test sample before subsampling and dilution of the test sample was accounted for. By additions of the Merck Arsenic ICP Standard As CertiPUR (987mg/kg ± 7 mg/kg) arsenic signal in the calibration blends was increased by factors from 1.2 to about 7.

Operation characteristics of the spectrometer were as presented in Table 1. Medium mass resolution was used for the measurements. Some part of data, usually at the beginning of the measurement sets, exhibited changes, partly because of the mass drift (Fig 2, compare [1]). Elimination of such data enabled to decrease appreciably the standard deviation of the signals, while was less essential for the ratios. Analysis of the raw data was recognized as an important part of the procedure. Fifteen points across the mass peak, covering 1.5 theoretical peak widths, were found enough to represent the integral signals used for the ratios. One measurement lasted for 10 ms (settling time 1 ms), and 200 - 250 measurements sets were used. The standard deviation of the signal

data set usually was about 4-8%. The standard deviation of the ratio data sets was about 6 or 7 percents resulting in the standard deviation of the mean ratio values lower than 0.5%. The full measurement sets were repeated from four to six times. Measurement of the ratios of the integral signals was essential to preserve the reproducibility of the data at the level corresponding to the standard deviation within a measurement set.
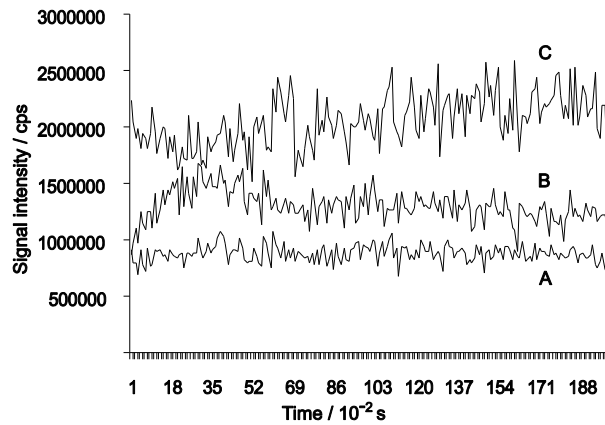

Fig 2. Example of absolute As signal measurement data from fast As/Se ratio measurement series : peak point (A), integral for 5 points from the right side (B) and integral for 5 points from the left (C). Time resolution 0.01s.

As an example, the measured ^{75}As and ^{66}Zn, ^{75}As and ^{77}Se signal ratios dependences on the added mass fractions for four blends are presented in Figs 3, 4. The analyte mass fraction was calculated from each measurement set and the obtained values averaged. Although the ratio of the signals in the test sample, R_x, is measured directly application of the ratio value determined from the graph by the least squares fitting for the mass fraction determination was preferred. The measurement results and their uncertainties are presented in Table4.
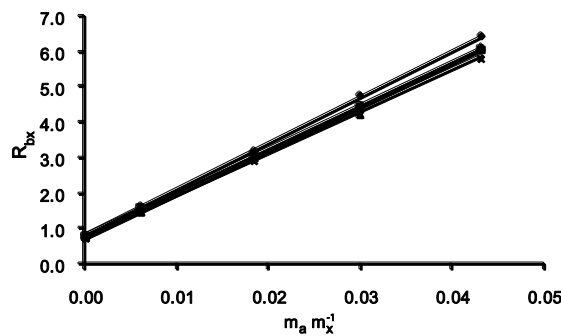

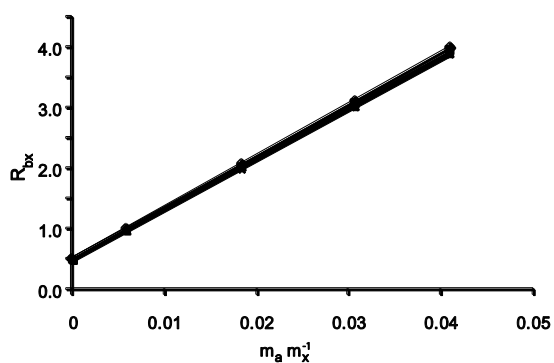**Fig. 3.** As/^{66}Zn signal intensity ratio calibration graphs.

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Fig. 4. As/^{77}Se signal intensity ratio calibration graphs.

Table 4 Arsenic measurement results

Internal standard	Result, ng/g	Expanded (k=2) relative standard uncertainty, %
^{66}Zn	61,6 ± 3,4	6
^{94}Mo	58.1 ± 1.6	3
^{77}Se	58,90 ± 1,20	2
Certified NIST SRM 1643e As mass fraction value: (58,98 ± 0.70)		1

The certified NIST SRM 1643e As mass fraction value is included in the table for comparison. It is clear that ^{77}Se acts as the best internal standard for As. The data show that application of the proper internal standard and full integration of the signals enable accuracy of the method of additions in analysis comparable to that of the isotope dilution.

3.3. Modeling of the matrix effect on analytical signal in close to equilibrium plasma.

Saha equation, in analogy to the law of active masses, is the main quantitative relationship between the densities of particles in the neighbor ionization states, i and $i+1$, of the element and electrons in local thermodynamic equilibrium (LTE) plasma. Because of the moderate temperatures characteristic to ICP, about or lower than 10 000 K, only atoms, the singly and double ionized ions are found at appreciable concentrations. Thus i

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takes values from 1 to 2. Namely, for each element and every pair of the neighbor ionization states,

$$\frac{N_{i+1}N_e}{N_i} = \frac{(2\pi m_e kT)^{3/2}}{h^3}\frac{2Q_{i+1}(T)}{Q_i(T)}e^{-(E_i-\Delta E_i)/kT}.$$

(1)

Here T is temperature, m_e is the electron mass, h and k are Planck and Boltzman constants correspondingly, Q are the partition functions, E is the ionization potential of the lower ionization state, and ΔE is the lowering of the ionization energy in the plasma. Various ideas are used to estimate the ΔE [2,3], between those the Debye shielding approach:

$$\Delta E_i = 2(z_i+1)e^3(\pi/kT)^{1/2}\left(\sum_i N_i z_i^2\right)^{1/2}$$

(2)

where e is the electronic charge, z_i is the elementary charge of the i-th ion ($z_i=i-1$).

As electrons are produced in any ionization step, the equations for each element or compound and all ionization states must be regarded simultaneously. In addition, balance of the total number of particles, N, and dependence of the total particle number density on temperature must be included. Asymptotic approach to the true electron density value N_e can be used. Correspondence of the electron density to the total concentration of all ions and sums of the densities of ions to the given gas composition for each element should be applied as accuracy tests.

If the values of the constants are introduced Saha equation can be rewritten in the form convenient for diagnostic purposes:

$$\frac{n_{i+1}}{n_i} = \frac{4.83\cdot10^{15}T^{3/2}}{N_e}e^{-\frac{11605}{T}(E_i-\Delta E_i)}.$$

(3)

Here $n_i = \dfrac{N_i}{Q_i}$ is population of a single statistical ionization state. Particle densities in equation (3) are expressed in cm^{-3}, T is in K and ionization energy is in eV. Both the index of the exponent and the coefficient before the exponent, number of the free electronic states attributed to one occupied state, can be determined from measurements enabling simultaneous determination of the plasma electron temperature and density.

For simplification let us take the Saha equation for atoms and the singly ionized ions of a single element in the form

$$N_e \cdot N_2/N_1 = K, \tag{4}$$

For single element at low temperatures $N = N_1 + N_2$, and $N_2/(N-N_2)=K/N_e$. The degree of ionization, $N_2/N=K/(N_e+K)$. It means that ionization is total, $N_2/N=1$, if $N_e \ll K$ independent on the real values of the ionization potentials (chemical species) and temperatures. Addition of the elements with low ionization potentials should increase the total electron density and reduce the ionization degree of any individual component. In a similar way decrease of the absolute analyte (and, consequently, electron) concentration at constant temperature must increase the ionization degree.

In modern analytical plasma sources plasma is created in foreign to the sample, usually inert gas, environment and only small quantities of the sample are introduced enabling to make almost no changes of the plasma state. Just the high ionization potential of the inert atmosphere, small sample quantities introduced and small concentrations of the analytes facilitate low electron densities, cumulatively increasing the ionization degree of the analyte and potential of the optical and mass spectrometric determination of ions from small quantities of a sample. Naturally, when sample throughput is to be increased, caution is needed on when the sample starts to change the plasma conditions. If it takes place, the absolute values of concentrations of all species must be specified for analysis of the data or comparison between experiments. Decisive role of the environment (relative to the analyte) in determining the electron density is the reason why the simplest form of the single Saha equation hardly can be observed.

As an example, comparison of the fraction of the singly ionized ions relative to the total number of particles of the element (degree of the first ionization, N_2/N) as dependences on the ionization potential of the neutral atoms in gas mixture characteristic to argon ICP (Ar 97%, H 2%, O 1% and 10^{-7}% of the analyte element, electron density below 10^{15} cm^{-3}, top) and pure monoelemental substances (bottom, electron densities up to 10^{17} cm^{-3} and higher) at atmospheric pressure and temperature 7000 K are presented in Fig.5. Essential increase of ionization in ICP is evident, especially for elements with ionization potentials from 6 eV to about 8 eV. Some decrease of the first ionization of the

elements with low ionization potentials (Ba, Sr) in ICP is because of the appreciable higher (secondary) ionization while at potentials about or higher than 8 eV the fraction of the neutral atoms increases. Dispersion of the data corresponding to different elements with high ionization potentials is due to the differences in partition functions.
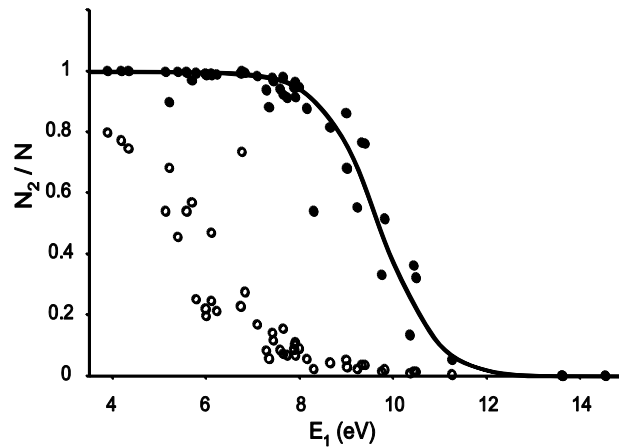

Fig. 5. Degree of the first ionization at T = 7000 K as dependence on the ionization potential of the neutral atom for pure elements (○) and in argon gas (●). Argon plasma composition: Ar 97%, H 2% , O 1%, other elements 10^{-7}%. Solid line represents hypothetic elements with partition functions equal to 1 and negligible secondary ionization.
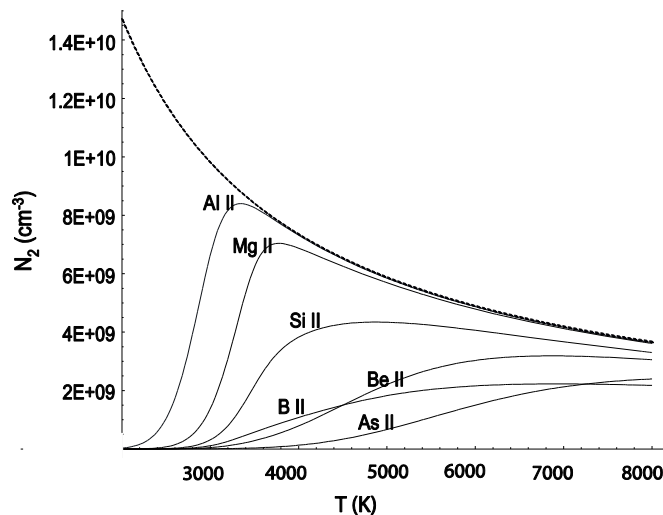
Fig.6. Dependence of the density of the singly ionized ions on temperature at argon ICP model conditions. Plasma composition: Ar 97%, H 2% , O 1%, other elements 10^{-7}%. Ionization potentials of the elements: Al 6.0 eV, Mg 7.6 eV, Si 8.1 eV, B 8.3 eV, Be 9.3 eV, As 9.8 eV.

Maximum of the ion density in ICP (Fig.6) for low ionization potential elements in comparison to the pure substance shifts to the lower temperatures. Decrease of the density of the singly ionized ions at higher temperatures takes place because of the law of

the ideal gases (dotted line for Al II in Fig.6) and, at low ionization potentials of the ions, due to successive ionization.
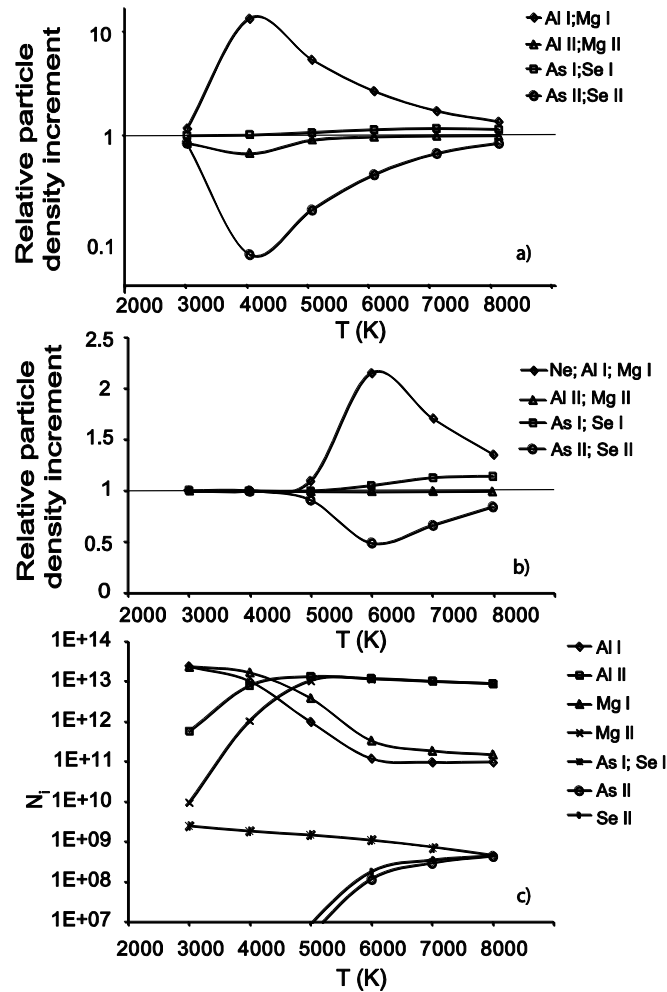

Fig. 7. Carbon content (particle fraction 0.01) effect on atomic particle and ion densities at different temperatures: a) plasma composition Al (10^{-9}), Mg (10^{-9}), O (0.01), H (0.02), other elements (10^{-9}) and Ar (the remaining gas)); b) plasma composition Al (10^{-5}), Mg (10^{-5}), O (0.01), H (0.02), other elements (10^{-9}) and Ar (the remaining gas); c) calculated particle densities (plasma composition as in case b, without carbon matrix).

If the electron density exhibit changes (e.g., because of the matrix) the ratio of the populations of the neighbor ionization states change in a reciprocal manner (eqn.(3)). Because of the preservation of the total number of particles, the main effect is to the less abundant component, i.e. to the densities of atoms when the ionization degree is high and to the densities of ions if the neutral atoms prevail. In addition, if the contents of the easy to ionize elements is increased then the electron density increases and the matrix effect shifts to higher temperatures (from the peak at 4000 K in Fig. 7a to 6000 K in Fig. 7b). In spite that in general the dependences seem similar, the changes are essential as the

plasma composition itself at different temperatures is different. Thus the results show extremely composition and temperature dependent character of the LTE matrix effects. Therefore any theoretical calculation must closely match the sample-plasma composition, measurements with space resolution would be of importance, or modeling ought to integrate space dependent changes.
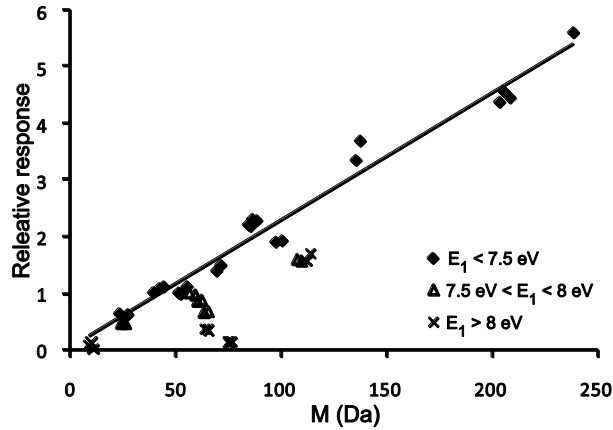

Fig. 8. Linear fit of the Element 2 response (normalized to ^{39}K) dependence on atomic mass, $y = 0.0225M + 0.0302$, $R^2 = 0.9731$. Data for elements with ionization potentials between 7.5 eV and 8 eV and for elements with ionization potentials exceeding 8 eV are given for comparison only.
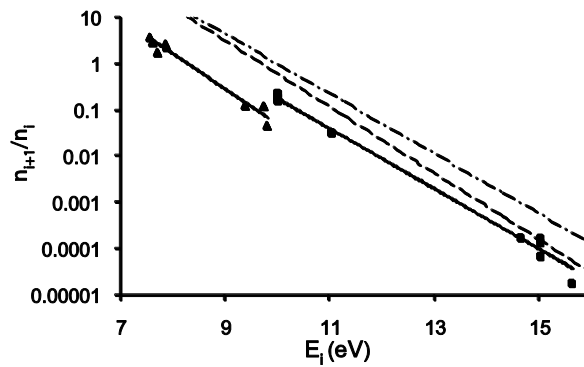

Fig. 9. Dependences of the ratios of populations of the neighbour ionization states on ionization potentials (populations of single statistical ionization states, $n_i=N_i/Q_i$, densities of ions divided by the corresponding partition functions, are used; see equation (3) also): experimental data for the ratios of populations of the states of the singly ionized ions and neutral atoms (($\blacktriangle$), $n_2/n_1 = 2 \cdot 10^6 exp(-1.7E_1)$); experimental data for the ratios of populations of the states of the double and singly ionized ions (($\blacksquare$), $n_3/n_2 = 6 \cdot 10^5 exp(-1.5E_2)$); LTE calculated dependences at 7000 K (dashed line, $n_{i+1}/n_i = 10^7 exp(-1.7E)$) and 7700 K (dashed-dotted line, $n_{i+1}/n_i = 3 \cdot 10^6 exp(-1.5E)$).

If the singly ionized ions prevail, as can be expected for the elements with ionization potentials of the atoms below 7.5 eV then the density of those ions and the ionic signal

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are proportional to the concentration of the elements. Such signals at equal concentrations of elements can be used as a measure of the sensitivity of the spectrometer (Fig. 8). Knowledge of the relative sensitivities of the equipment at different masses is inevitable for normalization of the measured signal to the common scale. If the ionization degree is far from total the real ionization degrees must be accounted for also. As follows from eqn. (3) knowledge of the ionization potentials and temperature only is enough to calculate the relative ionization ratios for different elements. The same equation as applied for different elements and ionization states is a key to plasma temperature (and electron density) measurements (Fig. 9). In parallel, monotonous dependence of the Saha ratios for the various elements are found as a confirmation of an applicability of the LTE concept to the plasmas under study. It enabled that the original plasma diagnostic method and calculated relative ionic signals could be applied for calibration of analysis of the complicated unique samples [A6]. However, the measurements show that matrix effects of some elements with very similar low ionization potentials of atoms are much larger than others [11]. Such an effect cannot be understood within the equilibrium approach and is analyzed in more detail in the next chapter.

3.4. Effect of matrices with low first and second ionization potentials on analytical signals in inductively coupled plasma mass spectrometry.

The matrix effects of Sr, Sm and Na on mass spectrometric signals of different elements were studied. The first ionization potentials of the elements are 5.69, 5.64, 5.13 eV correspondingly, while the second ones: 11.02, 11.08, 47.28 eV. Lowering of the number densities of ions due to the matrices were observed at matrix concentration in the range of milimoles. The effects increased in transition from Na to Sr and further to Sm, were similar for all analytes measured (Fig. 10) and no correlation of the magnitude of the effect with the first or second ionization potentials was observed. Correspondingly the effect on analytical signals could be reduced (up to about 20%) by application of the single internal standard.
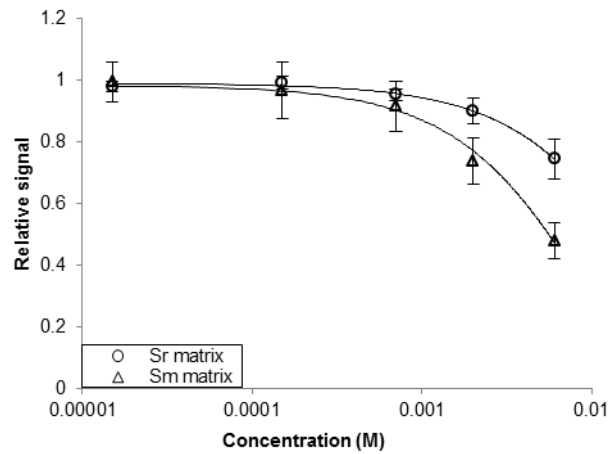
Fig. 10 Relative decrease of the signals of analytes in Sr and Sm matrices in dependence on the matrix concentration (mean for all analytes measured).

In addition, lowering of the degree of the double to single ionization of analytes (Fig. 11), difference in effects on the degree of the double to single ionization of matrices (Fig. 12), broadening of the radial distribution (Fig. 14) and indication of the possible increase of the electron temperature (Fig.13) were observed.
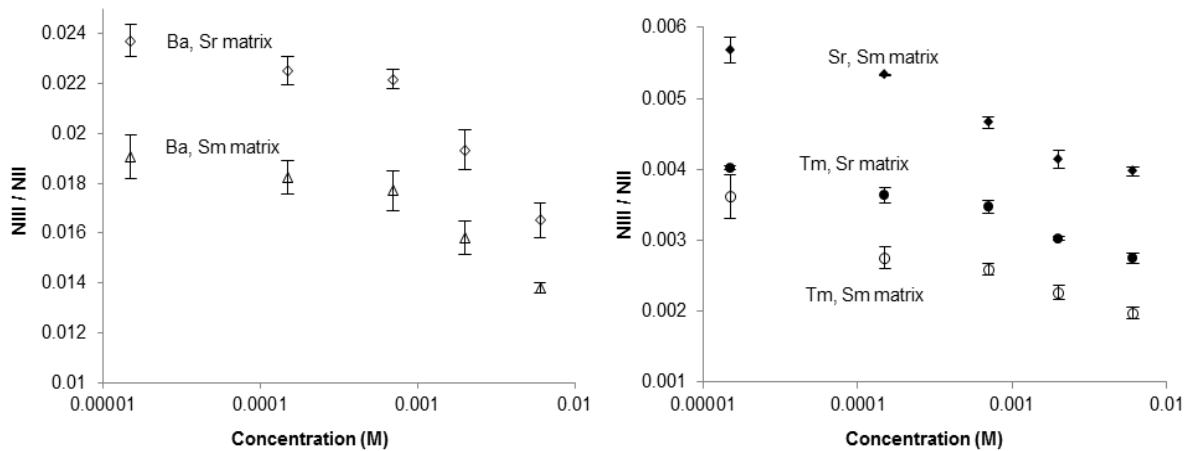

Fig. 11. Dependences of the ratios of signals of the doubly to singly ionized ions of different analytes in Sr and Sm matrices on the matrix concentration.
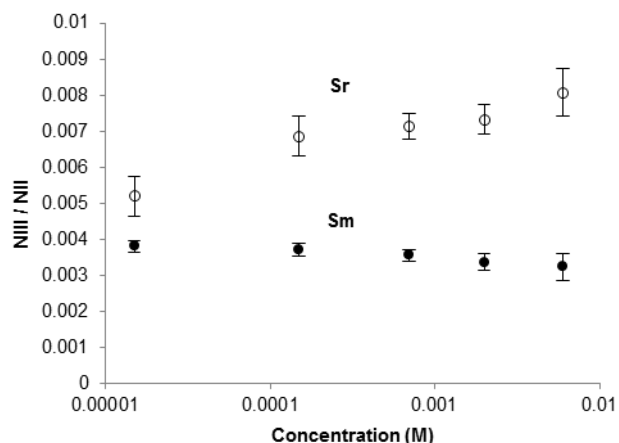
Fig. 12. Dependences of the ratios of the signals of the doubly to singly ionized ions for Sr in Sr matrix and Sm in Sm matrix on the matrix concentration.
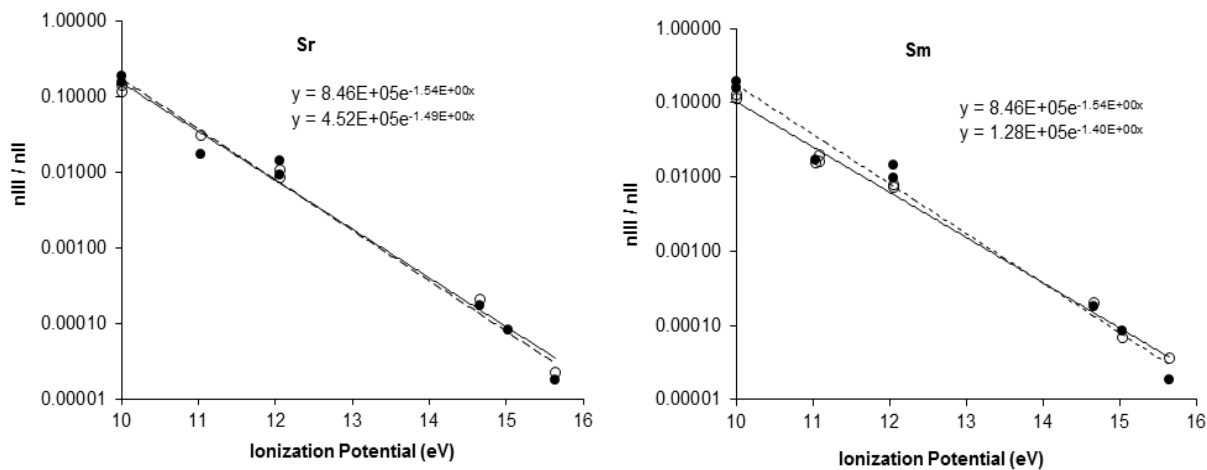

Fig. 13. Dependences of the ratios of populations of the single statistical levels of the doubly to singly ionized ions on the 2nd ionization potential in Sr (left) and Sm (right) matrices at a concentration of 6 mM. The relative populations of the single levels, *n,* are obtained by division of the measured signal value by the partition functions of the ions. The difference in sensitivity of the spectrometer to the doubly and singly ionized ions because of the different *m/z* values is accounted for according to [6]. The black points, a dotted line and the upper equation correspond to the sample without matrix, the white points, a solid line and the lower equations – to the samples with matrices.
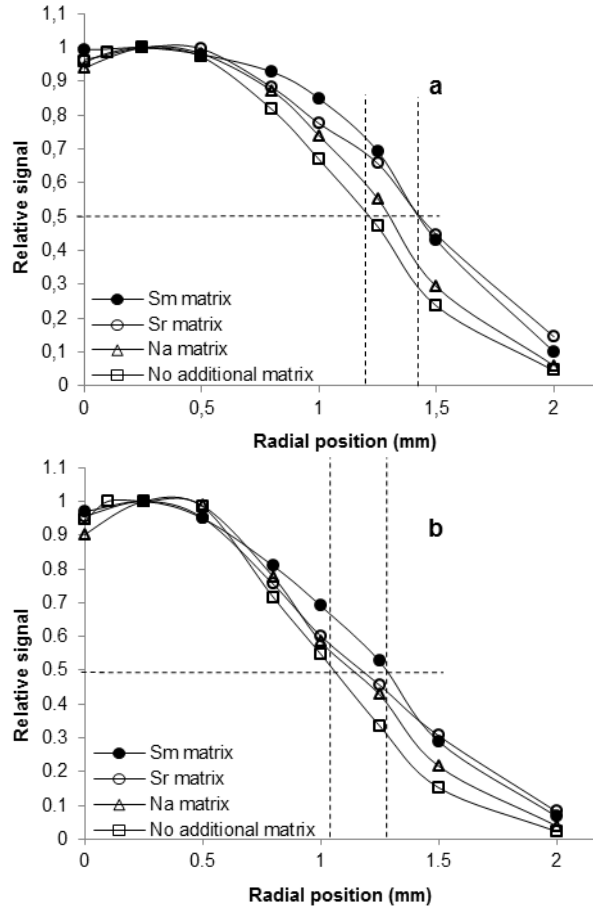
Fig. 14. Radial distributions of the relative intensities of the signals of the singly (a) and doubly (b) ionized ions of [137]Ba in different matrices as obtained from mass spectrometric measurements.

Increase in the ionization temperature (Fig.13), while relatively small, can serve as some indication of the mechanism of the phenomenon. It is at the level of the possible increase of the temperature due to the energy saved in the ionization process when the atoms with the low ionization potentials are ionized instead of argon (see [A7] for details) and as expected to explain the matrix induced increase in the radiation intensity observed in the earlier experiments [4.5]. Due to the Boltzmann exponent, the increased temperature must result in increase in the ionization and excitation rates, the ionization degree or excited level population by the factor

$$\eta = \frac{\Delta N}{N} = \frac{E}{T}\frac{\Delta T}{T} \qquad (5)$$

(energy E and temperature T are in the same units in the expression above). For low energy levels the increment is small but for excitation or ionization energies about or exceeding 5 eV at temperatures characteristic of argon ICP it approaches or exceeds a factor of 10 and can be effective in production of ions, especially of the doubly ionized ones.

Ambipolar diffusion seems to be a mechanism able to integrate the broadened distributions (Fig. 14), increased gradients and an increased electron temperature mentioned above. The ambipolar diffusion coefficient is proportional to the electron temperature. Additional heating of electrons is a widely used method for extracting charged particles from the plasma and leaving the neutral components almost undisturbed [6]. A decrease in the second to first ionization degree due to matrices (Figs. 11, 12) is a supplementary argument as the ambipolar diffusion field must act more efficiently on the second ions [7,8] increasing the ambipolar diffusion rate in general. In the regions of the highest temperature, which can be additionally increased by the matrix, the degree of the second ionization could be more appreciable, increasing the charged particle gradients in the low second ionization potential plasma and the difference in the diffusion rate as compared to the high 2nd IP matrices. A competition between the direct effect of the enhanced temperature and diffusion can be the reason why the simple arguments in favor of the diffusion mechanism [9,10] could not be applied.

The electron number density and density gradients depend on the whole ionization-recombination balance. Because of the high ionization potential of argon the ionization rate of this main plasma gas component is low and even the doubly ionized ions of the low 2nd IP elements can be important in determination of the electron density balance. As emphasized in [11] the energy level diagrams of the doubly ionized ions of most of the low 2nd IP elements are rich in energy levels at the energies close to the ionization potential of argon. Thus the reaction of the electron transfer from argon atom to the doubly ionized ion is possible [K3], e.g.,

$$Ar + Sm^{++*} \rightarrow Ar^+ + Sm^+. \tag{6}$$

In more detail, for example, according to [12] at a temperature of 8000 K the rate of ionization of the argon atoms is about 10^{-18} cm^{3}s^{-1} while the rate of the charge transfer

reaction (6) ought to exceed 10^{-10} cm^{3}s^{-1} [6,13]. As follows from Table 2 in [A7] the number densities of the doubly ionized ions of Sm only about 10^{12} cm^{-3} can be expected at such a temperature at the Sm matrix concentration of 6 mM in approximation of the even distribution of the matrix within the sampling gas (equation (1)). Yet the population of the excited levels at the energy of about 4.7 eV (in vicinity of the ionization potential of Ar as regarded relative to the ground state of Sm$^+$) will be much smaller. In reality there are some energy levels of the doubly ionized ion of Sm in the neighborhood of the Ar ionization potential (integral statistical weight 18 within ±0.1eV), resulting in the effective part of the partition function $\Delta Z/Z=5\cdot10^{-4}$ only at the temperature mentioned above. In spite of such small populations due to the high reaction rate mentioned above the electron transfer effect in the ionization balance can be comparable to the input by the electron collisions. Thus the particle number density of the doubly ionized ions of Sm ought to be lowered. The Ar ion instead of the doubly ionized ion of Sm is obtained at no change of the electron number density. But the electron recombination rate depends on the ion charge [11,14] and it will decrease also increasing the net electron density, density gradients and ambipolar diffusion yield in the electron and ion number density balance.

No reverse processes exist for both the charge transfer reaction (6) and ambipolar diffusion. Thus those processes destroy the detailed balance and increase deviation from the local thermodynamic equilibrium in the plasma. The kinetic approach is inevitable for the estimation of the rates of the processes, the ionization ratios and populations of the atomic states. The details of dynamics of the sample introduction, redistribution of heating within the discharge can be also important.

CONCLUSIONS

1. The results obtained demonstrate high potential of the multielement analytical data and the principal components data analysis for the wine pattern recognition, even when large variety of regions is included. Step by step approach from large to smaller classes was found a promising method for a better exploitation of the discriminating power of the most specific elements at the particular step. Selection of the specific elements is essential to reduce the noise level and can be carried out by the usual statistical procedures. Classification to sub-classes is not an effective way of reduction of the variety of the composition of samples and the matrix effects on the analytical results.

2. Selenium was identified as a high quality internal standard for arsenic measurements. Full integration of the peaks for double focusing high resolution mass spectrometer Element 2 ratio measurements and account for the low frequency noise provided high reproducibility and accuracy of determination. If the suitable internal standards can be selected, method of standard additions is found to provide the measurement accuracy comparable to that of isotope dilution. Comparison of the analytical signal of the test sample from direct measurements and calibration graph is recommended as a test of the level of the quality of the internal standard and elimination of the role of possible matrix effects on the measured analyte concentration values.

3. ICP is a plasma source essentially optimized for optical or mass spectrometric determination of low concentrations of analytes from measurements on ions. The inert gas atmosphere, low concentrations of analyte and matrix enable almost total ionization of most elements, low matrix effects and stability of the ion signals. Effects due to matrix ionization are most important on the minor plasma components and in the intermediate temperature region. Electron density and temperature measurement possibilities from mass spectrometric data were proposed and applied. LTE modeling if closely matching the sample composition was found essential for quantitative description of both the plasma state and the analytical signals. The approach can be perspective for the quantitative analysis of the phenomena in plasmas of the complex samples and semiquantitative analysis.

4. Lowering of the mass spectrometric analytical signals was observed at concentrations of the low first and second ionization potential elements in the range of

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milimoles. The role of the matrix effect can be reduced by application of the internal standards. The low ionization potential elements can increase the electron temperature, concentration and gradients in argon plasma. The increased role of the charge transfer between argon atoms and some doubly ionized ions and ambipolar diffusion are identified as essential in the balance of the charged particles in the presence of the low ionization potential elements.

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A6. A.Puzas, V.Remeikis, P. Serapinas, Ž. Ezerinskis, A. Plukis, G. Duškesas. Mass spectrometric determination of impurities in reactor core graphite for radioactive waste composition modelling. *Lithuanian Journal of Physics,* 2010, 50, No. 4, 445-449.

A7. P. Serapinas, Ž. Ežerinskis, V. Juzikienė. Effect of matrices with low second ionization potentials on analytical signals in inductively coupled plasma mass spectrometry *J. Anal. At. Spectrom.*, 2011, 26 (10), 1997 - 2005.

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K4. A. Puzas, V. Remeikis, Ž. Ežerinskis, P. Serapinas, A. Plukis, G. Duškesas. Determination of impurities of the reactor core graphite by neutron activation analysis, X-ray fluorescence and mass spectrometry techniques for graphite waste modeling. 16th Radiochemical conference, 18 - 23 April 2010, Marianske Lazne, Czech Republic.

CURRICULUM VITAE

2001-2005. Bachelor studies at Vilnius Pedagogical University, Bachelor degree in physics.

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SANTRAUKA

Medžiagų elementinės sudėties tyrimų reikia daugeliui šiuolaikinės technikos ir technologijų, aplinkos ir sveikatos apsaugos sričių. Todėl analitikams tenka tirti labai įvairius savo struktūra ir sudėtimi bandinius. Kartu keliami vis didesni reikalavimai analizės tikslumui, tenka matuoti nanogramų grame masės dalių ir žymiai mažesnes koncentracijas, tirti sunkiai besilydančias ir labai netirpias medžiagas. Pakankamos aptikimo ribos dažnai pasiekiamos tik fizikiniais, tame tarpe spektrometrijos, metodais. Tačiau, ypač spektrometrinio matavimo analizinis signalas ir analizės rezultatas priklauso ne tik nuo analitės koncentracijos, bet ir nuo bendros bandinio sudėties bei struktūros. Struktūros įtaka gali būti panaikinama tirpinant bandinį, tačiau bendros bandinio sudėties įtaka yra viena didžiausių cheminės analizės problemų. Dažniausiai ji sprendžiama įrangą kalibruojant labai panašios sudėties etaloninėmis medžiagomis. Vis plečiantis analizės taikymams, etaloninių medžiagų skaičius jau viršijo dešimt tūkstančių, bet, suprantama, negali patenkinti poreikių, nes naudojamų medžiagų įvairovė auga sparčiau.

Kita vertus, net turint panašios sudėties etaloninę medžiagą, ji niekada nėra identiška tiriamajai. Todėl vien etaloninių medžiagų nepakanka analizės rezultato tikslumui įvertinti. Pačių metodų fizikiniai ir cheminiai tyrimai, išsamesnis metode naudojamų ar pasireiškiančių reiškinių supratimas yra ne mažiau svarbus kelias metodų charakteristikoms pagerinti, jų patikimumui laiduoti bei tikslumui įvertinti.

Šio darbo tikslas yra ištirti paskirų paveikiųjų elementų ir bendros bandinio sudėties įtaką bandinių analizinių masių spektrometrinių matavimų rezultatams. Siekiant šio tikslo buvo tyrinėjami bandinio sudėties poveikiai vienos bandinių klasės riboje, parodyta skirstymas į smulkesnes klases nėra efektyvus būdas bandinio sudėties įtakai analizės rezultatams sumažinti.

Nustatyta, kad kai duomenų bei jų klasių yra daug, bandinių klasifikavimą tikslinga atlikti etapais, vis labiau detalizuojant klases. Kiekviename klasifikavimo etape reikia atrinkti tik būtent labiausiai išskiriančius tas klases požymius, siekiant kuo labiau sumažinti triukšmo įtaką. Nekontroliuojami paveikieji bandinio sandai gali sumažinti klasifikacijos patikimumą.

Priedų metodas yra vienas iš paplitusių būdų bandinio sudėties įtakai sumažinti cheminėje analizėje. Patikslinti metodo matematiniai sąryšiai leidžia realizuoti tiesinę priklausomybę tarp matuojamojo signalo ir analitės koncentracijos, tuo pačiu padidinant metodo tikslumą. Nustatyta, kad tinkamai parinkus vidinį etaloną ir matavimo metodiką masių spektrometrinės analizės priedų metodu tikslumas nenusileidžia izotopų skiedimo metodo tikslumui. Iš priedų nustatyto ir tiesiog bandinyje išmatuoto analitės signalų bandinyje atitikimo tikslumas gali būti naudojamas kaip kriterijus laipsnio, kuriuo bandinio sudėties įtaka analizės rezultatams priedų metode buvo eliminuota.

Ištirta, kad, siekiant sumažinti bendros bandinio sudėties įtaką cheminės analizės rezultatams, elementų matavimams reikėtų naudoti būtent jonus. Sudėtingiems bandiniams, kuriems nėra tinkamo lygio etaloninių medžiagų, analizinės sistemos jautrio priklausomybės nuo masės pataisos ir konkrečios plazmos diagnostikos duomenys įgalina patikslinti analizės rezultatus bei jų neapibrėžtis. Elementų su mažais pirmaisiais ir antraisiais jonizacijos potencialais įtaką analizės rezultatams galima efektyviai sumažinti vidiniais etalonais.

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