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Optimization, Calibration And Statistical Evaluation Of The New Spectrometric Tandem Method

Corresponding Author

Silvia Ruziekova
Department of Chemistry, Faculty of Metallurgy,
Technical University of Košice, Letná 9 SK-042
00 Košice, (SLOVAKIA)
E-mail: silvia.ruzickova@tuke.sk

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ABSTRACT

Analytical efficiency of the tandem spectrometric method, where the evaporation process is separated from the excitation process, was at first concentrated on the observation of the changes of the net intensities (I_L) as well as signal background ratios (I_L/I_B) in dependence on r value, which represents distance from the plasma centre to the zone of the observation of the emission radiation. In like manner were observed changes of the above mentioned parameters in dependence on the intensity of DC evaporation source. Verification of the optimal spectral lines selection was performed by exploratory statistical analysis by using of statistical QC Expert™ 2.5. software. Obtained results confirmed normal and homogeneous character of the intensities distribution. This statement confirmed justness and efficiency of the objective spectral lines selection. Analytical calibration was evaluated by the above mentioned software too. Analytical calibration without and with using of spectrochemical additives was also investigated. AgCl additive proved to be as optimal. Signification of the concentration range was studied and in term of linearity and precision the range of $c\in\langle 0.001,0.04\rangle$% was chosen as optimal. Linearity of the calibration lines was also confirmed. A coefficient of determination R was in the interval of $R\in\langle 96,98\rangle$%.

KEYWORDS

Tandem method;
DC arc;
Marinkovic plasma source;
Optimization;
Statistical verification;
Calibration.

INTRODUCTION

The direct trace element analysis of solid samples is still a challenge for the analyst. Plasma spectrochemical methods offer high precision and low detection limits. However, they require solid samples to be dissolved prior to analysis, which is often difficult and time consuming. Therefore, instrumental techniques that allow direct analysis of solid samples with little preparation are particularly interesting in the analysis of difficult soluble solid samples such as refractory, geological, ceramics and environmental materials.

There are a lot of techniques serving this purpose which can be divided into two main groups. Contact techniques involve classical atomic emission spectral analysis with spark or arc excitation (OES), direct powder injection into the plasma by carrier gas (DPI), direct sample insertion into the plasma using a graphite cup (DSI), and a technique using low pressure discharge for evaporation and excitation of solid samples (LPD). The second group represents the tandem spectral techniques, where the processes of evaporation and excitation are separated, incorporate slurry nebulization (SN), technique for production of aerosol by laser ablation of solid sample (LA), technique for production of aerosol by spark ablation (SA), and electro thermal evaporation of solid sample in a furnace (ETV). Advantages and limitations of mentioned techniques are summarized by several authors[1-8].

One of the major challenges remaining in the area of analytical atomic spectrometry today is the development of more universal methods for the direct analysis of solid samples. The novel technique based on evaporation of solid sample and production of aerosol by controlled high energy direct current (DC) arc discharge from the carrier electrode in a quartz chamber for aerosol production and following excitation of aerosol in a separated Marinkovic plasma source[3] has a chance to be suitable for analysis of various solid samples without any or minimal sample preparation and contamination. This problem was not studied in the spectroscopic literature till now because the combination of auxiliary DC arc with Marinkovic plasma is a novel technique of the authors. Every implementation of a novel method involves demanding optimization process of all operating parameters. The given paper has the aim to focus the investigation on the evaluation and optimization processes of the basic experimental parameters. From this reason it was needed to explore and verify the optical conditions of Marinkovicplasma source and processes which are preferably conditioned by plasma geometry[9].

From the group of the very toxic elements with strong trend of accumulation in the biological systems B, Cr, Mn, Ni, and V trace elements were determinated. From the group of toxic and medium toxic elements Al, Ca, and Mg subsidiary elements were evaluated. It was found out that it is impossible to determinate Si because sample aerosol was enriched by Si which comes from the silicon binder using for fixation of the quartz cell to the cooling brass holders[10]. Next, exploratory analysis of the one-dimensional input data was used for fitness checking of chosen spectral lines. Finally, the calibration process was evaluated and main figure of merit were determined.

EXPERIMENTAL

The new tandem technique of the atom spectra excitation is based on the separation of the thermal sample aerosol creation from the excitation process [11]. Aerosol of the solid samples (powders) is created in the separate quartz cell in the controlled DC arc. This enriched aerosol is transported by carrier Ar gas flow into the excitation plasma source. Emitted plasma radiation is registered in the distance r from the plasma centre and transmitted to the entry slit of spectrometer LECO 750 by means of optical fiber. The obtained integral intensities of the measured spectral lines of the single chosen elements are evaluated by Spectrumat software[12]. Operation of the whole experimental arrangement required to use a programmable DC arc generator[13] assigned for the sample evaporation, Marinkovic plasma source[14] with noncontrolled DC arc and multichannel, computer controlled simultaneous spectrometer with sensitive detectors and decoding unit. A scheme of the new unconventional instrumental equipment is described in figure 1.

INSTRUMENTATION

Cell for aerosol production

Realization of this type of tandem method needed to design thermal evaporation cell (Figure 2) with possibility of the accurate adjusting of the

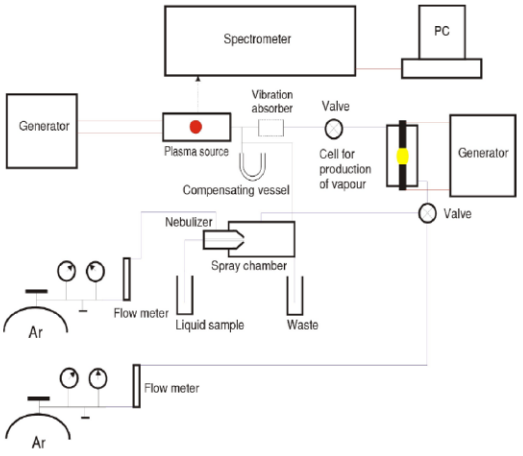


Figure 1: Scheme of the experimental equipment

interelectrode distance, centering of the electrode, tangentially input of the carrier Ar gas as well as effective water cooling of the whole system. For this purpose authors have designed a special quartz cell where aerosol of the solid samples (powders) is created in the controlled DC arc.

DC arc

A DC 301 instrument (Spectral sources Ltd., Germany) was used for evaporation of powder samples. It offers possibility to exactly adjust intensity of the direct current arc (from 1 to 30A) as well as time of evaporation. Controlled DC arc, in comparison with non-controlled DC arc, is characterized by considerably higher stability of intensity and "arc migration" is eliminated because arc is electronically programmable and controlled[15,16]. In case of controlled arc, the intensity fluctuations are lower than at non-controlled arc. All chosen elements, except from B, create only unstable carbides and nitrides and at the temperatures above 4000°C they recombine into the elementary form[17]. The intensity of the evaporation DC arc and exposition time was optimized and described in[18,19].It was approved that current intensities from 15A to 20A are sufficient. Using of higher current intensity than 20A was not suitable because plasma burnt very irregular and at current of 30A and more plasma quenched. Researches of evaporation processes[18,19] proved that all elements were at 20A of DC arc during 35-45s totally evaporated and evaporation process is uniform for all elements. From this reason, original 90s′ exposition time was abbreviated to 60s. This exposition time guaranteed for markedly different matrixes total sample evaporation (combustion). Next experiments were carried out under these optimized parameters.

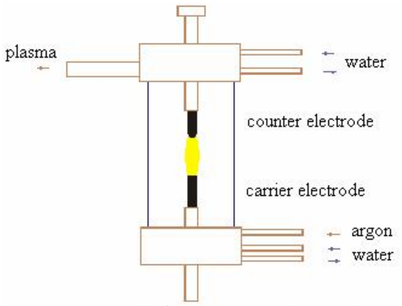


Figure 2 : Cell for aerosol production

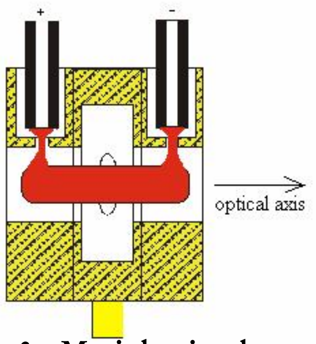


Figure 3 : Marinkoviæ plasma source

Plasma source

Marinkovic plasma source(Figure 3) which is characterized by sufficient temperature, intensity of spectral lines, stability and meaning tolerance to the gas flow fluctuations, was used for our purposes. In the previous work[20] was defined plasma shape of the Marinkovic source (Figure 4). There was stated that in the distance r∈⟨3.5; 4.0⟩mm from the plasma centre, the signal/background ratio value I_l/I_B can be regarded as optimal.

Sample

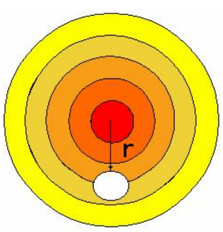


Figure 4: Scheme of the plasma radiation

TABLE 1. Parameters of the studied elements

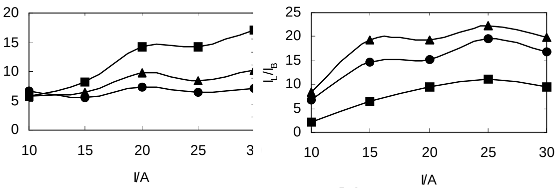
Element	Form	T_m/°C	T_b/°C	λ/nm	E_e/eV	E_e/kJ.M^{-1}
Al	Al_2O_3	2050	2980	396.15	5.98	577.61
B	H_3BO_3	450	1750	249.77	8.29	800.77
Ca	CaO	2580	2850	393.36	6.11	589.87
Cr	Cr_2O_3	2240	4000	425.43	6.64	652.00
Fe	Fe_2O_3	1565	3000	238.20	7.87	759.50
Mg	MgO	2800	3600	280.27	7.64	737.84
Ni	NiO	1960	2732	349.29	7.63	736.78
V	V_2O_5	690	1750	318.54	6.74	652.51

T_m - melting temperature, T_b - boiling temperature, λ - wavelength, E_e - excitation energy

Selection of the elements (TABLE 1) was carried out in accordance with research works of the place of work which are focused to the analysis of the environmental samples of the gravitation dust sediment and non-oxide ceramics materials. Boiling temperature (T_b) of single elements, except from B and V, were always higher than 2000°C and lower or equal 4000°C. Top of the carrier electrode is temperature limited by 4200°C[21], but achieved temperature guarantees total evaporation of all elements. Excitation energy (E_e) of single elements is in the interval from 650 kJ.$^{-1}$ to 800 kJ.M^{-1}. These parameters are perspicuously suitable for DC arc evaporation.

Experiments were carried out with the model mixtures consisting of oxides of the given elements (Al, B, Ca, Cr, Mg, Mn, Ni, and V) and graphite powder, because the main constituent of the gravitation dust sediments is the graphite powder. The J.Mathey, LONDON spectpure chemicals were exclusively used for the calibration.

RESULTS AND DISCUSSION



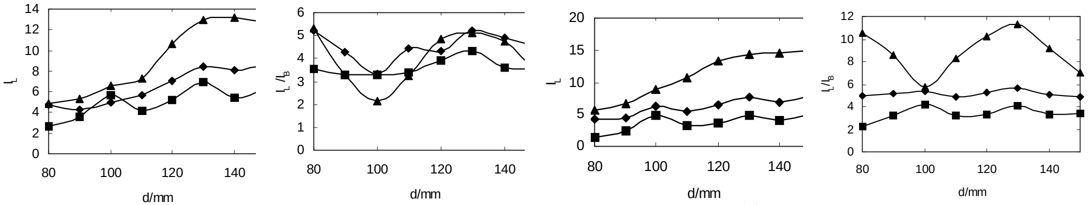
a) r = 3 mm b) r = 3.5 mm

Figure 6 : Influence of the current intensity on the I_L/I_B values.
● Al, ▲ Cr, ■ Mg

Evaluation and optimization of the experimental conditions

Whereas it was not possible to use a conventional instrument equipment, new modified experimental conditions required determination of optimal distance between optical fiber and plasma source, as well as distance between display lens and plasma source. The main optimizing criterion was experimentally determined maximum value of the net intensity (I_L) as well as maximum value of the signal/background ratio (I_L/I_B), which is calculated by Spectrumat software as integrated intensities in the time. DC arc of 15A intensity was used for these experiments (Figure 5) . Following obtained results, 130 mm distance between optical fiber and Marinkoviæ plasma source, and 165mm distance between display lens and plasma source were specified as optimal values. In like manner was optimized distance of the zone of the optical display r from the plasma centre. The maximal (I_L) and (I_L/I_B) values were obtained in the range of r∈⟨3.5,4⟩mm during 90s exposition time which guaranteed, nay exceed, total sample evaporation (combustion).

Next step of the optimization was to determine optimal DC arc intensity (Figure 6). According to above mentioned criterion, current interval of I∈⟨10, 30⟩A was investigated. At the current optimization



a) r = 2.5 mm b) r = 3 mm

Figure 5 : Influence of the distance d between lens and plasma centre on the I_L a I_L/I_B values
■ Mg, ◆ Cu, ▲ Cr,

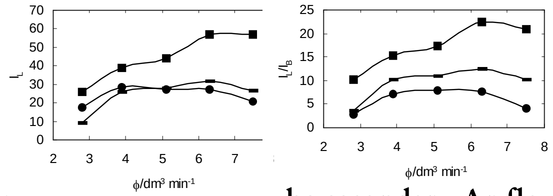


Figure 7 : Influence of the secondary Ar flow ϕ on the I_L a I_L/I_B values ● Al, – Ca, ■ Mg

was used the reduced exposition time of 60s. Graphical dependences in the figure 6 prove that application of the current from 10 to 20A causes gradually increasing of I_L/I_B value. Higher current than 20A has a negative influence on the (I_L) and (I_L/I_B) values. It sometimes causes unstable and irregular burning and even quenching of plasma that led to the imperfect excitation[19]. From this reason, all other experiments were realized at DC arc of 20A and 60s'exposition time.

Finally, carrier gas flow ϕ (Figure 7) and interelectrode distance d (Figure 8) in the evaporation cell were optimized. The secondary Ar flow of ϕ=3.9 dm^3min^{-1} and 1mm interelectrode distance were defined as optimal values. Previous our results [22,23] confirmed applicability of the graphite carrier electrodes SW 380 and carbon counter electrodes SU 206. Their thermal and electric properties are the most suitable for this type of excitation.

Preliminary experiments proved that spectrochemical additives have an expressive positive influence on the plasma source stability. It was found out that AgCl additive during the exposition increased the conductivity and the chlorinating effect and favorably the precision and the detectability too. Optimized parameters of the experimental conditions are shown in TABLE 2.

Exploratory analysis

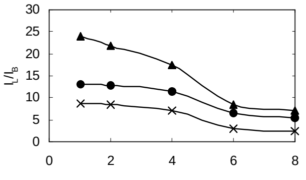


Figure 8: Influence of the interelectrode distance d on the I_L a I_L/I_B values
● Al, ▲ Cr, × Fe

In order to approve the well-founded selected spectral lines of the individual analytical elements, exploratory analysis of the one-dimensional input data was performed. From the statistical point of view, this process is important because of relevance of the spectral lines selection in keeping with given experimental technique. Representative selection of the input data should follow random sampling which is characterized by constant dispersion of the individual elements, reciprocal independence and selection should by characterized by normal and homogeneous dispersion. In term of statistical data processing are important shaped parameters like excess E(x) and asymmetry A(x). In TABLE 3 are summarized results of the exploratory analysis. This analysis required a 25-multiple repeated measurements of the 1 % oxide mixture of the selected elements at current

TABLE 2. Experimental conditions

General conditions	
Spectrometer	LECO – 750, simultaneous
Grating	2400 lines per 1 mm
Spectral range	220 – 766 nm
Evaporating conditions	
Evaporation source	Controlled direct current arc, generator DCA 301
Current of the DC arc	10,15,20,25,30A
Carrier electrode	SW 380, Elektrokarbon Topoľčany
Counter electrode	SU 206, Elektrokarbon Topoľčany
Distance between electrodes	1 mm
Concentration of the additive	9.3 mg cm^{-3} $AgNO_3$
Sample Sample amount	1% oxide mixture of the chosen elements 10 mg
Primary Ar flow	2.8 dm^3 min^{-1}
Secondary Ar flow	2 dm^3min^{-1}
Excitating conditions	
Excitation source	Marinković plasma source
Current intensity	11 A
Display and evaluating conditions	
Display plasma area	r=3.5 mm
Distance between lens and plasma	130mm
Distance between optical fibre and lens	165mm
Exposition time	90,60,42s
Software	SPECTRUMAT

TABLE 3: Results of the statistical analysis of the one dimensional input data

Element		Al	B	Ca	Cr	Fe	Mg	Ni	V
Wavelength	λ /nm	396.152	249.773	393.367	425.433	238.207	280.270	349.296	318.540
No. measur.	N	25	25	25	25	25	25	25	25
Arith. mean	$\bar{I}$ (x)/ppm	49.43	9.06	40.29	69.23	33.62	24.53	24.96	79.83
St. dev.	s($\bar{I}$)$_x$/ppm	3.03	1.60	2.80	5.19	3.02	2.51	2.35	7.12
RSD	s($\bar{I}$)$_{x,r}$/%	6.13	17.67	6.95	7.49	8.98	10.23	9.41	8.92
Median	$\bar{I}$ (x)/ppm	49.62	9.06	40.68	70.01	33.89	24.42	25.08	79.58
St. dev.	s($\bar{I}$)$_x$/ppm	1.06	0.67	1.09	2.18	0.80	0.76	0.78	2.45
RSD	s($\bar{I}$)$_{x,r}$/%	2.14	7.39	2.68	3.11	2.36	3.11	3.11	3.08
Modus	$\hat{I}$ (x)/ppm	49.96	9.06	41.37	71.43	34.38	24.21	25.29	79.13
Half sum	$\bar{I}$ (x)/ppm	49.01	9.28	39.97	69.03	33.99	24.20	25.03	79.30
Range	ΔI/ppm	10.58	1.33	9.65	15.22	12.19	9.38	7.93	24.84
Asymmetry	A(x)	-0.13	0.07	-0.28	-0.14	0.08	-0.07	0.16	0.04
Test asym.	$t_{A(x)}\neq 0$	–	–	–	–	–	–	–	–
Exces	E(x)	2.17	2.12	1.92	1.69	2.44	2.23	2.00	2.00
Test exces	$t_{E(x)}=3$	–	–	–	–	–	–	–	–
Test norm.	t_{norm}	+	+	+	+	+	+	+	+
Test homog.	t_{horm}	+	+	+	+	+	+	+	+
Box-Cox. T	r	1	1	1	1	1	1	0.4	0.8
Justness		No	No	No	No	No	No	No	No

–: Not accepted; +: Accepted

of 20A and evaluation of the obtained intensities at conditions shown in TABLE 1 and 2. Obtained data were evaluated by QC Expert™ 2.5. statistical software[24,25]. Precision of the estimation is expressed by relative standard deviation value (RSD). These data , except from B and Mg, are always lower than 10% but higher than 6%. This fact can be explained by complicated transport of aerosol into the plasma source because on the other hand, plasma sources are characterized by better precision. Values of the arithmetical mean ($\bar{I}$), median ($\tilde{I}$), modus ($\hat{I}$), and halfsum ($\hat{I}_P$) are in the frame of observational errors the same that is assumption for normal data distribution. RSD values for median are systematically lower than for arithmetical mean. It can be explained by fact that creation of median do not take into account leverages and out layers. Excess E(x) and asymmetry A(x) values and their tests prove relevance of normal distribution and homogeneity of the input data.

Finally, Box-Cox transformation was done for checking of normal distribution. Extreme cases of the most preferable and less preferable, but still suitable, spectral lines selection are shown in figure 9 and 10. Histogram of Mg intensities (Figure 9a) can be regarded symmetric. Circle plot (Figure 9b), which takes into account asymmetry A(x) and excess E(x), shows a good agreement with a theoretical curve.

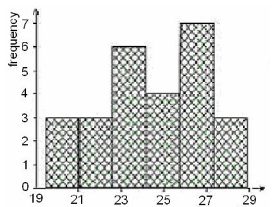


Figure 9α): Histogram of I_{Mg} values

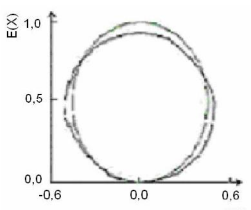


Figure 9b) :Circle plot of I_{Mg} values

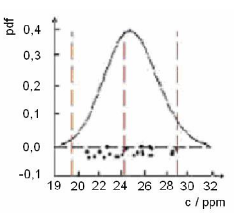


Figure 9c): Probability of density plot for I_{Mg} values

TABLE 4. Comparison of the parameters of the calibration lines without and with AgCl additive

Element		Al_1	Al_2	B_1	B_2	Ca_1	Ca_2	Cr_1	Cr_2
Wavelength	λ /nm	396.152	396.152	249.773	249.773	393.367	393.367	425,433	425.433
No. measur.	N	33	43	39	43	38	36	33	43
Model		linear	linear	linear	linear	linear	linear	linear	linear
Fitness		suit	suit	suit	suit	suit	suit	suit	suit
Abs. member	A(x)	-1.50	0.12	0.17	-0.51	-1.80	1.54	-2.43	0.57
St. deviation	$s_{A(x)}$	0.81	0.14	0.20	0.67	0.63	0.28	1.18	0.49
Test abs. m.	$t_{A(x)}=0$	+	+	+	+	+	+	+	+
Sensitivity	B(x)	586.22	316.69	99.44	1170.69	391.42	761.62	810.51	869.63
Min. conc.	c_{min} /%	0.005	0.001	0.005	0.001	0.005	0.001	0.005	0.001
Max. conc.	c_{max} /%	0.06	0.04	0.10	0.04	0.10	0.04	0.06	0.04
LOD	c_L /%	0.004	0.001	0.006	0.001	0.005	0.001	0.004	0.001
St. deviation	s(y)	2.92	0.66	0.85	3.23	2.54	1.26	4.27	2.34
Corel. coef.	r	0.97	0.99	0.97	0.98	0.98	0.99	0.97	0.98
Test corel.	$t_r=0$	-	-	-	-	-	-	-	-
Coef. deter.	$R=r^2$ .100	94.09	98.01	94.09	96.04	96.04	98,01	94.09	96.04
Element		Fe_1	Fe_2	Mg_1	Mg_2	Ni_1	Ni_2	V_1	V_2
Wavelength	λ /nm	238.207	238.207	280.270	280.270	349.296	349.296	318.540	318.540
No. measur.	N	31	43	35	43	31	43	37	43
Model		linear	linear	linear	linear	linear	linear	linear	linear
Fitness		suit	suit	suit	suit	suit	suit	suit	suit
Abs. member	A(x)	4.50	0.55	-1.53	0.11	2.54	-0.05	-0.19	0.51
St. deviation	$s_{A(x)}$	1.05	0.33	0.34	0.26	0.15	0.11	0.26	0.40
Test abs.	$t_{A(x)}=0$	+	+	+	+	+	+	+	+
Citlivosť	B(x)	562.36	837.31	383.06	544.73	123.91	331.97	114.54	1019.89
Min. conc.	c_{min} /%	0.005	0.001	0.005	0.001	0.005	0.001	0.005	0.001
Max. conc.	c_{max} /%	0.06	0.04	0.10	0.04	0.10	0.04	0.10	0.04
LOD	c_L /%	0.005	0.001	0.003	0.001	0.003	0.0009	0.006	0.001
St. deviation	s(y)	3.69	1.57	1.36	1.27	0.59	0.52	1.06	1.92
Corel. coef.	r	0.94	0.99	0.99	0.98	0.99	0.99	0.96	0.99
Test corel.	$t_r=0$	-	-	-	-	-	-	-	-
Coef. deter.	$R=r^2$ .100	88.36	98.01	98.01	96.04	98.01	98.01	92.16	98.01

+: identical with zero (accepted); –: not identical with zero (refuse); X_1 – without additive; X_2 – with AgCl additive

Finally, the probability density plot (Figure 9c) has an ideal Gaussian character. Set of these characteristics confirms normal scatter character. Al, Fe, Ni, and V elements achieved similar appropriate parameters. On the other hand, histogram of Ca intensity values (Figure 10a) and in like manner B

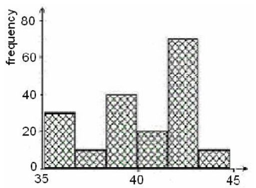


Figure 10a): Histogram of ICa values

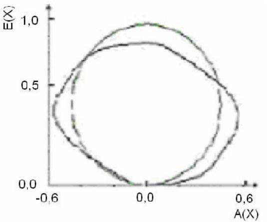


Figure 10b): Circle plot of ICa values

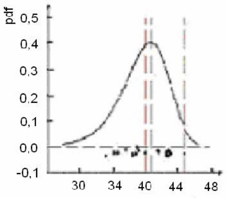


Figure 10c) : Probability of density plot for ICa values

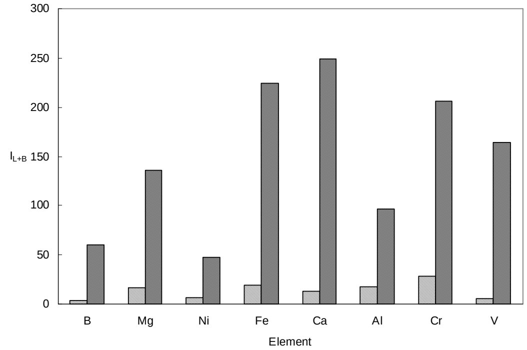


Figure. 11 Comparison of the influence of additive on the gross signal of analytical elements.
□ without AgCl additive, ■ with AgCl additive

TABLE 5: Recovery and its testing

Element	$c(X)_0$ /%	$c(X)_{calc}$	Δc	Test result
Al	0.020	0.021	0.001	-
B	0.020	0.0195	0.0005	+
Ca	0.020	0.020	0.000	+
Cr	0.020	0.022	0.002	-
Fe	0.020	0.019	0.001	+
Mg	0.020	0.019	0.001	+
Ni	0.020	0.021	0.001	+
V	0.020	0.022	0.002	-

and Cr values cannot consider symmetric. Overlapping of the theoretical curve of the circle plot with experimental data curve (Figure. 10b) confirms disordered character of normal distribution. The probability density plot (Figure. 10c) markedly confirms this break. Course of the curve is asymmetric and skewed in the direction of lower values. Following exploratory analysis data it can be stated that data in TABLE 3, in spite of some differences, which are typical for multicomponent analysis, confirm normal and homogeneous character of the intensities distribution of the single tested spectral lines. From this reason, selection of the spectral lines is in term of statistics relevant and it is allowed to use these lines for analytical calibration.

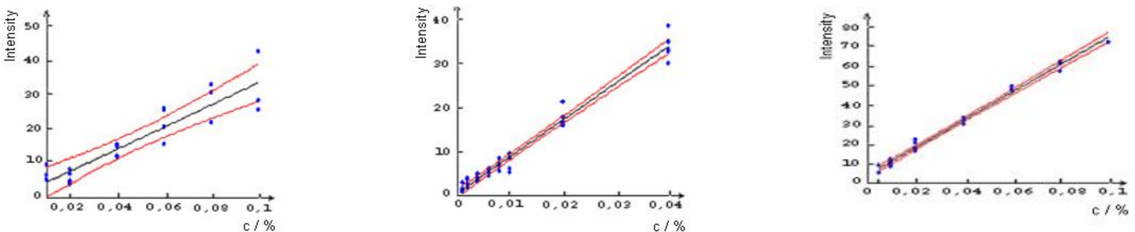
Analytical calibration

At first, the analytical calibration was performed without spectrochemical additive (X_1) and then (X_2) with AgCl additive. Into each empty electrode was added 10ml of $AgNO_3$ (c=9.3 mg cm^{-3}) and 10ml of concentrated HCl. After drying (105°C/1h), electrodes were filled with 10mg of mixture consisted of graphite powder and analyzed sample. Reaction (1) expresses creation of AgCl, which is during evaporation thermal decomposed into recombined atomic chlorine and silver.

$$AgNO_3 + HCl \rightarrow AgCl + HNO_3 \qquad (1)$$

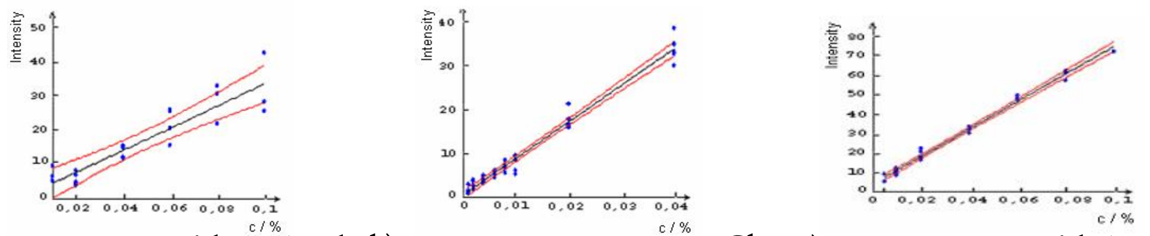
At spectra excitation was used not only "carrier" effect of AgCl but also "chlorination"effect of released chlorine too. Results confirmed expressive influence of AgCl additive on all spectral lines intensities (Figure 11) as well as total sample evaporation which was reduced to 42s.

In the all tested cases was confirmed availability of the linear model of the calibration line. Absolute member value (A(x)) was tested in disagreement with zero. This test was negative in the all cases that mean that the matrix effect of the appropriate influence only the slope of the calibration line. The sensitivity value (B(x)), except from Al line, was for cases with using of AgCl additive always markedly higher than in the cases without using of additive. In like manner, the expressive concentration differences Δc between $\langle c_{max}, c_{min} \rangle$ values were achieved without AgCl additive. Correlation coefficient value (r) for calibration without AgCl application was in the range of $r \in (0.94, 0.99)$ and appropriate determination coefficient R value has interval $R \in (88,98)\%$. AgCl



a) $\Delta c \in \langle 0.01, 0.1 \rangle$% without AgCl b) $\Delta c \in \langle 0.001, 0.04 \rangle$% with AgCl c) $\Delta c \in \langle 0.005, 0.1 \rangle$% with AgCl

Figure 12: Calibration lines for Fe



a) $\Delta c\in\langle 0.01,0.1\rangle$% without AgCl b) $\Delta c\in\langle 0.001,0.04\rangle$% with AgCl c) $\Delta c\in\langle 0.005,0.1\rangle$% with AgCl

Figure 12: Calibration lines for Fe

additive always increased correlation and it was achieved range of $r\in(0.98,0.99)$ and range of determination coefficient of $R\in(96.0,98.0)$%.

This result confirms hypothesis that it is allowed to use all input data for analytical calibration. Finally, LOD values confirm positive influence of AgCl additive for whole calibration process. Comparison of some figure of merit at the calibration for Fe element are summarized in TABLE 6 and graphically shown in figure. 12.

Final calibration results with AgCl application were tested by recovery estimation (TABLE 5). Synthetic oxides mixture of the chosen elements with concentration of $c(X)_o = 0.02\%$ was chosen as a confirmation value because obtained calibration lines of the mentioned concentration range showed high coefficients of correlation and determination. Defined concentration values those recovery was tested are marked as $c(X)_{calc}$. Concentration values difference $\Delta c = c(X)_o - c(X)_{calc}$ expresses "bias" (errors) measure of the determination. In the case of V element this value was 0.002% but in the other cases it was equal or less than 0.001%. In the aspect of theoretical value of 0.02% it is only 5% inaccuracy. Agreement of the concentration values of standards and proper analysis is sufficient and new tandem method can be regarded to be accurate.

TABLE 6: Comparison of some figure of merit at

Calibration		
without AgCl	with AgCl	
$\Delta c\in\langle 0.01,0.1\rangle$ % linear model	$\Delta c\in\langle 0.001,0.04\rangle$% linear model	$\Delta c\in\langle 0.005,0.1\rangle$% linear model
$c_L\in\langle 0.009,0.08\rangle$%	$c_L\in\langle 0.0009,0.01\rangle$%	$c_L\in\langle 0.001,0.005\rangle$%
$s_{A(X)}\in\langle 0.20,1.18\rangle$	$s_{A(X)}\in\langle 0.11,0.67\rangle$	$s_{A(X)}\in\langle 0.25,1.60\rangle$
$R\in\langle 82,86\rangle$%	$R\in\langle 96,98\rangle$%	$R\in\langle 96,98\rangle$%

CONCLUSION

Optimization of every new method is demanding and time consuming process mainly in the case of method which is special in the scientific field. From this reason it was necessary at first to optimize experimental conditions. We found out the maximum (I_L) and (I_L/I_B) value in the distance $r\in\langle 3.5;4.0\rangle$mm from tha plasma centre. The optimal intensity of DC arc for sample evaporation in the cell was 15A and during evaporation time of 60s was reached total sample evaporation. Using of AgCl additive increased the efficiency of evaporation and so exposition time could be reduced to 42s.

Exploratory analysis of the one-dimensional input data of the 25 repeated measurements confirmed normal and homogeneous data distribution. It was proved that values of arithmetical means, moduses, medians and halfsums are for single elements in the frame of observed errors identical and this fact suggests that spectral line selection is relevant. Shaping tests confirmed that values of asymmetry $A_x \neq 0$ and excess $E_x = 3$ are optimal. In the most cases was confirmed symmetrical probability density distribution that is condition for application of calibration by pair comparison.

Using of AgCl as a spectrochemical additive markedly influenced not only LOD values but also precision of method. The main attention was paid to the verification of linear model validity. Absolute member A(x) was statistically equal to zero that proves that matrix effects influence only slope of the straight line, sensitivity of the analytical method. LOD values are in the range of $c\in\langle 2.0,0.9\rangle$ppm and recovery of the method is high because measure of "inaccuracy" is only 5%.

Presented results warn necessity to use statistical evaluation mainly in the case of the optimization of new method because exploratory analysis informs us about efficiency parameters of the suggested analytical method. The more preferable statistical results we obtain the higher chance for optimal calibration we have.

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