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INDUCTIVELY COUPLED PLASMA OPTICAL EMISSION SPECTROSCOPY – DETERMINATION OF RARE EARTH AND PLATINUM GROUP OF ELEMENTS

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Abstract. The economic importance of rare earth elements and platinum group of elements has led to the development of analytical methods, which have to ensure their accurate quantification in different type of samples. Radial viewing 40.68 MHz inductively coupled plasma optical emission spectrometry (ICP-OES) and the Q - concept for the quantification of spectral interference were used in the determination of rare earth and platinum group of elements in materials with variable matrix constituents. Improvement of the detection limits was achieved by optimal line selection in the presence of different matrix constituents and by optimization of the operating conditions. The Mg II 280.270 nm/Mg I 285.213 nm line intensity ratios was measured to evaluate the robustness of the operating conditions. The lowest detection limits were obtained under non-robust conditions in a pure solvent and in the presence of rare earth matrices (excitation temperature ~ 6200 K). In the case of platinum group of elements in the presence of complex matrix, containing Al, Ca, Fe, Mg, Mn, P and Ti, the lowest detection limits were derived under robust conditions (excitation temperature ~ 7200 K).

Keywords: ICP-OES; rare earth elements; platinum group element; matrix effects; detection limits

Introduction

The great demand for rare earth element (REEs) and platinum group of elements (PGEs) requires large amounts of its production. This stimulates the development of methods for analytical control of various row minerals as well as in different technological and final products, which are of great interest for development of present

day technologies (McGee et al., 1991; Millett, 1980; Morris, 1980; 1990; Morris et al., 1991). Different research groups had focused on methods for the determination of these elements in samples with various compositions (Bayon et al., 2009; Barefoot & Van Loon, 1999; Burman, 1987; Brzezicka & Baranowska, 2001; Lichte et. al., 1987; Petrova et al., 2009; 2010; Ramanaiah, 1998; Li & Feng, 2006).

The determination of REEs in oxide crystal materials and in pure rare earth matrices requires taking into account the presence of matrix constituents, which are characterised with line rich emission spectra (Daskalova et al., 1992; 1996; 1997; 2002; Velichkov et al., 2000; Aleksieva et al., 2002; Kolibarska et al., 2008). The PGEs have to be determined in geological samples (Burman et al., 1987; Li & Feng, 2006; Petrova et al., 2010). The distribution of PGEs in geological samples depends upon the geochemistry. Therefore, knowledge of the PGEs distribution may shed new light on the mechanisms of noble metal mineralization and geneses, and thus provide additional useful information for mineral exploration (Boulyga & Heumann, 2005). The determination of PGEs in geological sample is of interest for geochemistry and for production of noble platinum group elements from different ores and waste materials (Petrova et al., 2010). PGEs are widely applied in the catalyst production. This fostered the development of accurate methods for determination of Pt, Pd and Rh in car catalysts (Kingdon et al., 1991). This fostered the development of accurate methods for determination of Pt, Pd and Rh in car catalysts in presence of aluminum as main element (Kallmann & Blumberg, 1980, Petrova et al., 2009). PGEs were included in automobile catalytic converters and the converters have been used in many car exhaust systems. As a result of the hot exhaust gases in motor car flowing through the converter cause abrasion and ablation of these units. These processes lead to the emission of the PGEs to the environment (Heinrich et al., 1999). Several PGEs and their complex salts cause allergy, asthma, rhino-conjunctivitis and different serious health problems (Merget & Rosner, 2001). The use of PGEs in catalyst production fostered the development of accurate methods for their determination in the environmental samples because of their wide distribution from the car exhaust system (Rauch et al., 2000; Wiseman & Zereini, 2009). Therefore the general analytic tasks in the determination of REEs and PGEs by ICP-OES require to take in consideration the spectral interferences, especially line overlaps, in order to ensure the both the lowest possible detection limits in the presence of matrices with line rich emission spectra and the accuracy of the analytical results.

The general purpose of the present paper is to show the possibilities of radial viewing 40.68 MHz ICP to lower the detection limits in the determination of Y, Sc and rare earth elements in europium oxide and PGEs in complex matrix, containing Al, Ca, Fe, Mg, Mn, P and Ti, in automobile catalytic converters and in environmental samples.

Experimental

Instrumentation

The measurements were performed with ICP-OES spectrometer JY Ultima 2 (Jobin Yvon, Longjumeau, France) with radial viewing. The characteristics of the spectrometer are specified in Table 1.

Table 1. Specification of the ICP-OES spectrometer JY ULTIMA 2 (Jobin Yvon, France)

Monochromator	JY ULTIMA 2 (Jobin Yvon, France)
Mounting	Czerny -Turner, focal length1 m
Grating	Holographic, 2400 grooves mm^{-1} – first order
Wavelength range	160 nm – 800 nm
Entrance slit	0.015 / 0.02 mm
Exit slit	0.02 / 0.08 mm
Practical spectral bandwidth	0.005 nm in the 2-nd order from 160 nm to 320 nm; 0.010 nm in the 1-st order from 320 to 800 nm
Detector	High Dynamic Detectors based on PMT‘s
Rf generator	Solid state RF 40.68 MHz
Frequency	40.68 MHz
Power output	0.5 – 1.50 kW
Nebulizer	Meinhard, concentric glass
Spray chamber	JY Glass cyclonic spray chamber
Pump	Peristaltic, two channels, twelve-rollers
Plasma torch	Fully demountable, injector tube with inner diameter-2 mm

Decomposition procedures

Europium oxide as pure rare earth matrix

1 g Eu_2O_3 is dissolved in HCl (12.0 mol l^{-1}) and the solution is transferred in 100 ml graduated flask. The blank contains 1 g high purity Eu_2O_3 (Johnson Matthey Chemicals, London, UK) dissolved in the same way, as the sample in the 100 ml graduated flask. The final acidity of the solution is 22 mg ml^{-1}. The reference solutions for the determination of the analytes were prepared on the basis of a blank containing the acids, used for digestion and the Eu_2O_3. The matrix blank contains the acid blank and the Eu_2O_3.

Enriched rare earth concentrate with composition Eu, Nd, Y, Tb and Dy

1 g of the enriched rare earth concentrate is dissolved in HCl (12.0 mol l^{-1}) and the solution is transferred in 100 ml graduated flask. The final acidity of the solution is 22 mg ml^{-1}.

Determination of Pt, Pd and Rh in samples with different matrix composition:

Geological sample - certified reference material SARM 7 (Pt - ore)

The digestion was performed in a microwave digestion system (Milestone 1200, USA) at 230 °C and at pressure of 70 bar in accordance with Ref. (Zischka et al, 2002). 0.5 g of the SARM 7 sample was weighed in a PTFE vessel. The digestion procedure in three steps was used: First step - 4 ml nitric acid (65%) and 1 ml hydrochloric acid (12.0 mol l^{-1}); Second step - 1 ml hydrofluoric acid (40%) for complete dissolution of the sample; Third step - 10 ml boric acid, saturated at 20 °C for complexing insoluble fluorides. Afterwards boric acid (in excess to HF) was added in order to bind the HF as a HBF_4 complex. HBF_4 solutions do not etch glassware used (volumetric flasks etc.) as well as the conventional ICP sample introduction system (glass nebulizer, glass chamber and silica ICP-torch). So a conventional ICP-OES can be used for the analysis of such solutions. The final sample solution was 50 ml. The concentration of boron in the sample solution is 1400 μg ml^{-1}. Duration of one digestion step, including cooling period, was 40 min.

Environmental material - certified reference material BCR-723 (road dust)

Extraction of traces of Pt and Pd in acid mixture HBr / HNO_3 in an apparatus, described in (ISO 11466:1995 (E)) was used for digestion of certified reference material BCR-723 (road dust). A total of 3.0 g subsample was weighed in a reaction vessel; 3 ml of bi-distilled water was added to obtain slurry, followed by 15 ml of HBr and 15 ml HNO_3. The sample was allowed to stand for 16 h at a room temperature for slow oxidation of the organic matter and reduction of the gases. They were heated under reflux until boiling for 2 h and allowed to cool slowly at room temperature. The content of the reaction vessel was transferred quantitatively to a 100 ml glass ware. The supernatant solution was filtered through a filter (blue band), the solution was collected in a 100 ml graduated flask, the residue was washed with 0.1 M HCl and final solution was filled up to the 100 ml with 0.1 M HCl.

Extraction of platinum and palladium, sorbed on activated carbon immobilized with 2- mercaptobenzimidazole

The following procedure was used: the resulting solution obtained in Section 2.3.2 was filtrated through a filter (blue band); the filter with activated carbon was dried in drying-oven at 90 °; the activated carbon along with a filter was transferred in quartz

crucible and the sample was heated at 450 °C (1 h) and 850 °C (1 h) in furnace; the quartz crucible was allowed to cool slowly at a room temperature and after that the crucible is placed into reaction flask of an apparatus, described in ISO 11466:1995 (E); an acid mixture HNO_3/HBr (3 ml HNO_3+ 3 ml HBr) was use for dissolution of the so prepared residue; the sample was heated under reflux until boiling for 1 h and allowed to cool slowly a at room temperature. The content of the reaction container was transferred quantitatively to a 10 ml graduated flask and filled up to the mark with 0.1 M HCl. The final solution was introduced to the ICP - OES.

Calibration procedures

ICP-OES is not free from acid matrix interferences (Todoli & Mermet, 1999). The correct calibration from the point of view of multiplicative interferences means a precise matching of the acid and matrix contents both in the reference and in the sample solutions.

Results and discussion

Methodology for quantification of spectral interferences in the presence of matrices with different composition

Spectral interferences may drastically deteriorate the analytical characteristics of the ICP-OES. Without full information on the type and magnitude of spectral interference levels, the correct calibration procedure cannot be applied. In this case, the spectral interferences will affect the intercept if the calibration curve is plotted on a linear scale, and accurate analytical results cannot be expected (Boumans, 1986).

Boumans and co-authors defined the "true detection limit", $C_{L,\,true}$, as a rational criterion for line selection (Boumans et al., 1988). This methodology was taken as a basis in the presence investigations (Velichkov et al., 1993; 1998).

As a first step is the identification of all matrix lines which influence the prominent lines of the analytes. The information about the type of spectral interferences was derived from wavelength scans centered on the candidate (prominent) analysis lines. The identification requires a detailed study of the spectrum of the interferents around prominent lines (Boumans et al., 1988; Daskalova et al., 1992).

In the case of a pure matrices, the following signals were measured: X_A, X_B, $X_W(\Delta\lambda a)$, $X_I(\lambda a)$.

X_B is the solvent blank (due to source and solvent); – $X_W(\Delta\lambda a)$ - the wing background level with respect to the solvent blank; $X_I(\lambda a)$ - the net interfering signals with respect to the wing background level $X_{WJ}(\Delta\lambda a)$ of the interferent.

The total background signal in the presence of pure matrix is:

$$X_{BL} = X_B + Xw\ (\Delta\lambda_a) + X_I(\lambda_a), \quad (1)$$

The measured signals were then reduced to sensitivities: the sensitivity of the analysis line [S_A] (defined as the net line signal [X_A] per unit analyte concentration [C_A]; the interferent sensitivities [S_{WJ} ($\Delta\lambda a$)] and [$S_{IJ}(\lambda a)$], defined as interferent signals [$X_{WJ}(\Delta\lambda a)$] and [X_{IJ} (λa)], respectively, per unit interferent concentration [C_I]). Finally, the sensitivities were used for the calculation of the Q-values for wing background interference [$Q_W(\Delta\lambda a)$]= [$S_W(\Delta\lambda a)$] / [S_A] in the spectral region $\Delta\lambda a$, the Q-values for line interference [$Q_I(\lambda a)=S_I(\Delta\lambda a) /S_A$] in the maximum of the prominent line λa.

The true detection limits ($C_{L, true}$) is defined by Eq. (2), and the conventional detection limits ($C_{L, conv}$) with Eq. (3):

$$C_{L\ true} = 2/5\ Q_I(\lambda_a)\ \ C_I + C_{L, conv} \quad (2)$$

$$C_{L, conv}\ = 22\ \ 0.01\ \ RSDBL\ \ [BEC + Q_I(\lambda_a)\ \ C_I + Q_W(\Delta\lambda_a)\ C_I] \quad (3)$$

The geological and environmental materials contain a complex matrix (Al, Ca, Fe, Mg, Mn, P and Ti). The total background signal can be represented by Eq. (4):

$$X_{BL} = X_B + \Sigma_J\ X_{WJ}\ (\Delta\lambda_a) + \Sigma_J\ X_{IJ}(\lambda_a) \quad (4)$$

The true detection limits is calculated by Eq. (5):

$$C_{L\ true} = 2/5\ \Sigma_J\ Q_{IJ}(\lambda_a)\ \ C_{IJ} + 220.01 RSDBL\ x[\ BEC + \Sigma_J\ Q_{IJ}\ (\lambda_a) \times C_{IJ} + \Sigma_J\ Q_{WJ}(\lambda_a) \times C_{IJ}] \quad (5)$$

where J= Al, Ca, Fe, Mg, Mn, P, Ti.

The magnitude of the true detection limits is determined from the $Q_I(\lambda_a)$ – values in the presence of given matrix, and the $Q_W\ (\lambda_a\ )$ - values influence the detection limits through the conventional detection limits (Eq. 3).

Line selection

The optimal line selection for trace analysis in pure matrices implies the choice of the prominent lines with minimum values of the true detection limits, i.e. these with the lowest line interference and background (wing) interference signals in the presence of the matrix. **Tables 2** and **3** show the selected analysis lines of neodymium (in bold) in the determination of neodymium in presence of europium as matrix and the selected analysis line of platinum (in bold) in the presence of complex matrix, containing Al, Ca, Fe, Mg, Mn, P and Ti.

The detection limits in pure solvent are calculated by Eq. (6):

$$C_L = 2\sqrt{2} \times 0{:}01 \times RSDB \times BEC \quad (6)$$

where: RSDB = 1% is the relative standard deviation of the pure solvent.

The results from Tables 2 and 3 show: (i) The true detection limit by using Nd II 406.109 nm in the presence of europium matrix is the lowest in comparison to the corresponding true detection limits by using the most prominent line in pure solvent (Table 2); (ii) The most prominent lines of platinum in pure solvent cannot be used for determination of this elements in certified reference material SARM 7 (Table 3); (iii) Cleary, detection limits obtained in pure solvent cannot be transferred as detection limits in matrices with different matrix composition.

Therefore, the magnitude of spectral interferences cannot be predicted by general considerations, but can be obtained only by systematic investigations.

In conclusion it should be underlined that the quantitative database for spectral interferences were used for optimum line selection, calculation of the total background signals in λa of the analytes, calculation of the true detection limits, selection of the type of background correction — in λa of a given prominent line or in the spectral window Δλa by a simple off-peak background measurement.

Table 2. Values of Q_W ($_a$), Q_I ($_a$), and $C_{L,\ conv}$, and $C_{L,\ true}$ for the prominent line of neodymium in the presence of europium. Interferent is europium – 8.6 mg ml^{-1}

Prominent lines, nm in accordance with detection limits in ICP-Tables (Boumans, 1980)	Detection limits in pure solvent, ng ml^{-1}	Q_W ($_a$)	Q_I ($_a$)	$C_{L,\ conv}$, (ng ml^{-1})	$C_{L,\ true}$, (ng ml^{-1})
Nd II 401.225	7.4	1.3×10^{-4}	1.0×10^{-5}	95	440
Nd II 430.358	8.0	2.6×10^{-4}	6.7×10^{-5}	276	508
Nd II 406.109	**11.0**	$\mathbf{9.7 \times 10^{-5}}$	$\mathbf{7.0 \times 10^{-6}}$	**75**	**100**
Nd II 415.608	14.0	1.4×10^{-4}	8.4×10^{-5}	110	400

Optimization of the plasma operating conditions for achieving the lowest detection limits

The Mg II 280.270 nm / Mg I 285.213 nm line intensity ratio (Mg II / Mg I ratio) was measured to evaluate the robustness of the operating conditions (Mermet, 1991).

For achieving the lowest detection limits, signal - to background ratios should be maximized and the relative standard deviation of the background signal should be minimized (Blades & Horlick, 1981; Kawaguchi et al., 1981; Boumanns, 1987). The methodologies for choice of the operating conditions for minimization of the detection limits in pure solvent and in pure and complex matrices are described in (Velitchkova et al., 2007; Velitchkova et al., 2013).

By using these methodologies the lowest detection limits were obtained under the following experimental conditions depending on the matrix composition listed in Table 4.

The excitation temperature was measured by the Boltzmann plot method with titanium lines (Mermet, 1987) for different combinations between incident power and sheathing gas flow rates (Velitchkova et al., 2007).

Table 3. True detection limits in solution (ng ml^{-1}) in the presence of matrix constituents in solution after dissolution of certified reference material SARM 7 (column 2), true detection limits with respect to the dissolved solid (column 3) by using the platinum prominent lines, located before selected analysis line (column 1). Column 4 shows the certified value for platinum. Comparison is shown and the true detection limit, obtained by selected prominent line

Analytical lines listed in accordance to detection limits in pure solvent, λ, nm	Detection limits in pure solvent, ng ml^{-1}	True detection limits in solution in the presence of matrix elements, ng ml^{-1}	Detection limits with respect to the dissolved solid sample (0.5 g sample in 50 ml), ng g^{-1}	Certified reference material SARM 7 Certified value for Pt in ng g^{-1}
Pt II 203.646 (1)	7	3 200 (5)	320 000	3740 ± 45
Pt II 214.423 (2)	8	65 (2)	6 500	
Pt I 217.467 (3)	12	790 (3)	79 200	
Pt I 193.670 (4)	13	1 150 (4)	115 000	
Pt I 265.945 (5)	**14**	**17 (1)**	**1 700**	

Detection limits in determination of Y, Sc and rare earth elements in europium oxide under optimal plasma operating conditions

The selected analysis lines and corresponding true detection limits with respect to

the dissolved solid, obtained under optimal plasma operating conditions (Table 4) are as follows: Sc II 358.094 nm - 6.5×10^{-6} %; Y II 360.073 nm - 4.1×10^{-6} %; La II 408.672 nm - 4.8×10^{-5} %; Ce II 413.380 nm -1.3×10^{-3} %; Pr II 422.293 nm - 1.2×10^{-4} %; Nd II 406.109 nm – 8.4×10^{-5} %; Sm II 359.260 nm – 5.2×10^{-5} %; Gd II 342.247 nm – 4.0×10^{-4} %; Tb II 356.852 nm - 5.9×10^{-4} %; Dy II 353.602 nm - 2.0×10^{-4} %; Ho II 339.898 nm – 1.5×10^{-5} %; Er II 337.271 nm - 5.5×10^{-5} %; Tm II 313.126 nm – 1.2×10^{-4} %; Yb II 328.937 nm – 1.0×10^{-6} %; Lu II 261.542 nm - 1.0×10^{-5} %. It should be underlined that the line interference level in the maximum of the selected prominent lines of Sc, Y и Yb is equal to (Q_l (λ_a) = 0) and the true detection limits are the lowest in comparison to the true detection limits by using the best analysis lines for the rest elements. The true detection limits shown in this section ensure 99.99 % purity of the europium oxide.

Table 4. Optimal plasma operating conditions for different type of samples

Analytical tasks	Optimal operating condition by using radial viewing 40.68 MHz ICP, JY ULTIMA 2
Determination of Eu, Nd, Y, Tb and Dy in enriched rare earth concentrate and traces of Y, Sc and rare earth elements in Eu_2O_3	***Non-robust operating conditions**:* Incident power = 700 W, Sum carrier and sheath gas flow rate 0.4 l min^{-1} + 0.4 l min^{-1}, Excitation temperature (T_{exc}) ~ 6000 K Mg II 280.270 nm / Mg I 285.213 nm = 3.6
Determination of Pt, Pd and Rh in geological samples	***Robust operating conditions**:* Incident power = 1000 W, Sum carrier and sheath gas flow rate 0.4 l min^{-1} + 0.2 l min^{-1}, Excitation temperature (T_{exc}) ~ 7200 K Mg II 280.270 nm / Mg I 285.213 nm = 11.4

By using the quantitative base data for spectral interferences in the presence of europium as matrix elements was determined Eu, Nd, Y, Tb and Dy in enriched rare earth concentrate. Rare earth concentrate was obtained by separation of europium from a rare earth concentrate, a by-product of the apatite processing (Minkova & Todorovsky, 1995). The authors studied the influence of the eluent concentration on the ion exchange separation of europium (II) from rest rare earth elements (Nd, Y, Tb and Dy) (Minkova & Todorovsky, 1997). The present ICP-OES method was applied for control of all technological process of separation and for the characterization of final product. By using this technology the obtained europium oxide was with purity 99.9%.

True detection limits in the determination of PGEs in certified reference materials

In Tables 5, 6 and 8 are shown the mean values X, for n=4 replicates; the confidence interval of the mean value ΔX for statistical confidence P=95% and f=n−1=3 (column 2) (Dörffel, 1984) as well as the RSD of the analytical results obtained by ICP-OES (column 3).

Certified reference materials SARM 7

Table 5 shows true detection limits with respect to the dissolved solid sample in the determination of Pt, Pd and Rh.

The experimental results were in good agreement with the certified values (column 3 versus column 5).

Table 5. True detection limits with respect to the dissolved solid sample for solid concentration 0.5 g in 50 ml solution in the determination of Pt, Pd and Rh in certified reference material SARM 7 (platinum ore)

Selected analysis lines, λ, nm	True detection limits, ng g^{-1}	ICP-OES		Certified values, X ± ΔX in SARM 7, ng g^{-1}
		Concentrations, X±ΔX, ng g^{-1}	RSD, %	
Pt I 265.945	1700	3725 ± 50	1.0	3740 ± 45
Pd II 229.651	1440	1515 ± 30	1.3	1530 ± 32
Rh II 233.477	900	≤ 900	-	240 ± 13

Certified reference material SRM 2556

Table 6 shows the detection limits for Pt, Pd and Rh with respect to the dissolved solid sample for solid concentration 1 g in 50 ml solution, by using the most prominent lines of the analytes, which were selected as analysis lines in the presence of aluminum as matrix element.

Using Student's criterion, no statistical differences between the experimental results (columns 3) and the certified values (columns 5) (Dörffel, 1984).

Determination of Pt, Pd and Rh in certified reference material BCR-723 (road dust)

Table 7 shows the corresponding results.

The true detection limits (Table 7, column 2) are significantly higher in accordance with the certified values in BCR-723 (road dust). In this case the true detection limits in the direct ICP-OES method cannot satisfy the requirements of environmental science (Table 7, column3).

Table 6. True detection limits with respect to the dissolved solid sample for solid concentration 1 g in 50 ml solution in the determination of Pt, Pd and Rh in certified reference material SRM 2556 (auto catalyst) by using selected analysis lines in the presence of aluminum as a matrix element

Selected analysis lines, λ, nm	True detection limits by direct determination by ICP-OES, ng g^{-1}	BCR-723 (road dust), Certified values, ng g^{-1} Requirements of the practice
Pt I 265.945	1540	81.3
Pd II 229.651	1150	6.0
Rh II 233.477	740	12.8

Table 7. True detection limits in the determination of Pt, Pd and Rh in certified reference material BCR-723 (road dust) and certified values

Selected analysis lines, λ, nm	True detection limits by direct determination by ICP-OES, ng g^{-1}	BCR-723 (road dust), Certified values, ng g^{-1} Requirements of the practice
Pt I 265.945	1540	81.3
Pd II 229.651	1150	6.0
Rh II 233.477	740	12.8

Improvement of the detection limits in the determination of Pt and Pd in the certified reference material BCR-723 (road dust) by pre concentration of the analytes and separation of the matrix elements - Al, Ca, Fe, Mg and Ti.

The new column method with 2-mercaptobenzimidazole immobilized on an activated carbon was developed for separation of the matrix element from the analytes and pre concentration of Pt and Pd. The final sample solution was introduced to ICP-OES with ultrasonic nebulizer. (Petrova et al., 2013).

Table 8 shows the detection limits in the determination of Pt and Pd with respect to the dissolved solid sample, in ng g^{-1} (column 2) by using the proposed pre concentration/ separation procedure, the content of Pt and Pd in the certified reference material BCR-723, obtained by ICP-OES (mean values X, for n=4 replicates and the confidence interval of the mean value ΔX for statistical confidence level of P=95% and f=n−1 =3 (column 3), as well as the RSD of the analytical results (column 4). Column 5 lists the certified values.

The results obtained by the present method agree well with the certified values of the reference material BCR-723. Therefore, this method can be used successfully in the determination of Pt and Pd in environmental materials.

Table 8. Detection limits with respect to the dissolved solid sample, in ng g^{-1} for the determination of Pt and Pd in certified reference material BCR-723 (road dust) by using the present method, contents of Pt, Pd in ng g^{-1}, RSD of the analytical results and certified values in ng g^{-1}

The most prominent lines in pure solvent λ, nm	Detection limits, ng g^{-1}	ICP-OES		Certified values, X ± ΔX in BCR-723, ng g^{-1}
		Concentrations, X±ΔX, ng g^{-1}	RSD, %	
Pt I 203.646	3.3	80.9 ± 0.05	3.0	81.3
Pd II 229.651	4.0	6.2 ±0.0.04	2.5	6.0

Conclusions

The problems with the spectral interferences in ICP-OES in the determination of rare earth element in the presence of pure rare earth matrices and in the determination of Pt, Pd and Rh in samples with different composition can be successfully solved by systematic investigations. In the present paper the quantitative information for spectral interference in the presence of europium as matrix constituent and in the presence of complex matrix, containing Al, Ca, Fe, Mg, Mn, P and Ti was obtained. The database was used for the optimum line selection, calculation of the total background signals in λa of analytes, calculation of the true detection limits, selection of the type of background correction — in λa of a given prominent line or in the spectral window Δλa by a simple off-peak background measurement. The improvement of the detection limits in pure solvent and the true detection limits in the presence of investigated matrices was achieved by optimization of the plasma operating conditions.

The new column method was developed for separation of matrix element from analytes and pre concentration of Pt and Pd in the determination of these elements in road rust. The final sample solution was introduced in ICP-OES with ultrasonic nebulizer. By this way the following detection limits in certified reference material BCR-723 (road dust) were reached: Pt – 3.3 ng g^{-1}, Pd – 4 ng g^{-1}. The accuracy of analytical results was experimentally demonstrated by certified reference materials.

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REFERENCES

Aleksieva, L., Daskalova, N. & Velichkov, S. (2002). Spectral interferences in the determination of traces of scandium, yttrium and rare earth elements in "pure" rare earth matrices by inductively coupled plasma atomic emission spectrometry; part VI: ytterbium. *Spectrochim. Acta Part B, 57*, 1339-1350.

Barefoot, R.R. & Van Loon, J.C. (1999). Recent advances in the determination of the platinum group elements and gold. *Talanta*, *49*, 1–14.

Bayon G., Barrat, J.A., Etoubleau, J., Benoit, M., Bollinger, C. & Révillon, S. (2009). Determination of rare earth elements, Sc, Y, Zr, Ba, Hf and Th in geological samples by ICP-MS after Tm addition and alkaline fusion. *Geostandards & Geoanalytical Res., 33*, 51-62.

Blades M.W. & Horlick, G. (1981). The vertical spatial characteristics of analyte emission in the inductively coupled plasma**.** *Spectrochim. Acta Part B, 36,* 861 - 880

Boulyga, S.F & Heumann, K. (2005). Direct determination of platinum group elements and there distributions in geological and environmental samples at ng g^{-1} levels using LICP-IDMS. *Anal. Bioanal. Chem., 383*, 442–447.

Boumans, P.W.J.M. (1980) Line coincidence tables for inductively coupled plasma atomic emission spectrometry. Oxford: Pergamon.

Boumans, P.W.J.M. (1986). A century of spectral interferences in atomic emission spectroscopy. Can we master them with modern apparatus and approaches. *Fresenius Z. Anal. Chem., 324*, 397–425.

Boumans, P.W.J.M. (1987). Basic concepts and characteristics of ICP-AES (pp. 100-257). In: Boumans, P.W.J.M. (Ed.). Inductively coupled plasma emission spectroscopy, part 1: methodology, instrumentation and performance. New York: Wiley.

Boumans, P.W.J.M., Tielrooy, J.A. & Maessen, F.J.M.J. (1988). Mutual spectral interferences of rare earth elements in inductively coupled plasma atomic emission spectrometry-I: rational line selection and correction procedure. *Spectrochim. Acta Part B, 43*, 173–199.

Brzezicka, M. & Baranowska, I. (2001). Methods for separation of trace amounts of platinum and investigation of the influence of interfering elements during platinum determination in copper ores and copper concentrates by graphite furnace atomic absorption spectrometry. *Spectrochim. Acta Part B* 56, 2513–2520.

Burman, J.-O. (1987). Applications: geological (pp. 27-47). In: P.W.J.M. Boumans, P.W.J.M. (Ed.). Inductively coupled plasma emission spectroscopy, part 2: applications and fundamentals. New York: Wiley.

Daskalova N.,Velichkov, S., Krasnobaeva, N. & Slavova, P. (1992). Spectral interferences in the determination of traces of scandium, yttrium and rare earth elements in ‚pure' rare earth matrices by inductively coupled plasma atomic emission spectrometry - I. Cerium, neodymium and lanthanum matrices. *Spectrochim. Acta, Spectrochim. Acta Electronica, Part B, 47*, E1595-E1620.

Daskalova, N., Velichkov, S. & Slavova, P. (1996). Spectral interferences in the determination of traces of scandium, yttrium and rare earth elements in ‚pure' rare earth matrices by inductively coupled plasma atomic emission spectrometry - III. Europium. *Spectrochim. Acta Part B, 51*, 733-768.

Daskalova, N., Velichkov, S., Slavova, P., Ivanova, E. & Aleksieva, L. (1997). Application of inductively coupled plasma atomic emission spectrometry (ICP-AES) in analytical control of the preparation of single crystals of potassium titanylphosphate. *Spectrochim. Acta Part B*, *52*, 257-278.

Daskalova, N., Aleksieva, L., Gentsheva, G. & Velichkov, S. (2002). Analytical control of the preparation of single crystal materials by inductively coupled plasma atomic emission spectrometry. *Spectrochim. Acta Part B, 57*, 755-768.

Dörffel, K. (1984). *Statistik in der analytichen Chemie*. Leipzig: Deutscher Verlag für Grundstorfindustrie, Leipzig.

Heinrich, U., Ruehle, T. & Schloegl, R. (1999). Bioavailability of fine dispersed platinum as emitted from automotive catalytic converters: a model study. *Sci. Total Environ. 228*, 219–242.

Kallmann, S. & Blumberg, P. (1980). Analysis of automobile-exhaust emission – control catalysts. *Talanta,* 27, 827–835.

Kawaguchi, H., Ito, T. & Mizuike, A. (1981). Axial profiles of excitation and gas temperatures in an inductively coupled plasma. *Spectrochim. Acta Part B, 36*, 615 – 623.

Kingdon A.I., Davis, R.F. & Thackeray, M.M. (1991). Engineering properties of multicomponent and multiphase oxides (pp. 758-774). In: Schneider, S.J. (Ed.). *Engineered materials handbook, volume 4: ceramic and glasses.* Metal City: ASM International.

Kolibarska, I.,Velichkov, S. & Daskalova, N. (2008). Inductively coupled plasma atomic emission spectrometry – detection limits in the determination of yttrium, scandium and rare earth elements in rare earth oxides. *Spectrochim. Acta Part B, 63*, 603-606.

Li, Z.. & Feng, Y. (2006). Determination of the platinum group elements in geological samples by ICP-MS after NiS fire assay and Te coprecipitation: ultrasound-assisted extraction of PGEs from Te precipitate. *J. Anal. Atom. Spectrom. 221*, 90–93.

Lichte F.E., Meier, A.L. & Crock, J.G. (1987). Determination of the rare-earth elements in geological materials by inductively coupled plasma mass spectrometry. *Analytical Chemistry, 59*, 1150-1157.

McGee, T.F, Bloom, G.M. & Kostecky, G. (1991). Growth and characterization of doped KTP crystals. *J. Cryst. Growth, 109,* 361–366.

Merget, R. & Rosner, G. (2001). Evaluation of the health risk of platinum group metals emitted from automotive catalytic converters. *Sci. Total Environ., 270*, 165–173.

Mermet, J.M. (1987). Spectroscopic diagnostics: basic concepts (pp. 353-386). In: Boumans, P.W.J.M. (Ed.). *Inductively coupled plasma emission spectroscopy, part 1: methodology, instrumentation and performance*. New York: Wiley, New York.

Mermet, J.M. (1991). Use of magnesium as a test element for inductively coupled plasma atomic emission spectrometry diagnostics. *Anal. Chim. Acta, 250*, 85–94.

Millett, E.J. (1980). Progress in the analysis of crystalline solids. *J. Cryst. Growth, 48*, 666–682.

Minkova, N. & Todorovsky, D. (1995). Separation of Eu from a rare earth concentrate, a by-product of the apatite processing. *Ann. Univ. Sofia, Fac. Chimie, 88*, 25-30.

Minkova, N.L.& Todorovsky, D.S. (1997). Influence of the eluent concentration on the ion exchange separation of europium (II) from rare earth concentrate. *Bulg. Chem. Commun., 29*, 84-88.

Morris P.A. (1990). Impurities in nonlinear optical oxide crystals. *J. Cryst. Growth, 106,* 76-88.

Morris P.A., Ferretti, A. & Bierlein, J.D. (1991). Reduction of the ionic conductivity of flux grown $KTiOPO_4$. *J. Cryst. Growth, 109*, 367–375.

Petrova P.P.,Velichkov, S.V., Havezov, I.P. & Daskalova, N.N. (2009). Inductively coupled plasma atomic emission spectrometry — line selection and accuracy in the determination of platinum, palladium, rhodium, barium and lead in automotive catalytic converters. *Bulg. Chem. Commun., 41*, 65–71.

Petrova P.,Velichkov, S.,Velitchkova, N., Havezov, I. & Daskalova, N. (2010). Problems, possibilities and limitations of inductively coupled plasma atomic emission spectrometry in the determination of platinum, palladium and rhodium in samples with different matrix composition. *Spectrochim. Acta Part B* 65, 130–136.

Petrova, P., Velitchkova, N., Velitchkov S., Havezov, I. & Daskalova, N. (2013). Determination of palladium and rhodium in environmental materials by high resolution inductively coupled plasma emission spectrometry (HR-ICP-OES).

Colloquium analytische Atomspectroskopie CANAS 2013, Freiberg, Germany, 17-19.03.2013.

Ramanaiah G.V. (1998). Determination of yttrium, scandium and other rare earth elements in uranium-rich geological materials by ICP–AES. *Talanta, 46*, 533-549.

Rauch, S., Motelica-Heino, M., Morrison, G.M. & Donard, O.F.X. (2000). Critical assessment of platinum group element determination in road and urban river sediments using ultrasonic nebulisation and high resolution ICP-MS. *J. Anal. Atom. Spectrom., 15*, 329–334.

Todoli, J.L. & Mermet, J.M. (1999). Acid interferences in atomic spectrometry: analytes signal effects and subsequent reduction. *Spectrochim. Acta Part B, 54*, 895–929.

Velichkov, S., Daskalova, N. & Slavova, P. (1993). Spectral interferences in the determination of traces of scandium, yttrium and rare earth elements in ‚pure' rare earth matrices by inductively coupled plasma atomic emission spectrometry – II: praseodymium and samarium. *Spectrochim. Acta Part B, 48*, E 1743-E 1789.

Velichkov S., Kostadinova, E. & Daskalova, N. (1998). Spectral interferences in the determination of traces of scandium, yttrium and rare earth elements in "pure" rare earth matrices by inductively coupled plasma atomic emission spectrometry; part IV: lutetium and yttrium. *Spectrochim. Acta Part B, 53*, 1863–1888.

Velichkov, S., Aleksieva, L., Kostadinova, E. & Daskalova, N. (2000). Spectral interferences in the determination of traces of scandium, yttrium and rare earth elements in "pure" rare earth matrices by inductively coupled plasma atomic emission spectrometry; part V: gadolinium and erbium. *Spectrochim. Acta Part B, 55*, 689-729.

Velitchkova N.,Velichkov, S. & Daskalova, N. (2007). Inductively coupled plasma atomic emission spectrometry - optimization of the operating conditions in the determination of trace of elements in line-rich emission matrices. *Spectrochim. Acta Part B, 62*, 386–402.

Velitchkova, N., Veleva, O., Velichkov, S., Markov, P. & Daskalova, N. (2013). Determination of As, Zn, Pt, B, Hg, Cd, Tl and U in environmental materials by high resolution radial viewing 40.68 MHz inductively coupled plasma optical emission spectrometry (ICP-OES). *Bulg. Chem. Commun.*, *44*, 229 – 243.

Wiseman, C.L.S. & Zereini, F. (2009). Airborne particulate matter, platinum group elements and human health: a review of recent evidence. *Sci. Total Environ., 407*, 2493–2500.

Zischka, M., Schramel, P., Muntau, H., Rehnert, A., Gomez, M.G., Stojanik,

B.,Wannemaker, G., Dams, R., Quevauviller, P. & Maier, E.A. (2002). A new certified reference material for the quality control of palladium, platinum and rhodium in road dust, BCR-723. *Trends Anal. Chem., 21*, 851–868.

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