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Short communication

ED XRF analysis of precious metallic alloys with the use of combined FP method

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Abstract

The "combined" FP method, which combines standardless FP method with empirical calibration, was applied to the analysis of Ir–Pt, Rh–Pt, Rh–Pd–Pt and Rh–Ir–Pt disk samples and Pt–Rh thermocouple wire. Four reference materials of binary Pt–Ir system, eight Pt–Rh systems, eight reference materials of ternary Pt–Ir–Rh system and 10 Pt–Rh–Pd systems were used for calibration of "combined" FP XRF method. Results of mentioned method agreed well with certified values, or ICP OES results respectively. For determination of elements, which were not present or certified in calibration standards (Ru in Rh–Pt–Pd disc and Fe in Pt–Rh thermocouple wire) the standardless FP method was used. This approach provides good results as well.

Keywords: Precious metals; ED XRF; Fundamental parameters

1. Introduction

The XRF spectroscopy is an analytical technique, which have begun to play a crucial role in the analysis of precious metallic alloys. Benefits of XRF technique are namely non-destructive quick measurement, very little or no sample preparation and expandability of the system to laboratory automation [1]. The XRF methods based on empirical calibration curves provide very good results if composition of reference materials used as calibration standards correspond to that of the sample under study. The large set of calibration standards is in general necessary for calculation of coefficients for matrix effects correction. Accuracy of this method is in addition strongly depend on correspondence between samples and standards in size and surface quality [2].

Local analysis with the use of X-rays focused to small measurement spot can be solution of this problems, but only for highly homogenous materials. The XRF methods based on fundamental parameter (FP) calculation modelling usually less depend on sample size and surface preparation quality. The FP calculation method can result in better statistical precision, namely for irregular samples as gold rings or some archaeological artefacts, than empirical calibration curve method. However accuracy complicates some practical FP applications in analysis of precious metals. The algorithm for the FP in combination with semi-empirical calibration method using set of matrix specific standards, can considerably improve accuracy of precious metals analysis [3].

In this paper, results obtained by application of "combined FP" method to the quantitative analysis of components in binary (Pt–Ir, Pt–Rh) and ternary (Pt–Ir–Rh, Pt–Rh–Pd) precious metal systems, are described. The "combined FP" method is joint method, which combined standardless FP method with empirical calibration. The concentrations of elements of interest are in the first step calculated using standardless FP method. This calculated concentration values, which are as a matter of fact independent on sample size and surface quality, therefore substitute intensities of corresponding analytical lines in calibration module. The systematic error of standardless FP method, which is significant for materials such Pt–Ir alloys, is in a wide range of concentration corrected by this method.

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2. Experimental

2.1. Instrumentation and analytical conditions

Measurements were performed using desktop energy-dispersive XRF spectrometer (Elva X Industrial, Elvatech Ltd., Kiev, Ukraine) equipped with a W anode X-ray tube. Excitation X-ray beam was pre-treated by collimator (gap diameter 2 mm) and Ni filter. The tube was operated at 45 kV/8–40 μA. Thermo-electrically cooled solid state Si-pin detector (PF-550, MOX-TEK, USA) with 5.5 mm^2 active area and 5 μm thick Be window was used. Its energy resolution is 180 eV at 5.9 keV (Fe^{55} radioisotope source). The count rate was stabilised between 2000 and 2200 count per second (cps). The spectrum collection time was usually 200 s per analysed sample. The instrument control, signal acquisition, spectrum treatment and quantitative analysis were carried out using Elvatech commercial software package, which contains also "combined FP" module. Integral USB camera served for accurate selection of analysed part of sample.

2.2. Calibration of "combined FP" method

Four reference materials of binary Pt–Ir system, eight Pt–Rh systems, eight reference materials of ternary Pt–Ir–Rh system and 10 Pt–Rh–Pd systems (all produced by Safina, Czech Republic) were used for calibration of "combined FP" XRF method. The ranges of declared concentrations of individual component were following: Ir 2–10%, Pt 64–99%, Rh 0.5–25% and Pd 0.5–25%. Each reference material was in the form of plate with thickness more than 1 mm. Three independent measurements on both sides of each calibration standard were performed. The presence of Ru in two Rh–Pd–Pt systems was found out after treatment of proper XRF spectra (Fig. 1). Ru content in used alloys were not certified, consequently "combined FP" method had not been calibrated for this element and Ru had been measured only by standardless FP method. However the presence of Ru in matrix of standards was necessary to take into account in calculation of calibration models for other elements.

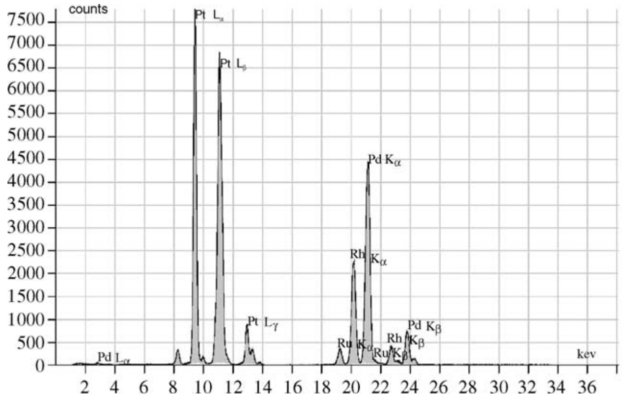

Fig. 1. Spectrum of Rh–Pd–Pt alloy with the presence of Ru.

The following calibration model was suggested for each element

$$C_i = a_0 + c_i\left(a_i + a_{ii}c_i + \sum_j a_{ij}c_j\right) + c_j\left(a_j + a_{jj}c_j + \sum_{k\neq j} a_{jk}c_k\right) \qquad (1)$$

where C_i is the certified concentration of analyte in the standard (%, w/w), c_i the concentration of analyte calculated by standardless FP module (%, w/w), c_j and c_k are the concentrations (%, w/w) of other elements in the standard (including Ru) calculated by standardless FP method. The best model selection by elimination of statistically insignificant parameters from group a_0, a_i, a_{ii}, a_{ij}, a_{jj}, a_{jk} and subsequently determination of significant parameters were performed using quadratic stepwise multiple regression algorithm.

3. Results and discussion

The accuracy of method was tested on reference materials. Quantitative results obtained with using of "combined FP" method for two Pt–Ir and two Pt–Rh reference materials of

Table 1
Results obtained for binary systems, the specimens form is like a standard

Sample	Element	Certified (%, w/w)	XRF (%, w/w)						Mean	*s*	*Δ* (XRF − Cert.)
			Side A			Side B					
			A1	A2	A3	B1	B2	B3			
RM 13	Ir	2.0	1.95	2.11	1.84	1.82	1.82	2.03	1.93	0.11	−0.07
	Pt	98.0	98.05	97.89	98.16	98.18	98.18	97.97	98.07	0.11	0.07
RM 15	Ir	7.5	7.58	7.64	7.33	7.39	7.32	7.40	7.44	0.12	−0.06
	Pt	92.5	92.42	92.36	92.67	92.61	92.68	92.60	92.56	0.12	0.06
RM 01	Rh	0.5	0.47	0.45	0.47	0.47	0.46	0.46	0.46	0.01	−0.04
	Pt	99.5	99.53	99.55	99.53	99.53	99.54	99.54	99.54	0.01	0.04
RM 08	Rh	20.0	20.04	20.09	20.01	20.12	20.16	20.13	20.09	0.05	0.09
	Pt	80.0	79.96	79.91	79.99	79.88	79.84	79.87	79.91	0.05	−0.09

Table 2
Results obtained for ternary (quaternary) systems, the specimens form is like a standard

Sample	Element	Certified (%, w/w)	XRF (%, w/w)						Mean	s	Δ (XRF − Cert.)
			Side A			Side B					
			A1	A2	A3	B1	B2	B3			
RM 22	Rh	5.0	4.94	4.93	4.95	4.97	5.01	4.92	4.95	0.03	−0.05
	Ir	5.0	4.89	4.96	5.06	5.05	5.17	5.06	5.03	0.09	0.03
	Pt	90.0	90.17	90.10	89.99	89.98	89.82	90.02	90.01	0.11	0.01
RM 25	Rh	1.5	1.39	1.44	1.46	1.50	1.48	1.49	1.46	0.04	−0.04
	Ir	3.5	3.52	3.40	3.49	3.46	3.57	3.28	3.45	0.09	−0.05
	Pt	95.0	95.09	95.16	95.06	95.04	94.96	95.22	95.09	0.08	0.09
RM 8343	Rh	9.3	9.07	9.07	9.23	9.51	9.43	9.35	9.28	0.17	−0.02
	Pd	0.8	0.81	0.86	0.84	0.92	0.89	0.85	0.86	0.04	0.06
	Pt	89.9	90.12	90.07	89.93	89.57	89.68	89.79	89.86	0.20	−0.04
RM 35	Ru	[a]	0.83	0.83	0.84	0.87	0.87	0.87	0.85	0.02	[a]
	Rh	9.4	9.41	9.41	9.41	9.40	9.41	9.39	9.40	0.01	0.00
	Pd	20.2	20.35	20.31	20.17	20.11	20.17	20.34	20.24	0.10	0.04
	Pt	69.4	69.41	69.45	69.58	69.62	69.56	69.40	69.50	0.09	0.10

[a] Ru concentrations were not certified, content of Ru was determined by standardless FP method.

Table 3
Results obtained for thermocouple wires, the specimens form is very different from standards

Sample	Element	ICP OES (%, w/w)	XRF (%, w/w), measurement					Mean	s	Δ (XRF − ICP OES)
			M1	M3	M4	M5	M6			
3813	Pt	91.51	91.53	91.62	91.69	91.39	91.30	91.506	0.144	−0.004
	Rh	8.49	8.47	8.38	8.31	8.61	8.70	8.494	0.144	0.004
3914	Pt	90.71	90.72	90.75	90.69	90.62	90.64	90.684	0.048	−0.026
	Rh	8.52	8.67	8.66	8.51	8.67	8.53	8.608	0.072	0.088
	Fe	0.77	0.61	0.59	0.80	0.71	0.83	0.708	0.097	−0.062

Fe concentrations were not certified, content of Fe was determined by standardless FP method.

binary alloys (Safina, Prague, Czech) are presented in Table 1. The form of samples was the same as form of calibration standards. Three independent measurements on both sides of each sample were performed. Differences between mean XRF and certified values were always below 0.1% for all measured metals. Precision expressed as a standard deviation s ($n = 6$) was 0.11–0.12 for components of Pt–Ir alloys and 0.01–0.05 for components of Pt–Rh alloys.

The results of the analysis of two ternary Rh–Ir–Pt and one Rh–Pd–Pt samples respectively are shown in Table 2. Spectrum treatment of the sample RM 35 proved Ru presence in this alloy. The fact, that total sum of certified values of individual components in RM 35 equal to 99% (w/w), agrees with qualitative analysis outcome. The results of quantitative analysis of quaternary Ru–Rh–Pd–Pt system RM 35 are summarised in Table 2 as well. For all elements in above mentioned systems differences between mean XRF and certified values were $\leq 0.1\%$ and $s \leq 0.2$.

In Table 3, the results of "combined FP" XRF analysis of two thermocouple wires (0.5 mm diameter) are compared with the results of the analysis performed by ICP OES. Wires were measured in the form of clot with diameter 5 mm, five times each. The presence of Fe in second sample was detected after spectrum treatment. Its concentration was determined by standardless FP method (by the same way as Ru in above mentioned RM 35).

4. Conclusions

The "combined FP" method applied to the analysis of samples of precious metals provided good estimation of the element concentrations. The method was successfully applied to the element determinations in Ir–Pt, Rh–Pt, Rh–Pd–Pt and Rh–Ir–Pt samples of the same form as standards. Results of "combined" FP analysis of Pt–Rh wire were in good agreement with those from using ICP OES. Determination of elements which are presented in calibration standards by combined FP method and determination of other elements by standardless FP method were performed in case of Ru–Rh–Pd–Pt sample (form like standards) and Pt–Rh–Fe thermocouple wire (form different from standards). Obtained results were in good agreement with certified values or ICP OES values respectively.

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