

Analysis of Mine Waters Using X-ray Fluorescence Spectrometry

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Abstract

In this paper investigations on the application of XRF method with the helium system for liquid analysis and for the determination of the composition of saline mine water have been presented. The applied procedure allows determination of various elements in broad concentration range of analyzed elements (g/dm^3 - mg/dm^3).

Keywords: mine water, XRF

Introduction

Mine waste water management is an important problem in the field of environmental protection. Water, penetrating layers of rock mass, dissolves various salts. Most often they are sodium, potassium, calcium and magnesium chlorides, carbonates, sulphates and heavy metal compounds.

Complexity and diversity of chemical composition of mine water requires the application of several analytical methods.

Used in the presented work X-ray fluorescence spectrometry with the helium system for the analysis of liquids allows determination of mine water composition in the wide concentration range of analyzed elements.

Analysis of literature data concerning methods commonly applied for the determination of saline mine water components has revealed that most often contents of heavy metals are analyzed by stripping voltammetry [1], AAS, ICP [2-3] after previous separation and concentration of analyzed elements. Calcium and magnesium were usually analyzed titrimetrically with EDTA [4, 5], by flame photometry and AAS [5], while sodium and potass-

ium were determined by flame photometry [7, 8] and AAS [6]. Mohr's method [9] or ion-selective electrode [10] were applied for chloride determination, while gravimetry [11] for sulphate analysis.

Experimental Procedures

Analysis of mine waters of diverse salinity was carried out by semi-quantitative XRF method on the basis of SemIQ program and calibration curves. The following concentration ranges for the particular elements in solutions for calibration were applied:

Na	6.0-20.0 g/dm^3
K	0.2-1.0 g/dm^3
Ca	0.4- 2.5 g/dm^3
Mg	0.1- 1.0 g/dm^3
Cl	9.4-31.7 g/dm^3
Cu, Cd, Ni, Zn, Pb	$2 \cdot 10^{-4}$ - 0.1 g/dm^3
Cr	$2 \cdot 10^{-4}$ - $5 \cdot 10^{-2}$ g/dm^3
S	$2 \cdot 10^{-3}$ - $7.8 \cdot 10^{-2}$ g/dm^3

Calibration for Pb was carried out using La line while other elements were determined on K α line. Two collimators were applied: 550 μm for Cl, Mg, Na and S and 150 μm for other elements. Detection of Cl and S was

carried out on a PE 002 crystal, Mg and Na on PXI crystal; whereas LiF 200 was applied for other elements.

Correction for mutual multi-element interactions was calculated.

For Mg and Ca determination the α factor to correct the effect of Na was introduced; for K determination α correction factor to correct the effect of Cl was calculated and for Cl and Fe determination α factor to correct the effect of Ca was used. Measurement parameters for the "mine water" application are in Table 1. In Table 2 regression parameters of analytical curves for analyzed elements are gathered. Next, analysis of mine water samples of various salinity was carried out by both semi-quantitative and calibration curves methods.

Table 1. Set of measurement channels for the "mine water" application.

Channel	kV	mA	Angle (°2T)	Offset Bgl (°2T)	PHD1 LL	PHD1 UL
Cd	60	50	15.2454	-0.3430	17	67
Pb	60	50	33.8682	-0.3524	22	72
Zn	60	50	41.7228	-0.4718	16	78
Cu	60	50	44.9900	-0.3756	23	64
Ni	60	50	48.6884	-0.4320	20	66
Fe	60	50	57.4984	-0.3692	15	68
Cr	50	60	69.2834	-0.5102	15	67
Ca	40	50	113.0824	-0.7406	34	69
K	40	50	136.6062	-0.5074	33	69
Cl	40	50	65.4594	1.3222	33	69
Mg	40	50	22.2206	-0.9104	29	86
Na	40	50	26.9158	-1.3290	28	80
S	30	100	75.7834	0.8602	27	74

Portions of 20 cm³ of mine waters were taken for analysis. Samples 1, 2, 5, 6 were diluted 5 times, sample 4 twice. Results obtained by semi-quantitative XRF method and calibration curves method are presented in Table 3. Apart from those elements in tested water samples additionally the presence of the following elements was found: Si, Br, Cu, Ni. Because the results of Ni and Cu contents obtained by both methods differ significantly and Zn, Fe, Cd and Pb were not found in the samples, the following procedure was developed to check the results:

Table 3. Results of the analysis of mine water samples obtained by semi-quantitative XRF method (a) and by calibration curves method (b).

Water		g/dm ³						
		Na	Mg	Ca	K	Cl	S	Al
Water 1	a	76.050	4.060	3.445	1.185	130.000	0.670	1.180
	b	73.695	3.970	3.445	1.100	121.625	0.635	x
Water 2	a	49.400	2.445	1.325	0.520	91.410	0.660	0.000
	b	50.930	2.025	1.330	0.625	86.795	0.610	x
Water 3	a	2.307	0.100	0.090	0.060	3.082	0.231	0.000
	b	2.370	0.112	0.072	0.051	3.090	0.250	x
Water 4	a	32.116	0.391	0.824	0.309	48.902	0.946	0.164
	b	32.604	0.390	0.780	0.302	48.404	0.866	x
Water 5	a	41.755	1.650	2.745	0.505	75.725	0.100	0.000
	b	40.520	1.895	2.675	0.115	74.380	0.099	x
Water 6	a	53.250	4.045	3.380	0.980	109.035	0.050	0.000
	b	56.485	4.075	3.385	0.965	105.610	0.005	x

x – no determination.

Table 2. Regression coefficients for calibration curves ($C = D + E.R.M.$) for analysed elements for the "mine water" application.

Compound	D	E	RMS	RE	K
Na	-0.06841	7.13083	0.01498	0.01173	0.01293
Mg	0.07968	0.97707	0.00286	0.02101	0.00768
Cl	0.00000	0.52089	0.71709	0.03800	0.15672
K	-0.02073	0.64129	0.01499	0.01035	0.01235
Ca	-0.03066	0.43440	0.03468	0.01782	0.02472
Cr	0.00040	0.10740	0.00011	0.00113	0.00036
Fe	-0.00975	0.21150	0.00524	0.00512	0.00518
Ni	-0.03193	0.19860	0.00253	0.00247	0.00250
Cu	-0.00640	0.03870	0.00013	0.00128	0.00041
Zn	-0.00005	0.01030	0.00013	0.00125	0.00040
Cd	0.00277	0.09990	0.00210	0.00205	0.00208
Pb	0.00169	0.00640	0.00065	0.00065	0.00065
S	-0.02129	0.14590	0.01487	0.01236	0.01346

Table 4. Results of the determination of Mg, Ca, Cl contents obtained by XRF method (a) and by volumetric methods (b).

Water sample		Determined element		
		Mg mg/dm ³	Ca mg/dm ³	Cl mg/dm ³
W1	a	3.970	3.445	121.625
	b	4.128	3.609	120.550
W2	a	2.025	1.330	86.795
	b	1.909	1.443	84.200
W3	a	0.112	0.072	3.090
	b	0.121	0.064	3.234
W4	a	0.390	0.780	48.404
	b	0.414	0.731	47.120
W6	a	4.075	3.385	105.610
	b	3.952	3.162	110.803

(agreement) with those obtained by calibration curves method. The presence of Zn, Cr, Cd, Pb was not found in the investigated samples of mine water. Application of standard addition method revealed that Zn can be determined with the accuracy ± 0.1 mg/dm³, Cr ± 1.1 mg/dm³ while Cd and Pb ± 0.3 mg/dm³ and Cu ± 0.2 mg/dm³. It indicates that the concentration of mentioned elements in the tested mine water samples was lower than the detection limit. Application of XRF method for this purpose needs additional separation and pre-concentration of those elements.

Applied in the work XRF method with the helium system for liquid analysis allowed the determination of the composition of saline mine water samples in the broad concentration range of analyzed elements (g/dm³ - mg/dm³).

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Table 5. Statistical evaluation of the results of trace elements determination obtained by XRF method with the application of calibration curves.

Determined element	Cr g/dm ³	Fe g/dm ³	Cu g/dm ³	Zn g/dm ³	Cd g/dm ³	Pb g/dm ³	Ni g/dm ³
x	0.0061	0.0045	0.00520	0.0051	0.0047	0.0047	0.00530
S	0.00144	0.0044	0.000919	0.000316	0.001709	0.000483	0.000919
Sx	0.0004553	0.0014	0.000291	0.0001	0.000539	0.000152	0.000291
L	0.0061 \pm 0.0011	0.0045 \pm 0.0005	0.0052 \pm 0.0002	0.0051 \pm 0.0001	0.0047 \pm 0.0003	0.0047 \pm 0.0003	0.0053 \pm 0.0002

X – mean value taken from 10 measurements; S – standard deviation; Sx – standard deviation of the mean value; L – confidence interval.

To the 100 cm³ measuring flask 20 cm³ of mine water sample 6 and standard solutions of Cr, Cu, Cd, Fe, Ni, Pb, Zn ions were introduced to reach the final concentration of 5 mg/dm³. Next, 20 cm³ portions were taken and 10 measurements for each analyzed ion were carried out. Results are gathered in Table 5.

In Table 4 results of the determination of chlorides, calcium and magnesium contents obtained by volumetric methods (for chlorides-Volhard's method, for Ca and Mg - complexometric titration) are presented and compared with those obtained by XRF method.

Analyses carried out by means of sequential x-ray spectrometer Philips PW 2400.

Discussion of Results

The obtained results of Na, Ca, Mg, Cl, S determination by semi-quantitative method are in good accordance

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