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VALIDATION OF THE ICP-MS METHOD FOR DETERMINATION THE HEAVY METALS IN WATER

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Abstract

The subject of this paper is validation the analytical method of determining the content of heavy metals Al, As, Cd, Cu, Fe, Mn, Ni, Pb i Zn in water using the mass spectrometry with inductively coupled plasma. The validation parameters that were studied are: linearity, limit of detection (LoD), limit of quantification (LoQ), recovery and precision (RSD). For determined analytes, the values of validation parameters were: LoD (0.011-2.23) μg/L, LoQ (0.03 - 3.4) μg/L, recovery (above 96 %) and the RSD (0.9-3.1) %.

***Keywords**: ICP-MS, validation, heavy metals*

1. INTRODUCTION

Monitoring the emission of polluting substances in the urban and industrial zones is an important task in many countries and one of the biggest challenges of the modern era. Water is the basic condition of life, but everyday human activities lead to its contamination. To prevent contamination of the water system, it is necessary to control the quantity and type of pollutants in it.

The City of Bor, where is located the largest mining center in Serbia, is the best example how the mining activities affect the quality of surface and underground water. River pollution in the city of Bor is the subject of many studies dealing with the influence of mining activity, acidic waste water, waste drainage water and other water. The following heavy metals: Al, As, Cd, Cu, Fe, Mn, Ni, Si, Pb and Zn were detected [1,2,3].

In order to monitor the content of pollutants, it is necessary to develop a fast, accurate and precise method of analysis. One of them is the mass spectrometry with the inductively coupled plasma, which can detect a large number of analytes, in a concentration range of several μg/L or mg/L, in a very short time.

The subject of this paper is development and validation the ICP-MS method for determining the content of heavy metals in water: Al, As, Cd, Cu, Fe, Mn, Ni, Pb and Zn. The validation parameters that were tested are: limit of detection (LoD), limit of quantification (LoQ), linearity, accuracy (recovery) and precision (RSD).

2. EXPERIMENTAL

2.1 Instrumentation and Operating Parameters

The method was validated on a mass spectrometer (quadrupole analyzer) with inductively coupled plasma, model NexION 1000 (Perkin Elmer, USA), equipped with an autosampler, model S25 (Perkin Elmer, USA). Before starting the analysis, the working conditions of the instrument were checked using a tunning solution (Be, Ce, Fe, In, Li, Mg, Pb and U, 1 μg/L, Perkin Elmer, USA). All instrument conditions and function are controlled by the Syngistix v.3.2 software. The optimal operating conditions of the ICP-MS instrument and selected metal isotopes are shown in Table 1.

Table 1. *Operating conditions of the ICP-MS instrument and method parameters*

Instrument parameter	Value / type
ICP RF power	1600 W
Nebulizer Gas Flow	1 $Lmin^{-1}$
Auxiliary Gas Flow	1.2 $Lmin^{-1}$
Plasma Gas Flow	15 $Lmin^{-1}$
Analogue State Voltage	-1825 W
Pulse Stage Voltage	1500 W
Detector	Dual
Nebulizer	Glass
Spray Chambers	Glass Cyclonic High Sensitivity Spray Chamber
Metod Parameters	
Sample loop	3.0 mL
Replicates	3
Readings/Replicate	1
Read Delay	20s
Pump Speed	-30 rpm
Time Wash	30s
Measured isotopes *	^{27}Al-STD mod, ^{75}As-Ked mod, ^{111}Cd-Ked mod, ^{63}Cu-Ked mod, ^{57}Fe-Ked mod, ^{55}Mn-Ked mod, ^{60}Ni-Ked mod, ^{208}Pb-STD mod, ^{66}Zn-Ked mod
Optimization	Criterion: ^{9}Be>4500, ^{115}In>80000, ^{238}U>60000, Bkgd<=3, ^{156}CeO/^{140}Ce<=0.025, $^{70}Ce^{++}$/^{140}Ce <=0.03 Optimization results: ^{9}Be>11087, ^{115}In>87142, ^{238}U>92857, Bkgd<=0.17, ^{156}CeO/^{140}Ce<=0.017, $^{70}Ce^{++}$/^{140}Ce <=0.020

*- Analyte isotopes were chosen according to the recommendation of Perkin Elmer.

2.2 Reagents and Standards

The reagents used in the validation study are of analytical grade as follows nitric acid (65%, w/w), Zorka Šabac, multi-element standard solution XXI for ICP, 10μg/mL; standard solutions of rhenium and rhodium, 1000μg/mL, AccuStandard, USA; certified reference material VHG-QWTPM-15 (VHGLABS, USA) and ultrapure water (χ=0.055Ms cm^{-1}).

Multi-element standard solution XXI was used to prepare the calibration solutions in concentrations of 1, 5, 10, 50, 100 and 200 μg/L, with the addition of HNO_3. Rhodium and rhenium were used as the internal standards at concentration of 10 μg/L.

The blank is a 1% aqueous solution of nitric acid with the addition of internal standard.

Accuracy and precision of the method are determined analyzing the certified reference material QWPTM.

3. RESULTS AND DISCUSSION

3.1. Validation

The method performance was evaluated on the basis of linearity, limit of detection and quantification, accuracy and precision [4,5].

3.2 Linearity, LoD and LoQ

Linearity was determined on the basis of calibration curves, where the correlation coefficient was from 0.9998 to 0.9999 (Table 2). The LoD and LoQ values are calculated on the basis of blank measurements (n=10).

LoD = Blank concentration average + 3S (1)

Limit of detection is in the range of 0.011 µg/L for Cd to 2.23 µg/L for Zn.

LoQ = Blank concentration average + 10S (2)

Limit of quantification is in the range of 0.032 µg/L for Cd to 3.36 µg/L for Zn.

The values of linearity, correlation coefficient, LoD and LoQ are shown in Table 2.

Table 2. *Values of linearity, correlation coefficient, LoD and LoQ*

Elements	r (correlation coefficient)	linear range (ug/L)	LoD (µg/L)	LoQ (µg/L)
Al	0.9999	0-200	0.38	1.23
As	0.9999	0-200	0.084	0.25
Cd	0.9999	0-200	0.011	0.032
Cu	0.9999	0-200	0.38	1.07
Fe	0.9999	0-200	0.52	1.69
Mn	0.9999	0-200	0.029	0.071
Ni	0.9999	0-200	0.12	0.16
Pb	0.9996	0-200	0.058	0.16
Zn	0.9999	0-200	2.23	3.36

3.3 Accuracy and Precision

The accuracy and precision of the method were determined analyzing the certified reference material, which was analyzed 10 times. The obtained values are shown in Table 3.

Table 3. *Accuracy and precision of the ICP-MS method*

Elements	Certified value	Experimentally obtained value	Recovery, %	RSD, %
As	637	611	95.9	2.2
Cd	497	542	109.0	0.9
Cu	516	529	102.4	0.9
Fe	368	397	108.9	1.6
Mn	1680	1757	104.6	1.1
Ni	1100	1179	107.2	1.3
Pb	543	522	96.8	3.1
Zn	857	842	98.4	2.0

The method accuracy, evaluated through the efficiency, was from 96% for Pb to 109% for Cd, and precision, expressed through the RSD, was from 0.9% for Cd and Cu to 3.1% for Pb. The recovery and RSD values were in the acceptable range for the measured concentration, according to the procedure [6].

4. CONCLUSION

The obtained values of the validation parameters (correlation coefficient, LoD and LoQ, accuracy and precision) give the satisfactory results meaning that the studied analytical method can be applied for the analysis of water samples. The LoQ values were from 0.032 to 3.36 μg/L for Cd and Zn, respectively. Such low values are suitable for monitoring the ecological status of the rivers. The method accuracy was above 96% and precision ranged from 0.9 to 3.1% indicating that a reliable method was developed. In the future study, the validation should be extended to a larger number of analytes; the other validation parameters should be studied, and the method should be applied for the analysis of real water samples. In this way, a fast, accurate and precise method for ecological water monitoring would be developed.

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