PHYSICAL CHEMISTRY 2012

11th International Conference
on Fundamental and Applied Aspects of
Physical Chemistry

Under the auspices of the
University of Belgrade

Proceedings
Volume II

The Conference is dedicated to
Professor Ivan Draganić

September 24-28, 2012
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XRF ANALYSIS OF HEAVY METAL CONTENT IN SOIL SAMPLES USING MINIPAL 4 SPECTROMETER

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Abstract

Monitoring of heavy metal content in urban park soil is important, as their elevated concentrations can have detrimental effect on human health. We present preliminary results of test of performance of MiniPal 4 XRF spectrometer for analysis of heavy metal content in soil and the results of analysis of soil from a city park in Belgrade center. The obtained results are generally in agreement with heavy metal content in soil in Belgrade central area, including parks, reported in some other studies.

Introduction

Heavy metals are naturally present in soil. Their elevated concentrations in urban soil can affect human health. Children are at higher risk of exposure to toxic heavy metals in park soil, and more sensitive to their effects. Thus, it is important to monitor level of heavy metals in urban park soil. For this purpose, X-ray fluorescence (XRF) spectrometry is a convenient method, as it is nondestructive, requires little sample preparation and allows multielemental analysis. PANalytical MiniPal 4 is a compact benchtop energy dispersive XRF spectrometer, used primarily in mining and cement industries, but also for research purposes [1]. Here we test the performance of this spectrometer in analysis of heavy metal content in soil samples, and present our preliminary results of the analysis of soil samples collected at different depths from a city park in the center of Belgrade, in Spring of 2011.

Experimental

The soil samples were taken from several locations in the park, from three layers at depths of 0-10 cm, 10-20 cm and 20-30 cm, using steel corer. For each of the layers a composite sample was made. After drying, sieving and milling, 5g of each of the soil samples was pressed into a pellet at the pressure of 30 tons for 60 s. In this study a MiniPal 4 XRF spectrometer was used for elemental analysis. It is equipped with 9W Rh tube and silicon drift detector, with resolution FWHM = 145eV for 5.9keV 55Fe. The calibration of the instrument was performed using six reference materials (soil and lake sediment), pressed into pellets. The following elements have been measured: Ba, Ca, Cr, Cu, Fe, K, Mn, Ni, Pb, Rb, Ti, V, Zn and Zr. Optimal measurement parameters (tube voltage, current and filter) were found for different sets of elements. The analysis of the spectral data was performed using MiniPal/MiniMate software.

Results and Discussion

In this study we focus primarily on Cr, Cu, Fe, Mn, Ni and Zn, as common heavy metal pollutants for urban soil. Lead and V are excluded from the analysis because the calibration results for these elements were not satisfactory. The values of the calibration parameters are shown in Table 1.

Table 1. Calibration results for analyzed elements.

Element	Correlation	Relative RMS (%)	Concentration range (ppm)
Cr	0.9982	6.2	75.0 - 4310.0
Cu	0.9999	1.4	16.9 - 390.0
Fe	0.9832	6.1	32733.0 - 67400.0
Mn	0.9984	3.7	390.0 - 3460.0
Ni	0.9863	12.9	27.8 - 291.0
Zn	0.9981	4.0	44.0 - 345.0

Prior to analysis of soil samples, we analyzed two soil reference materials (SARM42 and GBW07406) as unknown samples, in order to test our calibration method. The average values of element concentrations obtained from three repeated measurements are in agreement with the corresponding certified values, as shown in Table 2.

Our analysis showed very low concentration of Cr, close to the limit of detection, both in the top (0-10 cm) and the deeper layers of soil samples from the park. The concentrations of other elements in the top layer are the following: 27 ppm for Cu, 35431 ppm for Fe, 795 ppm for Mn, 54 ppm for Ni and 100 ppm for Zn. These values are in agreement with those reported in some earlier studies on elemental analysis of soil in the Belgrade central area [2, 3]. Copper and Zn concentrations showed increase with depth, which could indicate washing out of these elements from the top layer of soil. Manganese and Fe concentrations are higher in the top layer than in deeper layers. Variability of Ni concentration with depth was not significant.

More details related to the performance of MiniPal 4 spectrometer in analyzing heavy metals in soil samples from the Belgrade park will be presented.

Table 2. Measured and certified values of concentrations of analyzed elements for SARM 42 and GBW07406 soil reference materials

Element	SARM42		GBW07406	
	Certified (ppm)	Measured (ppm)	Certified (ppm)	Measured (ppm)
Cr	4310	4032	75	62
Cu	17	19	390	390
Fe	32733	33394	56584	57121
Mn	774	785	1450	1489
Ni	125	153	53	51
Zn	44	50	97	95

Conclusion

Test of the applicability of PANalytical MiniPal 4 energy dispersive XRF spectrometer for the analysis of heavy metal content in soil samples showed that it can be successfully used for this purpose. The obtained values for concentrations of

Cr, Cu, Fe, Mn, Ni and Zn are in agreement with those reported for soil in the Belgrade central area in some other studies [2,3].

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