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Quantification of metals in sewage sludges by X-ray spectrometry

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Abstract. The application of sewage sludge on soils is a common practice, but the heavy metals should be determined before disposal. Sewage sludges composition is mainly organic and the amount of heavy metals is variable. Usual methods for heavy metals determination are based on dissolution of the sample. The results depend, partially, on the efficiency of the dissolution of the heavy metals, which may vary from sample to sample. We studied the feasibility of analyzing pressed pellets of sludges by wavelength dispersive X-ray fluorescence spectrometry (WD-XRF), with fundamental parameters matrix effects correction. Several ways of introducing the carbon content in the corrections were tested. Accuracy was evaluated by analysis of four international certificate reference materials. Results were within or very close to the confidence interval of the available certified values for most elements (Al, As, Cr, Cu, Fe, Mn, Ni, Pb, S, Se, Si, V, Zn). Other metals, like Cd and Hg were below the detection limits (15 and 9 mg kg^{-1}, respectively). Despite the limitation concerning the proper matrix correction, the uncertainty of the XRF results is probably similar to the methods normally used in sludge analysis, with the advantage that sample preparation is much faster.

1. INTRODUCTION

In many developing countries, sewage treatment procedures are just being implemented. In highly populated areas, huge amounts of solid residue are generated, and they need to be properly disposed. The application on soils is a common practice, but the sludge should be characterized before disposal and soils should be monitored. Sewage sludges composition is mainly organic and the amount of metals is variable. The metals more commonly determined in sewage sludges are Cd, Co, Cr, Cu, Hg, Mn, Ni, Pb, Zn. Other metals can be included as well as metalloids (e.g. As). Usual methods for heavy metals determination are based on dissolution of the sample and determination by inductively couple plasma optical emission spectrometry (ICP-OES) or atomic absorption spectrometry (Radojevic and Bashkin [1]). The results depend, partially, on the efficiency of the dissolution of the heavy metals, which may vary from sample to sample.

An alternative method for heavy metals determination in sludges is X-ray fluorescence spectrometry (XRF). With this technique, samples can be analyzed as pressed pellets, which is faster compared to the solution methods. But in XRF, the accuracy of results depends on the efficiency of matrix corrections. Frequently, when complex samples are concerned, matrix corrections are made with influence coefficients calculated using as standards, certified reference materials (CRM) of similar composition to the unknowns. Few CRMs of sewage sludges are available so this method of calibration is not feasible. An alternative is to correct the matrix effects with the fundamental parameters method. In this method the elemental sensitivities are obtained from single elements or simple compounds standards, but the full composition of the sample needs to be measured or, at least, considered. Carbon and associated light elements, the main matrix elements in sludges, are not detected in common XRF spectrometers, but they strongly attenuate the X-ray fluorescence intensities.

Few works in literature used XRF for sludges analysis. West *et al.* [2] analyzed industrial sludges, using a fundamental parameters method just as a semi-quantitative method. Our main objective was to evaluate the feasibility of determining heavy metals in sludges by wavelength dispersive X-ray fluorescence spectrometry using commercial software based on fundamental parameters to correct the matrix effects.

2. EXPERIMENTAL

Samples were analyzed with a Philips PW2404 XRF spectrometer equipped with a rhodium anode tube and SuperQ 3.0 software. Matrix corrections and results for elements of interest were obtained with UniQuant 5.0 (ODS, Holland). Normally, for this software more than 80 analytical lines are measured, with counting times between 4 and 10 s, depending on the region of the spectrum. In the present application just a selected number of elements was measured and counting times were increased to allow better statistics and quantitative determination. Instrumental conditions are summarized in Table 1.

Table 1. Instrumental conditions

Element	Crystal	Detector	kV	mA	Average time (s)
Ba, Sb, Cd, Mo, Pb, As, Se, Bi, Hg	LiF 220	C	60	40	20
Zn, Cu, Ni, Co, Fe, Mn, Cr, V	LiF 220	duplex	60	40	40
Ti, Ca, K, Cl, S, P	Ge111	F	40	60	8
Si, Al, Mg, Na	PX1	F	40	60	10

F= flux; duplex: F + sealed Xe; C= scintilation

Samples were analyzed as pressed pellets, prepared by mixing 9.0 of sample (as received or dried at 105 °C, as recommended by the supplier) and 1.5 g of wax powder (Hoechst, Germany) and pressing for 1 min at 119 MPa. Originally the software is calibrated with single element or compound standards. But it can be personalized with the user standards. For some elements, two international sludge certificate reference materials (SRM 2781 and SRM 2782 from NIST, USA) were used to refine the calibration of some elements.

3. RESULTS

Results were obtained after testing several ways of numerically introducing the carbon and some of associated in compounds found in sludges. The number of compounds, which can be introduced by this version of the software, is limited to two. Results presented here considered the presence of cellulose and of another carbon compound, hypothetical, containing, C, N, O and H. These components were chose because it is known that sludges can contain 15-41% proteins and 8-15% cellulose [1]. Accuracy was evaluated by analysis of four certificate reference materials. The results obtained for SRM 2781 and SRM 2782 (NIST, USA), a domestic and an industrial sludge, respectively are presented in Table 2. The uncertainties associated with the results are the sum of three combined errors: counting statistics, systematic errors in background and spectral corrections and on sensibilities used to calibrate the spectrometer. The uncertainties associated with the certified values correspond to the 95% confidence interval. When uncertainties are absent, the values given in the certificate are only informative. The concentration values obtained for most elements fall within or very close to the confidence interval, indicating the robustness of the matrix corrections method. Some discrepancies between results and

certified values probably arise from the inaccurate modeling, i.e., not knowing exactly the composition of the non-measured constituents. This difficulty could be solved by separate elemental analysis, especially C, N and H, which is frequently done in routine analytical laboratories of such matrices.

The concentration of Se in SRM 2781 was obtained after increasing the measuring time from 20 to 100 s. The same was tested for other elements, which concentrations are below the detection limits, like As in SRM 2781 and Cd and Hg in both samples, but they were not detected. The difficulties for detecting As and Hg were already expected, because the samples were dried. Cadmium is normally a difficult element for detection by XRF, because it is inefficiently excited by the Rh X-ray primary source.

Table 2. XRF results obtained by XRF in sludge certified reference materials

	SRM 2781		SRM 2782	
%	XRF	Certified value	XRF	Certified value
Al	1.55 ± 0.04	1.6 ± 01	0.69 ± 0.03	1.37 ± 0.09
Ca	4.17 ± 0.01	3.9 ± 0.1	0.62 ± 0.01	0.67± 0.06
Fe	2.86 ± 0.12	2.8 ± 0.1	25.5 ± 0.3	26.9 ± 0.7
K	0.54 ± 0.01	0.49 ± 0.03	0.29 ± 0.01	0.32 ± 0.01
Mg	0.57 ± 0.03	0.59 ± 0.04	0.15 ± 0.01	0.26 ± 0.02
Na	0.21 ± 0.01	0.21 ± 0.02	0.79 ± 0.04	1.30 ± 0.5
P	2.64 ± 0.05	2.42 ± 0.09	0.49 ± 0.02	0.50 ± 0.06
S	1.32 ± 0.04	-	0.21 ± 0.01	0.2
Si	4.93 ± 0.07	5.1 ± 0.2	17.4 ± 0.11	20.3
Ti	0.34 ± 0.01	0.32 ± 0.03	0.08 ± 0.01	0.088 ± 0.009
mg kg^{-1}	-	-	-	-
As	-	7.82 ± 0.28	158 ± 33	166 ± 20
Ba	545 ± 50	-	151± 50	254 ± 24
Cd	-	12.78 ± 0.7	-	4.17 ± 0.09
Cl	2990 ± 150	-	762 ± 40	-
Co	-	-	-	66.3 ± 4.8
Cr	207 ± 10	202 ± 9	109 ± 10	109 ± 6.0
Cu	651± 10	627.4 ± 13.5	2470 ± 20	2594 ± 52
Mn	829 ± 10	745 ± 33	258 ± 10	258 ± 15
Ni	71 ± 10	80.2 ± 2.3	153 ± 10	154.1± 3.1
Pb	218 ± 10	202.1 ± 6.5	550 ± 10	574 ± 11
Se	14 ± 4	16.0 ± 1.6	-	-
Sr	263 ± 10	-	62 ± 5	-
V	89 ± 4	-	76 ± 10	80 ±10
Zn	1290 ± 30	1273 ± 53	1250 ± 30	1254 ±196

In Table 3, results obtained for two other certified reference materials are presented. CRM 144R and CMR 145R (IRMM, Belgium) are domestic sludges. These CRMs have less certified elements than NIST samples. The calculation procedure previously described was used, but pellets were prepared without drying the samples. The results show a slight tendency for lower values compared to their respective certified concentrations.

Table 3. XRF results obtained by XRF in sludge certified reference materials

	CRM 144R		CRM 145R	
mg kg^{-1}	XRF	Certified value	XRF	Certified value
Cd	-	1.82 ± 0.10	-	3.50 ± 0.15
Co	-	15.0 ± 0.6	-	5.61 ± 0.31
Cr	96 ± 3	104 ± 3	-	-
Cu	268 ± 3	308 ± 7	677± 5	696 ± 12
Hg	-	3.14 ± 0.23	-	2.01 ± 0.22
Mn	174 ± 4	208 ± 3	136 ± 4	156± 4
Ni	28 ± 5	47.7± 1.1	217± 5	247± 7
Pb	109 ± 9	106 ± 4	292 ± 9	286 ± 5
Zn	857± 23	932 ± 23	2040 ± 60	2122 ± 23

As already mentioned, probably results could be improved by considering the elements, which cannot be determined by XRF, after accurate analysis by another technique.

The application of sewage sludges on soils for agriculture use has requirements concerning heavy metal concentration. Each country has specific norms, i.e., concentration limits below which the sludge can be applied. The concentration values of metals and metalloids in sludges can be variable, depending on many factors. Domestic derived sludges tend too have lower content in heavy metals compared to industrial sewage sludges. In Table 4 the detection limits obtained by XRF are presented, with counting times mentioned in Table 1 and with extended counting times, i.e., 100 s.

Table 4. Detection limits of heavy metals determination in sludges by XRF

Element	Detection limits	
	20-40 s	100 s
As	24	7
Cd	15	5
Cu	26	10
Hg	9	3
Pb	9	3
Ni	18	3
Se	-	5
Zn	30	10

4. CONCLUSIONS

The metal content of sludges can be accurately determined by XRF if proper matrix corrections are applied. This means knowing the amount of carbon and other elements which cannot be detected by XRF, but are frequently determined in sludges by independent methods. Despite such limitation, the uncertainty of the XRF results is probably similar to the methods normally used in sludge analysis, with the advantage that sample preparation is much faster. Detection limits of some critical elements can be further improved, with longer analysis time. But some of the elements that occur at low concentration, e.g. Hg and Cd, are better analyzed by other analytical techniques. Compared to traditional techniques used in sludge analysis, XRF is faster and the total amount of each element is determined, which is more reliable regarding sludge disposal.

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