APPLICATION NOTE

Analysis of heavy metals in sewage sludge with ARL QUANT'X EDXRF Spectrometer

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Introduction

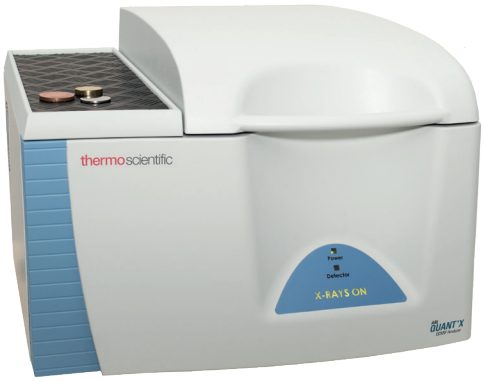
Sewage sludge is a byproduct of domestic sewage and waste water treatment. Sludge consists mainly of organic matter rich in nutrients such as N and P and can therefore be used to replenish farmlands of depleted soil. Due to the nature of the physicochemical process involved in waste water treatment, sludge tends to concentrate heavy metals and other harmful constituents present in waste water. The heavy metals content of sludge is restricted by governmental regulations such as the Sludge Directive 86/278/EEC of the European Union and EPA Part 503 of the United States. Concentrations of up to 10 heavy metals (As, Cr, Cd, Cu, Pb, Hg, Mo, Ni, Se and Zn) are typically monitored in sewage sludge. When maximum permissible concentrations are not met, sludge is mainly disposed of by incineration.

Energy-Dispersive X-Ray Fluorescence (EDXRF) is ideally suited to determine heavy elements in sewage sludge. The technique relies on a single highly-sensitive detector to measure the emission lines of all elements from Sodium (Na, Z=11) to Uranium (U, Z=92) at concentrations of a few ppm to % w/w. Sample preparation is minimal so that a complete sample analysis takes less than 15 minutes.

Instrumentation

The Thermo Scientific™ ARL™ QUANT'X EDXRF Spectrometer is equipped with a Silicon Drift Detector (SDD) and a 50 Watt Rh target X-ray tube which is air cooled with a maximum excitation voltage of 50 kV. A set of nine primary beam filters is designed to optimize the peak-to-background signals for all elements from Na to U. The 10-position auto-sampler with spinner allows for unattended analysis of multiple samples.

The SDD remains the performance benchmark for all energy-dispersive detectors. Its large active area of 30 mm^2 enables effective capture of characteristic element X-rays emitted by the sample.



Excitation conditions

In EDXRF, sensitivity and precision are achieved by targeted excitation of the sample to fluoresce only the elements of interest. The ARL QUANT'X EDXRF Spectrometer offers a virtually unlimited combination of excitation voltages (4-50 kV) and multiple primary beam filters for optimal background control.

As shown in Table 1, seven spectra were collected from each sludge sample for a total live time of 6 minutes, corresponding to less than 12 minutes real time (including detector dead time).

Table 1. Analytical conditions.

Condition	Voltage (kV)	Tube filter	Medium	Live time (s)	Elements
Low Za	4	No Filter	Vacuum	30	Na, Mg, Al, Si, P, S
Low Zb	8	C Thick	Vacuum	30	Cl, K, Ca
Low Zc	12	Al	Vacuum	60	Ti, V, Cr
Mid Za	16	Pd Thin	Vacuum	60	Mn, Fe, Co
Mid Zb	20	Pd Medium	Vacuum	60	Ni, Cu, Zn
Mid Zc	28	Pd Thick	Vacuum	60	As, Se, Mo, Hg, Pb
High Za	40	Cu Thin	Vacuum	60	Ag, Cd

Sample preparation

Concentrations of heavy metals in sludge are expressed as mg/kg (ppm) of dry matter. Sample preparation consists of grinding dry sludge in a mill to produce particle size of less than 50 microns (325 mesh) to minimize particle-size effects. Although the powder can be analyzed directly, accuracy and sample-to-sample repeatability are improved by pelletizing the powder with or without binding agent using a manual press at 15 tons.

Calibration

The fundamental parameters (FP) approach was used for the quantitative analysis of these sewage sludge samples. The FP model was calibrated using 20 pure element/compound standards taken from the common element kit for quantitative analysis, optionally available with the ARL QUANT'X EDXRF Spectrometer. The kit contains all necessary elements to span the entire periodic table. Sewage sludge contains a significant organic matrix fraction (up to 65 % w/w) which generates no characteristic signals in the spectrum. It is necessary to define the unknown matrix as part of the FP analysis routine. For typical sludge samples the organic fraction is well-characterized by cellulose ($C_6H_{10}O_5$).

Validation

Four sewage sludge reference materials (BCR 144R, BCR 145R, BCR 146R and NIST 2781) were used as "unknowns" to validate the calibration. The reference materials were sewage sludge samples of both domestic and industrial origin. Table 2 shows the analysis results for these reference materials.

As shown by these results, a quick and straightforward FP calibration using pure element standards allows for results that are generally accurate within 5 % to 10 % relative. With additional work using type standards for a more exact calibration, results can be further improved. As such, the ARL QUANT'X EDXRF Spectrometer serves as an excellent tool to screen sewage sludge samples.

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Table 2. Analysis results of sewage sludge using ARL QUANT'X Spectrometer.

	Reference values				Analysis results			
	BCR 144R	BCR 145R	BCR 146R	NIST 2781	BCR 144R	BCR 145R	BCR 146R	NIST 2781
	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg
Cd	1.82	3.5	18.8	12.78	1	3	16	10
Cr	104.3	307*	196	202**	95	312	198	214
Cu	308	696	838	627.4	288	723	800	665
Hg	3.14	2.01	8.6	3.64	< 3	< 3	12	< 3
Ni	47.7	247	70	80.2	43	239	69	87
Pb	106	286	609	202.1	99	286	545	214
Zn	932	2122	3060	1273	887	2154	2943	1304
Ag	-	-	-	98**	-	-	-	94
As	-	-	-	7.82	-	-	-	< 10
Mn	207.9	156	323	-	222	171	339	-
Mo	-	-	-	46.7	-	-	-	35
Se	-	-	-	16	-	-	-	16

* Aqua regia soluble content
** Noncertified values

Detection limits

Detection limits for these samples have been derived using standard reference material NIST 2781. Detection limits depend heavily on the type of sample matrix and the presence of any interfering elements at relatively high concentrations. Table 3 shows the typical detection limits for this type of samples.

Table 3. Typical detection limits when analyzing sewage sludge samples.

Detection limits (ppm in 60s live time)			
Cr	3	Se	2
Mn	5	Mo	1
Ni	2	Cd	1
Cu	2	Hg	3
Zn	2	Pb	3
As	3		

With some exceptions, detection limits of a few ppm are attainable for all elements. Of particular interest are the very low detection limits for heavy elements such as Mo and Cd.

Conclusion

The ARL QUANT'X EDXRF Spectrometer is ideally suited to screen and monitor the heavy element content of sewage sludge. An easy, straightforward calibration using Fundamental Parameters and pure element compounds offers a fast semi-quantitative analysis method with very little sample preparation required. The SDD allows for excellent element sensitivities.

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