PANalytical

EPSILON 5

Analysis of heavy-metal contaminants in soils and sludges

Soil: its contamination and regulation
Soil is an important, but limited, resource essential for many human activities, including the production of food, raw materials and energy. One requirement of the sustainable management of soils is that they are protected from chemical contamination. Contamination can affect the fertility of soils as well as introducing toxic levels of metals (and other chemicals) to the human food chain.

Contamination may occur indirectly by atmospheric deposition from industry, mining or vehicle exhaust. However, direct application of sewage sludges, manures, inorganic fertilizers and industrial wastes used to improve soil fertility can cause long-term build up of contaminants.

A wide range of contaminants may affect soils, but problems usually arise from a small number of elements. Elements such as zinc, copper, nickel, cadmium and arsenic can reduce yields or kill plants if they are present in high enough concentrations; whereas elements like lead, arsenic, cadmium, copper and molybdenum can be particularly harmful to animals.

In the European Union regulations restrict the maximum permissible concentrations of potentially toxic heavy metals in soils and in sludges used on the land. These regulations were introduced in 1986 and will be revised to lower levels in future.

Elements	Soil Limit Values (mg/kg ~ ppm)*	
	Directive 86/278/EEC	Future
As	50	~
Cd	1 - 3	0.5 - 1.5
Cr		30 - 100
Cu	50 - 140	20 - 100
Mo	4	~
Ni	30 - 75	15 - 70
Pb	50 - 300	70 - 100
Zn	150 - 300	60 - 200

Table 1. Limit values for heavy metals in soil according to EU Directive 86/278/EEC

Elements	Sludge Limit Values (mg/kg ~ pm)*	
	Directive 86/278/EEC	Future
Cd	20 - 40	10
Cr	-	1000
Cu	1000 - 1750	1000
Ni	300 - 400	300
Pb	750 - 1200	750
Zn	2500 - 4000	2500

Table 2. Limit values for heavy metals in sludge according to EU Directive 86/278/EEC

* Limits depend on pH of the soil.

Epsilon 5: the essential element
The Epsilon 5 is a fully integrated energy-dispersive XRF analyzer, consisting of a spectrometer, X-Y sample handler and software. It has a unique combination of features including a three-dimensional, polarizing geometry, together with a 600 W Gd-anode X-ray tube and 100 kV generator, up to 15 polarizing and secondary targets and a high-resolution PAN-32 detector. Designed for accuracy, precision and sub-ppm detection limits the Epsilon 5 excels in the analysis of medium to heavy metals, targeting a wide range of elements of environmental significance.

Epsilon 5 is ideal for the analysis of heavy metal contaminants in soils and sludges. Combining the required analytical performance with simple, inexpensive sample preparation it is a cost-effective method of analysis.

What is sewage sludge?

Sewage sludge is a by-product from the treatment of sewage and it is sometimes referred to as "biosolids". Untreated sludge is produced by primary (settlement) or secondary (biological) stages of treatment. Both untreated and treated sludge may be supplied in liquid form (similar to animal manure slurry) or as dewatered sludge cake.

Pressed powder samples

Planetary ball mill

Standards, samples and their preparation

A series of soil and rock standards were used to calibrate the application. These were the GSS-, GRS-, and GSD- series of geochemical reference materials (Institute of Geophysical and Geochemical Prospecting, PRC), together with NIST-2709, NIST-2710, NIST-2711 (National Institute of Standards and Technology, USA) and the soil standards SO-1, SO-2, SO-3 and SO-4 (Canadian Certified Reference Materials Project). Three powdered sewage sludge reference materials (WT-H, WT-L and WT-M) were also added to the calibration.

The soil samples were analyzed in the form of pressed powder pellets. The sample preparation technique is easily mastered, safe and relatively inexpensive. Samples were oven dried, then pulverized for approximately 20 minutes in a planetary ball mill together with 20 % wax/styrene additive. The additive acted as a binder as well as a grinding agent, resulting in a uniform grain-size distribution (≤ 40 μm). Approximately 12 g of the mixture was pressed into 36 mm diameter pellets using a hydraulic press operated at 20 tonnes pressure. Both standards and unknown samples were prepared in the same way.

Measuring with Epsilon 5

The measuring program was set up in the software using the Epsilon 5 Wizard, which guides the user through the steps required to calibrate the application. The software proposes the polarization targets and instrument settings that give the best performance for the selected analyte elements. For each of these instrument conditions a measurement time of 200 s (live time) was specified.

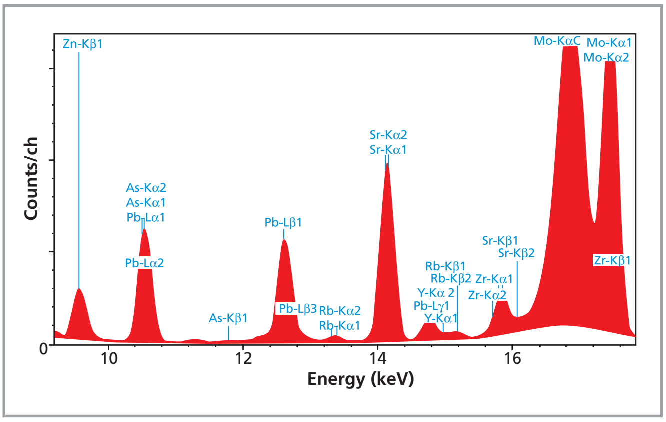


Figure 1. Spectrum obtained using a molybdenum secondary target, which gives optimum excitation for lead

Performance

The Epsilon 5 software features a very powerful deconvolution algorithm, which analyzes the sample spectrum and determines the net intensities of element peaks, even when they overlap one another.
The accuracy with which this is carried out is essential to trace element analysis.

Accuracy

The accuracy of the results is presented in Table 3. The calibration RMS value is a statistical comparison (1 sigma) of the certified chemical concentrations of the standards with the concentrations calculated by regression in the calibration procedure. What this means for the accuracy of determination within individual samples is presented in Table 3.

	Calibration range (ppm)	Calibration RMS (ppm)	GSS-1		GSD-7		WT-H (Sludge)	
			Certified	Measured	Certified	Measured	Certified	Measured
As	0.23 - 412	1.39	33.5	34.7	84	84	146	146
Cd	0.03 - 55	0.63	1.05	0.92	4.30	4.39	55	56
Cr	4.8 - 1340	17.44	62	58	122	119	1340	1265
Cu	4.1 - 3140	10.53	21	20.9	38.0	36.0	3140	3106
Mo	0.09 - 92	0.93	1.40	1.22	1.40	1.02	78	74
Ni	1.6 - 1140	5.42	20.4	19.7	53	54	1140	1147
Pb	4.4 - 2290	7.57	98	89	350	358	2290	2278
Zn	16 - 6360	10.98	680	679	238	246	6360	6359

Table 3. Results of calibration and verification of the accuracy of the analysis

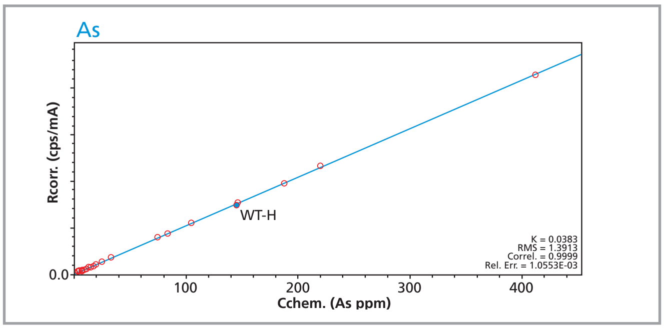


Figure 2. Calibration graph for As

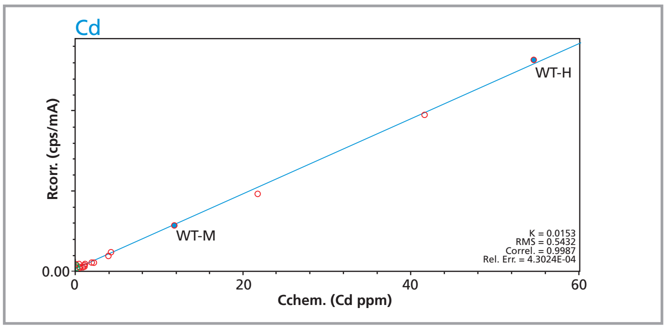


Figure 3. Calibration graph for Cd

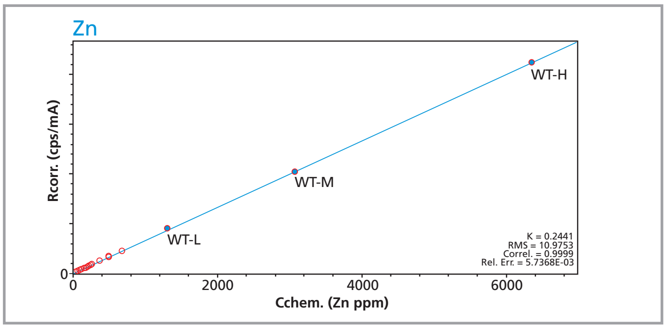


Figure 4. Calibration graph for Zn

Calibration plots for arsenic, cadmium and zinc (Figures 2, 3 and 4) give graphic illustrations of the accuracy of the method. In the case of zinc the wide dynamic range of the calibration is also shown. Furthermore, both soils and sewage sludges may be analyzed using the same calibration.

Precision and instrument stability

The analytical repeatability of the XRF method is unrivalled and measurements made with the Epsilon 5 are no exception (Table 4). 20 consecutive measurements of a sample demonstrate standard deviations better than 4 % relative at the 25 ppm level (i.e. 25 ± 1 ppm). More importantly, this level of reproducibility is maintained for measurements carried out over a period of 10 days, illustrating the long-term stability of the Epsilon 5 spectrometer. Comparison of these precision measurements with the counting statistical error (theoretically, the minimum possible error) emphasizes the inherent stability of the instrument.

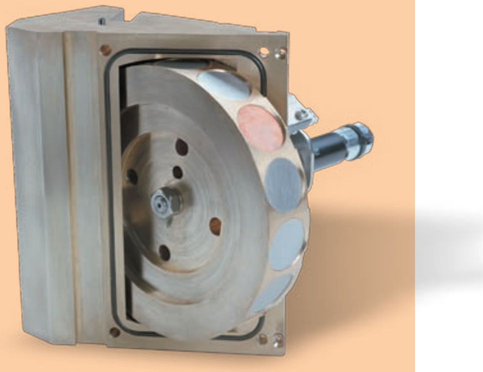
Element	As	Cd	Cr	Cu	Mo	Ni	Pb	Zn
REPEATABILITY (20 consecutive measurements) (200 s live time)								
Mean ppm	25.4	0.86	165.5	25.4	0.79	30.8	25.9	40.7
RMS	0.89	0.35	2.08	0.88	0.23	0.67	0.92	0.49
RMS rel%	3.5	40	1.3	3.4	28	2.2	3.5	1.2
REPRODUCIBILITY (Measurements carried out over 10 days) (200 s live time)								
Mean ppm	25.4	0.74	166.5	25.8	0.82	30.7	26.1	40.0
RMS	0.92	0.24	2.54	0.49	0.15	0.69	0.90	0.67
RMS rel%	3.6	32	1.5	1.9	18	2.2	3.5	1.7
COUNTING STATISTICAL ERROR (200 s live time)								
CSE	0.373	0.126	0.505	0.382	0.186	0.296	0.305	0.536
CSE rel%	1.31	3.97	0.99	1.31	2.69	1.69	1.64	0.93

Table 4. Analytical precision

Analytical flexibility

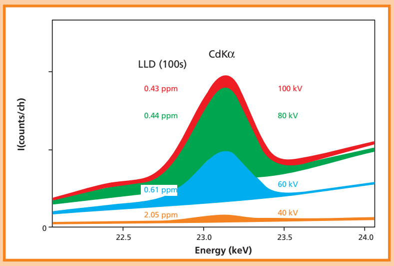
The Epsilon 5 can be “tuned” to get the lowest detection limits for a large number of elements. This flexibility is achieved using a set of programmable polarization and secondary targets. Up to 15 targets can be mounted in the Epsilon 5. The basic system is configured with 9 targets, giving comprehensive coverage of the periodic table. The additional 6 target positions can be configured when optimum excitation conditions are required for the lowest possible detection limits in specific applications.

A cost-effective alternative – making X-ray tube changes for optimum performance a thing of the past.



High-voltage Gd X-ray tube

PANalytical introduces its new Gd-anode X-ray tube. Operating at a maximum power of 600 W and voltages between 25 and 100 kV it is unique among energy-dispersive XRF spectrometers.
The characteristic tube lines of the Gd-anode enhance the fluorescence of elements in the range rhodium to barium. Furthermore, the 100 kV capability has clear advantages for the excitation of heavy element K-lines, for example cadmium, as illustrated below.



Detection Limits

Typical detection limits for heavy metals in soil are given in Table 5. For most elements the LLDs calculated in 100 s are well within the requirements laid down by the EU soil directive (Table 1). However, for Cd meaningful measurements at the 1 – 3 ppm level require a lower LLD, which can be obtained through longer measuring times. A total application measurement time of 30 minutes is sufficient to measure the concentrations regulated in EU Directive 86/278/EEC.

The lower limit of detection (LLD) is calculated from:

$$LLD = \frac{3}{s}\sqrt{\frac{r_b}{t_b}}$$

Where:
s = sensitivity (cps/ppm)
r_b = background count rate (cps)
t_b = live time (s)

Detection limit	As	Cd	Cr	Cu	Mo	Ni	Pb	Zn
100 s*	1.5	1	4	2.5	0.7	4	2.5	2
Application time (30 min.)	1.5	0.4	4	2.5	0.7	4	2.5	2

Table 5. Detection limits

* The LLDs quoted are typical for soil samples. LLDs for individual samples vary according to sample composition.

Conclusions

The Epsilon 5 is capable of analyzing heavy metal contaminants in soils and sludges to the limits that are currently regulated in Europe. A single calibration can be used to analyze both soil and sludge. Measurements are accurate and precise and the method benefits from simple, essentially hazard-free, sample preparation. The stability of the Epsilon 5 is such that individual calibrations can be used for months. Time-consuming re-standardizations are unnecessary and the resultant data are highly consistent over time.

Equipment Configuration		
Epsilon 5 energy-dispersive X-ray fluorescence spectrometer and controlling software.		
X-ray tube:	Type:	side-window tube
	Anode:	Gd
	Window:	Be (300 μm)
	Rating:	25 – 100 kV, 0.5 – 24 mA,
		maximum power 600 W
	Internal water cooling	
Detector type:	PAN-32:	Ge X-ray detector
	Crystal:	30 mm², 5 mm thick
	Window:	Be (8 μm)
	Energy range:	0.7 – 100 keV
	Resolution:	typically 135 eV but ≤140 eV (2000 cps, Mn Kα)
	Liquid nitrogen cooling	
Polarizing optics:	3-dimensional design	
Targets:	Al, Ti, Fe, Ge, Zr, Mo, Ag, Ce_2O_3, Al_2O_3, CsI, KBr	

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