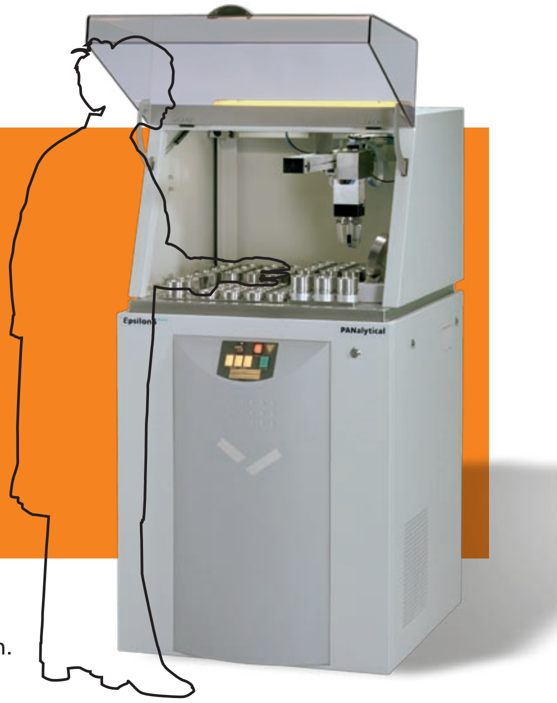
PANalytical

EPSILON 5

Analysis of Cd, Sn, Sb, Cs, Ba, La, Ce and Nd in rocks and soils – improved detection limits using K-series lines



Introduction
X-ray fluorescence spectrometry is used extensively for geochemical analysis. Simple sample preparation, accuracy, precision and good to excellent detection limits across large parts of the periodic table are the principal reasons for this choice. Detection limits for typical medium-power wavelength-dispersive spectrometers (WDXRF) configured for geological applications are illustrated in Figure 1.

This diagram shows ≤ 1 ppm detection limits for the majority of elements between scandium and uranium. However, the exceptions to this trend are the detection limits for elements from rhodium to the light rare earths. These elements have detection limits up to an order of magnitude worse than elements between zinc and molybdenum. The reasons for this are sub-optimal excitation and detection of analyte K-lines and as a consequence, the need to use L-series lines for the analysis of Cs to Ce. The Epsilon 5 overcomes these problems by making K-line analysis of heavy elements a reality by combining high excitation voltages and a superior solid-state detector.

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 at 110 °C, 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.

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 geological and environmental significance.

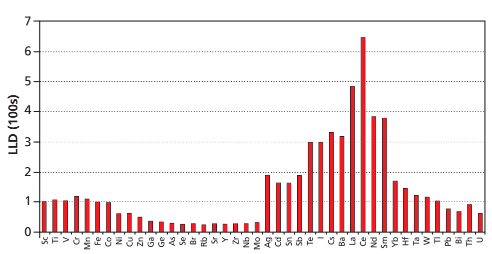
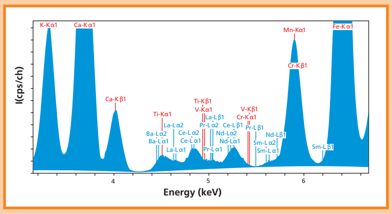


Figure 1. Typical detection limits from Sc-U for medium-power WDXRF spectrometers configured for geochemical analysis

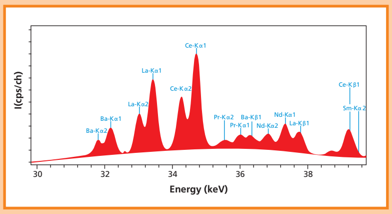
The Analytical X-ray Company

Spectral resolution

One of the main problems with using L-series lines for the analysis of heavy metals and rare earth elements is that they lie in crowded parts of the spectrum, commonly overlapped by lines of elements that are usually present at much larger concentrations. This is illustrated by comparing K- and L-line spectra for barium and rare earth elements in the same sample.



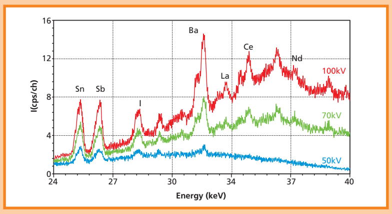
L-line spectra



K-line spectra

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 barium and rare earth elements.



Measurement criteria
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.

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.

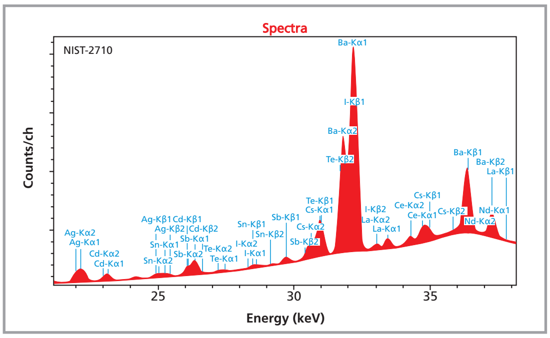


Figure 2. Spectrum obtained using a Barkla secondary target

	Calibration	Calibration	GSD-10		GSD-12		GSS-1	
	range (ppm)	RMS (ppm)	Certified	Measured	Certified	Measured	Certified	Measured
Cd	0.03 - 42	0.58	1.1	0.6	4.0	3.6	4.3	4.5
Sn	0.5 - 370	0.78	1.4	1.8	54	55	6.1	5.9
Sb	0.04 - 43	0.79	6.3	6.3	24.3	25.2	0.87	0.48
Cs	0.17 - 107	1.1	2.3	4.6	7.9	8.8	9.0	8.2
Ba	8.6 - 1899	24	42.0	42.7	206	203	590	588
La	13 - 90	2.0	13.0	15.8	32.7	32.8	34.0	33.5
Ce	34 - 242	5.0	38.0	38.8	61	59	70	70
Nd	11.8 - 92	4.2	11.8	13.9	25.6	26.9	28.0	26.0

Table 1. Calibration accuracy data based on 200 s live time measurements

Accuracy
The accuracy of the results is presented in Table 1. 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 also presented in Table 1. Calibration plots (Figure 3, 4 and 5) for antimony, barium and cerium give a graphic illustration of the accuracy of the method.

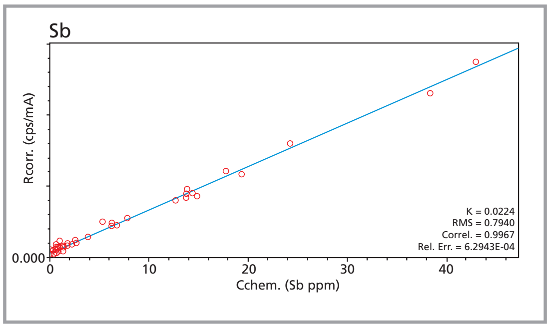


Figure 3. Calibration graph for Sb

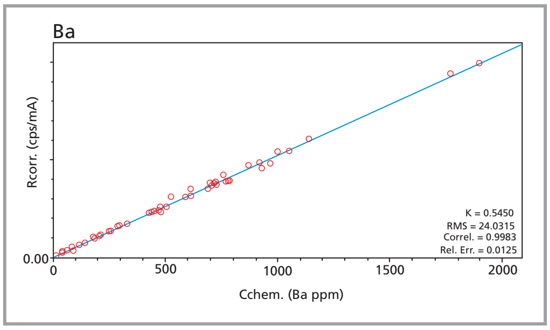


Figure 4. Calibration graph for Ba

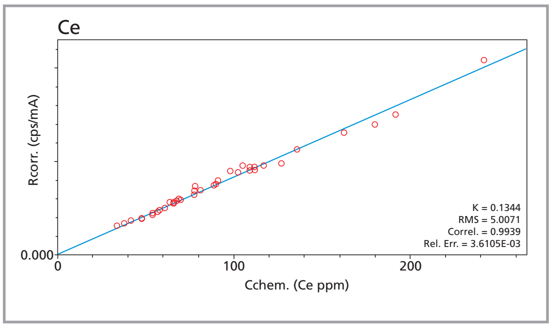


Figure 5. Calibration graph for Ce

Precision and instrument stability
The analytical precision of the XRF method is unrivalled and measurements made with the Epsilon 5 are no exception (Table 2). 20 consecutive measurements of a sample demonstrate standard deviations better than 3 % relative at the 40 ppm level (i.e. 40 ± 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.

Element	Cd	Sn	Sb	Cs	Ba	La	Ce	Nd
REPEATABILITY (20 consecutive measurements) (200 s live time)								
Mean ppm	1.38	1.63	6.21	4.99	43.9	15.1	39.6	14.4
RMS	0.34	0.34	0.42	0.47	1.00	1.20	1.18	1.28
RMS rel%	24.9	20.8	6.8	9.4	2.3	7.9	3.0	8.9
REPRODUCIBILITY (Measurements carried out over 10 days) (200 s live time)								
Mean ppm	1.45	1.56	6.40	4.70	43.7	15.1	39.6	13.2
RMS	0.48	0.36	0.32	0.72	0.62	0.64	1.20	1.5
RMS rel%	33.1	21.5	5.11	15.3	1.4	4.2	2.9	11.5
COUNTING STATISTICAL ERROR (200 s live time)								
CSE	0.153	0.165	0.319	0.322	0.783	0.434	0.676	0.549
CSE rel%	3.26	3.04	1.57	1.55	0.64	1.15	0.74	0.91

Table 2. Analytical precision

Detection limits
Detection limits for the analytes of interest in typical geological matrices are given in Table 3.

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

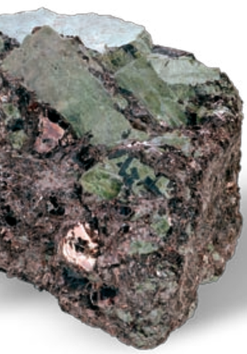
$$LLD = \frac{3}{s}\sqrt{\frac{r_b}{t_b}}$$

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

Detection limit (ppm)	Cd	Sn	Sb	Cs	Ba	La	Ce	Nd
LLD (100 s)*	1.2	1.3	1.4	2.1	2.5	3.2	3.5	5.0
Application LLD (800 s)**	0.42	0.46	0.49	0.74	0.88	1.13	1.24	1.77

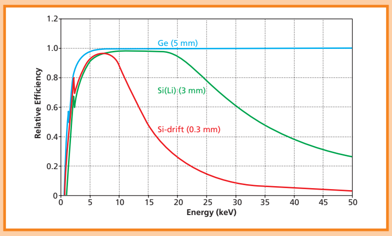
Table 3. Detection limits

* The LLDs quoted are typical for soil samples. LLDs for individual samples vary according to sample composition.
** Total measurement time for sequential WDXRF assumes 100 s measurements on peak and background, with background sharing between adjacent element peaks. Measurement of interfering elements lines is also taken into consideration. The Epsilon 5 measurements were made using a single Barkla polarizing target (Al_2O_3) and assume 50 % detector dead-time.



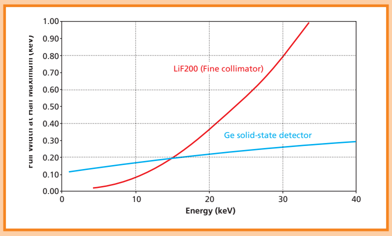
X-ray detector efficiency

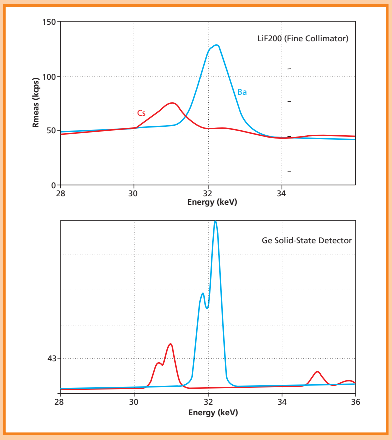
The PAN-32 detector is a liquid nitrogen-cooled solid-state Ge detector. Compared to other types of detectors it is characterized by a high degree of detection efficiency across the periodic table. Unlike other common solid-state detectors it maintains 100 % efficiency for heavy elements K-lines – a perfect match for Epsilon 5's high-voltage excitation source.



Detector resolution

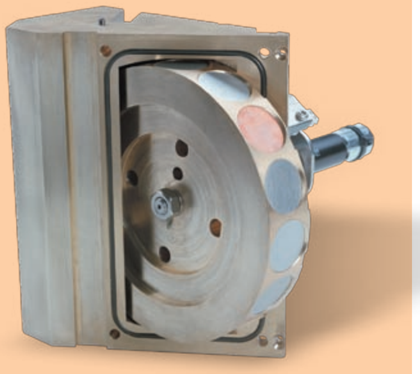
The PAN-32 detector also demonstrates superior spectral resolution at high energies compared to that obtained in WDXRF using dispersion crystals.





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.



Although, the LLD values for a counting time of 100 s in the Epsilon 5 are only slightly better than those obtained for WDXRF (Figure 1), a direct comparison is misleading. This is because the Epsilon 5 measures several elements simultaneously.

Figure 6 shows a comparison between the detection limits obtained in the same total measurement time (application time) where the Epsilon 5 shows significantly lower LLDs.

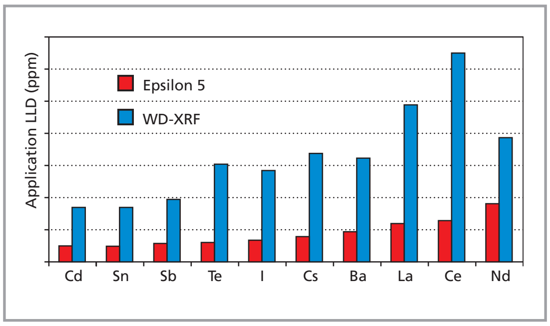


Figure 6. Comparison of application LLDs for the Epsilon 5 with typical WDXRF

Conclusions
The Epsilon 5 is capable of measuring heavy elements (Cd – Ce) in rocks and soils with significantly improved limits of detection. 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 resulting 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:	≤135 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, BaF_2	

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