AN APPLICATION BRIEF FROM
SPECTRO ANALYTICAL INSTRUMENTS

XRF-113-AB

Bio-Geochemistry: Analyzing Trace Elements in Sediment Using ED-XRF

Introduction

Multi-elemental analysis of sediment samples for bio-geochemistry applications represents a critical task for spectrometric instruments.

Users in science routinely use such spectrometric analysis on materials of widely varying composition. Energy-dispersive X-ray fluorescence (ED-XRF) instruments are often preferred for this work. ED-XRF methodology is an accepted technique for elemental analyses of sediment. So, these instruments' stability and ease of use let them excel at critical tasks from rapid screening analysis to precise elemental determination. They provide fast, precise, accurate, and economical solutions for analysis of major, minor, and trace elements in these and similar applications.

This paper covers the use of one such instrument to analyze trace elements in samples of geological materials with focus on the analysis of sediment, prepared as pressed powder pellets. Using polarization, band-pass filter, and direct excitation technologies, it proved a powerful analytical tool to satisfy the needs of high precision and low detection limits.

ED-XRF

The energy-dispersive X-ray fluorescence instrument treated in this paper identifies and quantifies the elements present in a substance using the following principle and methodologies:

A sample is subjected to X-rays emitted from a high-intensity X-ray tube. Some energy is absorbed by the atoms of elements in the sample. These excited atoms then emit X-ray fluorescent signals — along a spectrum of energies characteristic of the elements present. Element-specific signals are measured simultaneously, using a fixed, energy-dispersive semiconductor detector.

The radiation intensity of each elemental signal is proportional to the concentration of the element in the sample. This signal is processed in a multichannel analyzer, and the measured spectra are used to determine intensities. Concentrations are calculated using a calibration, as described in this paper.

Sample preparation

Standard reference materials in fine powder form with a grain size less than 63 micrometers (μm) were dried. Approximately 5 grams (g) of the dried powder was mixed and homogenized with 1 g wax. The powders were then pressed into steel rings with a pressure of 15 kilonewtons (kN) to produce the final pellets. This preparation concentrates sample components and introduces some degree of homogeneity, for improved analytical accuracy and precision.m For the accurate analysis of major elements in geological samples, these are typically prepared as fused beads. The performance for this application is described in a separate application brief.

Note that the analyzer used can routinely process solid, powder, pressed powder, fused bead, or liquid samples.

Analyzer

All measurements were made using a SPECTRO XEPOS simultaneous ED-XRF spectrometer from SPECTRO Analytical Instruments. This instrument is equipped with an air-cooled, 50 W end-window X-ray tube. The tube anode consists of a unique thick, binary- alloy cobalt-palladium. It is combined with an adaptive excitation system to excite specific elements for further increased sensitivity.

The analyzer also features a large area high-resolution silicon drift detector (SDD), plus the fixed excitation optics and a filter changer in front of the X-ray tube. The highly stable spectral resolution of the SDD amounted to <130 eV (Mn Kα) at an input rate of 1 million counts per second (cps).

SPECTRO XEPOS analyzers package high-quality components into a compact benchtop housing with a small footprint. In terms of analytical performance, they are known for low detection limits and high spectral resolution at high count rates, leading to reduced measurement times and improved accuracy.

Measurement parameters are given in Table 1.

Detection limits and sensitivities

A pure quartz sample was measured 10 times to determine the limits of detection (LODs). The absolute standard deviation (ASD) of the counts within the element-specific regions of interest (ROIs) (1.1*FWHM) of the quartz sample spectra and sensitivities was used to calculate the lower LOD values of Table 2. See Equation 1.

$$LOD = \frac{3^* ASD}{t_L} / S \qquad \text{(Eqn 1)}$$

ASD: Absolute standard deviation of the counts in a region of interest (1.1* FWHM) of an element specific line i at ten repeat measurements of a pure quartz sample

t_L: Live time in s

S: Sensitivity in kcps/% (see Table 2)

Note that instead of using a pure quartz sample, another suitable standard may be used to calculate LODs. The concentration of the observed element in the reference standard should be 100 times higher than the detection limit. See Equation 2.

$$LOD = 3^* C_o \frac{\sqrt{B}}{N} \qquad \text{(Eqn 2)}$$

N: Counts of an element specific line of a standard within an ROI having a width of 1.1* FWHM

B: Background behind the line within the same ROI

C_o: Concentration of the observed element in the standard

Table 1: Measurement conditions (measurement times shown are clocked real times; comparable live time specifications — which disregard processing intervals — would on average be 50% shorter)

Element	kV/mA	Mode	Measurement Time/s
Na – Cl	22.5/2.0	Polarization	300
K – Mn Pr – Sm	22.5/2.0	Co-band pass fiter	300
Fe – Nb Yb – U	45.0/1.0	Direct excitation	300
Mo – Ce	60.0/0.75	Direct excitation	600

SPECTRO XEPOS ED-XRF analyzer. Providing high resolution and sensitivity, reduced measurement times, low detection limits, low consumables use, and good long-term stability for accurate, precise, reliable analysis of geological materials in pressed pellet form.

The instrument's limit of spectral resolution, its full width of half maximum (FWHM), is calculated from the Gaussian width over energy calibration. Both methods used to calculate LOD (Equations 1 and 2) give similar values within the error of determination.

Calibration

Calibration for major, minor, and trace elements was performed by measuring a series of international reference materials. Validation was performed using another such set.

The mass absorption coefficient of the Compton-scattered palladium Kα line was calibrated via Compton intensity (Figure 1). Measured Compton intensities were corrected for volume effects. Absorption and enhancement effects within the sample were calculated based on the new SPECTRO XEPOS matched fundamental

Table 2: Calibration ranges, sensitivities, and lower limits of detection (3 sigma) in a pure silica (SiO_2) matrix

Other elements present in the sample at significant concentration level will influence the LOD

Element or oxide	LOD in µg/g	Calibrated concentrations range in µg	Average sensitivity of traces in kcps%	Element or oxide	LOD in µg/g	Calibrated concentrations range in µg	Average sensitivity of traces in kcps%
Na_2O	160	440,000		Ru	0.2	2,000	24
MgO	60	1,000,000		Rh	0.2	1,000	25
Al_2O_3	50	1,000,000		Pd	0.2	1,000	26
SiO_2		1,000,000		Ag	0.2	930,000	27
P_2O_5	5	600,000	20	Cd	0.2	880,000	28
S	0.6	300,000	14	In	0.2	830,000	29
Cl	0.8	600,000	37	Sn	0.3	770,000	31
K_2O	1.5	500,000	15	Sb	0.4	750,000	32
CaO	1.3	1,000,000	36	Te	0.7	800,000	29
Ti	0.3	600,000	70	I	0.9	760,000	25
V	0.3	560,000	120	Cs	1	690,000	23
Cr	0.2	680,000	210	Ba	2	700,000	20
Mn	0.2	750,000	220	La	2	850,000	18
Fe_2O_3	1.7	1,000,000	9	Ce	3	820,000	16
Co	0.8	740,500	12	Pr	2	830,000	50
Ni	1.0	790,000	15	Nd	2	860,000	53
Cu	0.5	800,000	21	Sm	2	860,000	57
Zn	0.2	800,000	39	Yb	2	880,000	8
Ga	0.2	750,000	53	Hf	1	850,000	9
Ge	0.1	700,000	60	Ta	1	820,000	10
As	0.1	760,000	82	W	0.6	800,000	11
Se	0.09	720,000	90	Pt	0.5	10,000	17
Br	0.06	1,000	110	Au	0.4	1,000	21
Rb	0.07	9,000	180	Hg	0.3	930,000	25
Sr	0.09	600,000	200	Tl	0.3	90,000	27
Y	0.1	1,000	210	Pb	0.2	170,000	33
Zr	0.2	480,000	230	Bi	0.2	900,000	37
Nb	0.2	700,000	260	Th	0.1	1,000	74
Mo	0.2	2,500	290	U	0.2	1,500	100

parameter approach, using the instrument's powerful TurboQuant II software, which is specialized to identify unknown samples. All elements measured in direct excitation were calibrated with a Compton model as well. The Compton model used as part of TurboQuant II allowed correction of different sample densities and correlated volume effects.

Of course, absorption jumps between an analyte and the palladium Kα Compton peak are also correctable with the model. Nevertheless, if an element has a concentration higher than a given limit (for example, 5000 µg/g), all elements with characteristic radiation energies below the energy of the 5000 µg/g element and the Compton peak will be analyzed with the SPECTRO XEPOS matched fundamental parameter model. Calibration data for the instrument's specific fundamental parameters is given in Tables 2 and 3; results of applying the calibration are shown in Figures 2 through 6.

Table 3: Number of used standards, correlation coefficient, RSD (Residual Standard Deviation), and number of calibration parameters for all calibrated elements

Element	Nr. of standards	Correlation coefficient	RSD in µg/g	Nr. of parameters
Ti	61	0.9998	487	1
V	54	1.0	20	1
Cr	77	1.0	36	1
Co	59	0.9993	23	6
Ni	57	0.9999	95	5
Cu	73	1.0	57	5
Zn	72	1.0	61	3
As	55	1.0	56	2
Br	17	0.9999	4	1
Rb	64	0.9999	23	3
Sr	63	0.9991	16	2
Y	54	0.9996	3	2
Zr	58	1.0	28	1
Nb	63	1.0	35	2
Mo	52	0.9991	17	2
Ag	31	0.9998	12	3
Cd	44	0.9999	6	3
In	18	0.9999	16	3
Sn	53	0.9998	22	3
Sb	38	0.9999	3	4
Te	10	0.9999	48	4

Element	nr. of standards	Correlation coefficient	RSD in µg/g	Nr. of parameters
I	10	0.9999	14	2
Cs	34	1.0	20	4
Ba	56	0.9999	33	1
La	61	0.9999	56	3
Ce	62	0.9999	66	2
Pr	30	0.9999	42	3
Nd	64	0.9999	36	1
Hf	42	0.9999	17	5
Sm	19	0.9999	52	1
Yb	24	0.9999	98	2
Hf	40	1.0	15	5
Ta	31	0.9999	273	3
W	38	0.9999	24	4
Au	13	0.9992	13	2
Hg	18	0.9999	1.4	3
Tl	33	0.9998	48	5
Pb	62	1.0	13	2
Bi	21	0.9998	27	2
Th	61	0.9998	2	3
U	57	0.9999	3	4

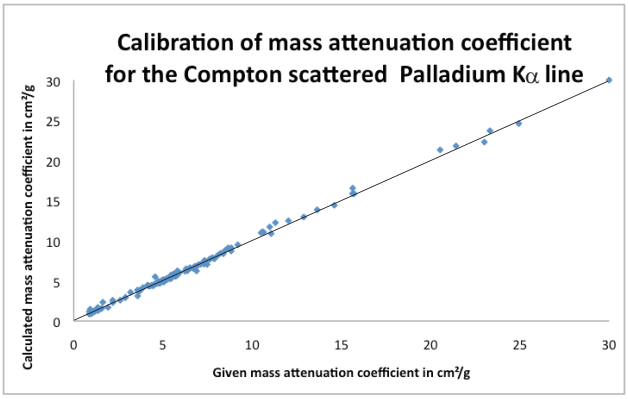

Figure 1: Calibrated mass absorption coefficients for the Compton- scattered palladium Kα line via given coefficients based on sample composition (correlation coefficient: 0.9993)

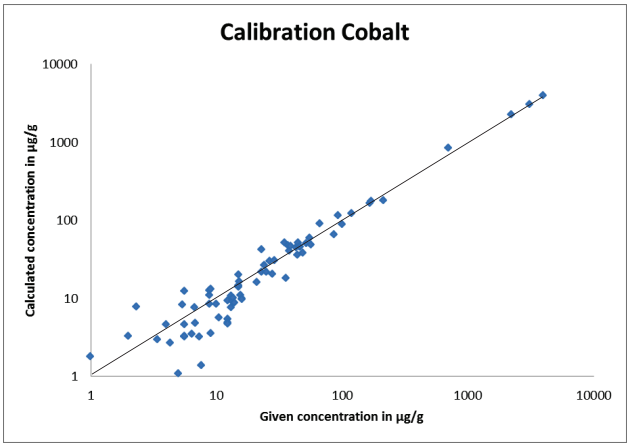

Figure 2: Comparison (log scale) between analyzed cobalt concentrations and given values (correlation coefficient: 0.9993)

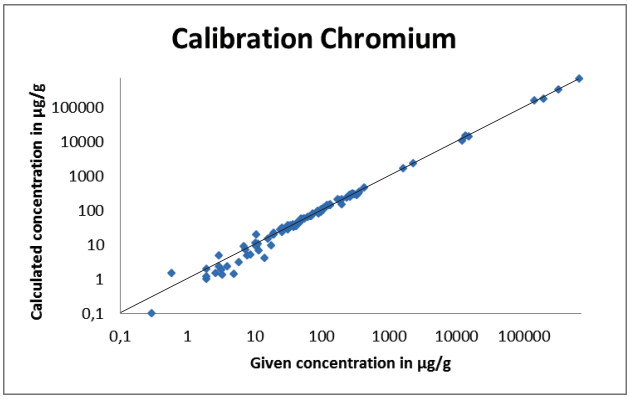

Figure 3: Comparison (log scale) between analyzed chromium concentrations and given values (correlation coefficient: 0.99999)

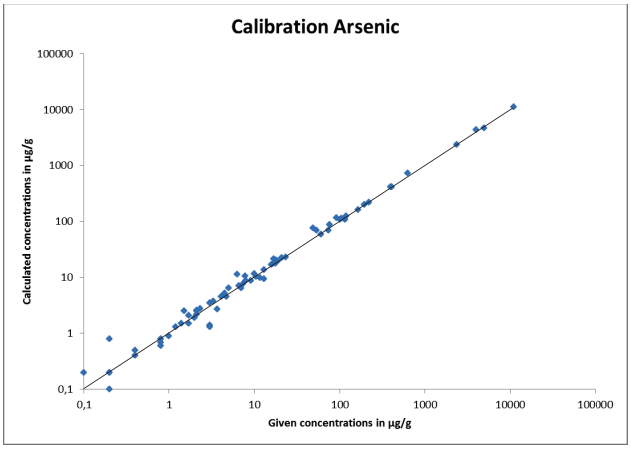

Figure 4: Comparison (log scale) between analyzed arsenic concentrations and given values (correlation coefficient: 1.0)

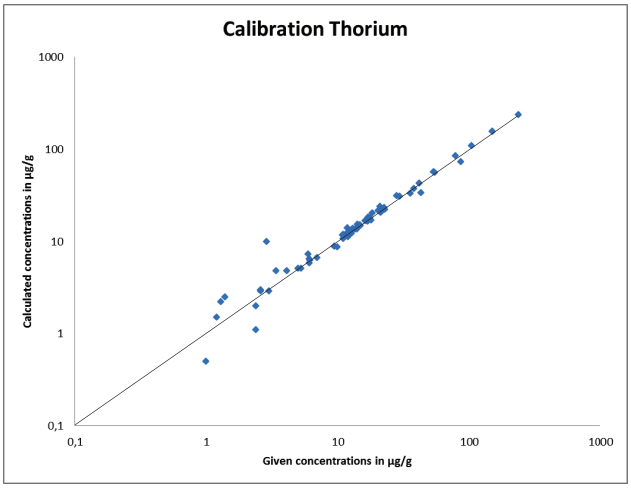

Figure 5: Comparison (log scale) between analyzed thorium concentrations and given values (correlation coefficient: 0.9997)

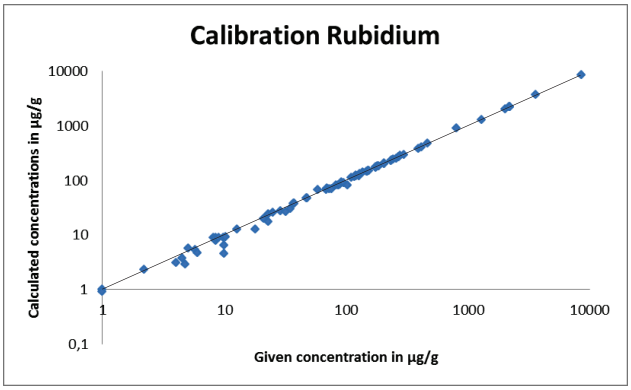

Figure 6: Comparison (log scale) between analyzed rubidium concentrations and given values (correlation coefficient: 0.99998)

Analytical performance

The exceptional performance of the SPECTRO XEPOS is demonstrated below. Analytical results for samples from a metal-rich sediment (SdAR-M2), are shown in Tables 4.

Table 4: Analytical results including counting statistical error (CSE) (95% confidence limit) for the metal-rich sediment SdAR-M2; values printed in italics are not certified

Element or oxide	Unit	Analyzed conc. ± error	Certified/ recommended conc. ± error
Na_2O	%	2.68 ± 0.04	2.58 ± 0.03
MgO	%	0.752 ± 0.01	*0.49 ± 0.02*
Al_2O_3	%	13.56 ± 0.02	12.47 ± 0.06
SiO_2	%	74.30 ± 0.02	73.45 ± 0.17
K_2O	%	5.31 ± 0.01	5.00 ± 0.03
CaO	%	0.93 ± 0.002	0.84 ± 0.01
Fe_2O_3	%	2.65 ± 0.002	2.63 ± 0.02
P_2O_5	µg/g	897 ± 12	*790 ± 20*
SO_3	µg/g	2783 ±12	*2422 ± 202*
Sc	µg/g	< 3	4.1 ± 0.02
Ti	µg/g	1680 ± 4	1798 ± 18
V	µg/g	26 ± 1	25.2 ± 0.7
Cr	µg/g	48.4 ± 0.6	49.6 ± 1.7
Mn	µg/g	1211 ± 2	1038 ± 15
Co	µg/g	10 ± 4	12.4 ± 0.4
Ni	µg/g	50 ± 1	48.8 ± 1
Cu	µg/g	237 ± 2	236 ± 4
Zn	µg/g	787 ± 2	760 ± 13
Ga	µg/g	18.5 ± 0.8	17.6 ± 0.4
Ge	µg/g	0.7 ± 0.2	*1.5 ± 0.2*
As	µg/g	89 ± 2	*76 ± 5*
Se	µg/g	1.8 ± 0.2	*2.7 ± 0.5*
Br	µg/g	1.2 ± 0.2	
Rb	µg/g	147 ± 0.6	149 ± 2
Sr	µg/g	142 ± 0.4	144 ± 3
Y	µg/g	33.5 ± 0.4	32.7 ± 0.7

Element or oxide	Unit	Analyzed conc. ± error	Certified/ recommended conc. ± error
Zr	µg/g	232 ± 0.6	259 ± 7
Nb	µg/g	25 ± 0.4	26.2 ± 0.7
Mo	µg/g	14.9 ± 0.6	13.3 ± 0.4
Ag	µg/g	13.1 ± 0.2	*15 ± 2*
Cd	µg/g	5 ± 0.2	5.1 ± 0.2
In	µg/g	2.4 ± 0.2	*2.1 ± 0.2*
Sn	µg/g	3.7 ± 0.4	*2.4 ± 0.2*
Sb	µg/g	102 ± 0.8	*107 ± 5*
Te	µg/g	2 ± 0.4	*2.1 ± 0.4*
Cs	µg/g	4.1 ± 0.6	1.82 ± 0.1
Ba	µg/g	1012 ± 4	990 ± 12
La	µg/g	46 ± 2	46.6 ± 1
Ce	µg/g	95 ± 3	98.8 ± 1.7
Pr	µg/g	6 ± 2	11 ± 0.2
Nd	µg/g	45 ± 2	39.4 ± 0.8
Yb	µg/g	< 2	3.6 ± 0.1
Hf	µg/g	6 ± 2	7.29 ± 0.23
Ta	µg/g	< 5	1.8 ± 0.1
W	µg/g	3 ± 1	*3.5 ± 0.4*
Hg	µg/g	1.7 ± 0.4	1.44 ± 0.1
Tl	µg/g	3.9 ± 0.6	*2.8 ± 0.2*
Pb	µg/g	807 ± 2	808 ± 14
Bi	µg/g	1.6 ± 0.6	1.05 ± 0.1
Th	µg/g	15.3 ± 0.6	14.2 ± 0.4
U	µg/g	2.5 ± 0.4	2.53 ± 0.1

Repeatability

Short-term repeatability of the SPECTRO XEPOS instrument was examined by analyzing the reference material GSD-14 NCS DC 73374 (stream sediment), performing 5 runs within 1 day.

As an example, Table 5 shows the absolute standard deviation (ASD) (95% confidence limit) of the repeats for one sample compared to the counting statistical error (CSE) (95% confidence limit). Also shown: the comparison between average and certified values. The values (95% confidence limit) of the element-specific CSE and the ASD of the repeats are similar for trace elements (highlighted in green). However, the CSE is dominant at concentrations less than about 1000 times LOD.

If the relative CSE is less than 0.2% (95% confidence limit), systematic errors appear. A relative error of about 0.27% (95% confidence limit) can be estimated by using the SiO2 results of Table 5. This error is mainly caused by three factors: the methodology of using the mass absorption coefficient of the palladium Kα radiation as an internal standard; the stability of the pellet; and some inaccuracies inherent in any instrument.

Thus, when evaluating this instrument for this application, sample preparation is identified as the main source of uncertainties in major and minor element analysis. In trace level analysis, sample preparation uncertainties fall below counting statistical error.

Figure 7: SPECTRO XEPOS schematics

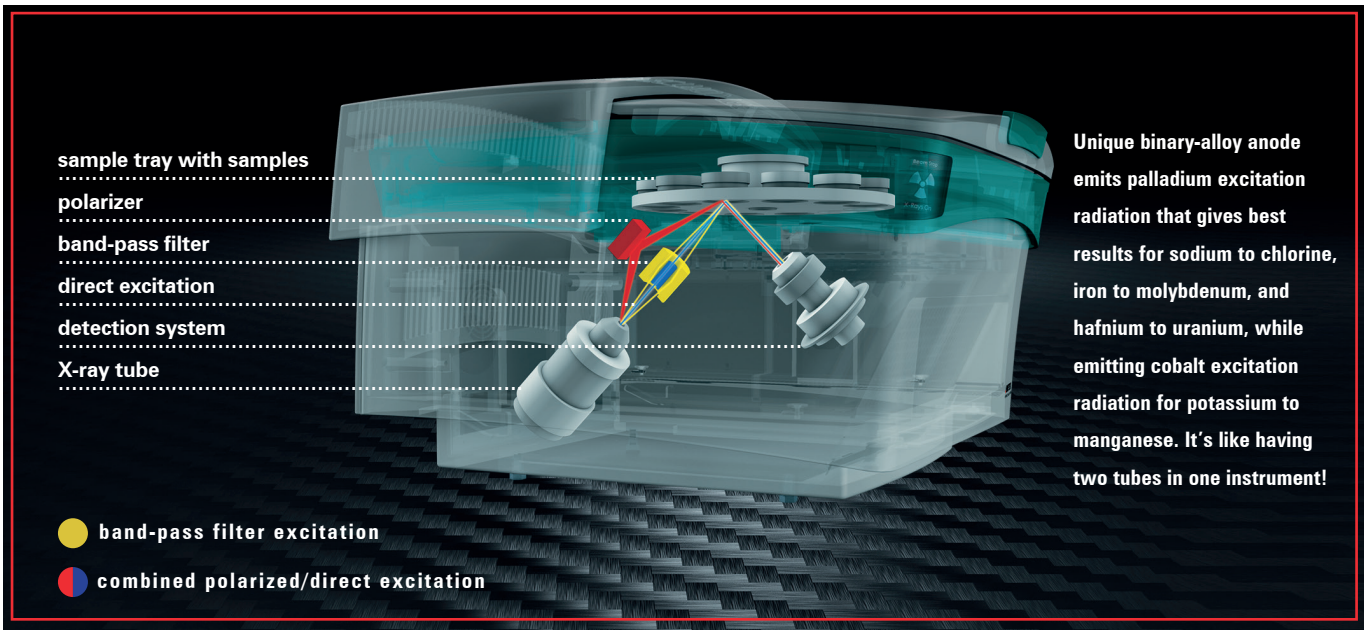

Table 5: Comparison between ASD (95% confidence limit) of five repeats and CSE (95% confidence limit), measured for geological reference material GSD-14 NCS DC 73374 (stream sediment). Comparison between the average value and the certified value (95% confidence limit) is also shown. Elements highlighted in yellow have concentrations 10 times greater than lower LOD); values printed in italics are not certified

Element or oxide	Unit	Certified/ recommended conc. ± error	Analyzed conc. ± ASD	CSE
Na_2O	%	2 ± 0.1	1.763 ± 0.02	0.03
MgO	%	3.4 ± 0.1	4.12 ± 0.03	0.02
Al_2O_3	%	13.39 ± 0.16	14.09 ± 0.12	0.02
SiO_2	%	57.25 ± 0.31	51.46 ± 0.14	0.02
K_2O	%	2.3 ± 0.1	2.202 ± 0.004	0.002
CaO	%	3.5 ± 0.1	3.26 ± 0.02	0.002
TiO_2	%	2.4 ± 0.08	2.230 ± 0.02	0.003
Fe_2O_3	%	9.5 ± 0.1	9.15 ± 0.036	0.008
P_2O_5	µg/g	2291 ± 30	2064 ± 34	16
SO_3	µg/g	*275*	363 ± 30	4
Cl	µg/g	*58*	47 ± 6	6
Sc	µg/g	18 ± 2	30 ± 3	2
V	µg/g	190 ± 25	197 ± 2	3
Cr	µg/g	243 ± 16	228 ± 1	1
Mn	µg/g	1230 ± 82	1243 ± 6	2
Co	µg/g	28 ± 2	22 ± 8	6
Ni	µg/g	87 ± 9	85 ± 1	2
Cu	µg/g	66 ± 6	67 ± 2	1.4
Zn	µg/g	165 ± 15	170 ± 0.6	1.4
Ga	µg/g	25 ± 3	23.1 ± 0.8	0.6
Ge	µg/g	1.6 ± 0.3	1.4 ± 0.2	0.2
As	µg/g	18 ± 2	19.9 ± 1.2	0.6
Br	µg/g	*2.6*	2.2 ± 0.2	0.2

Element or oxide	Unit	Certified/ recommended conc. ± error	Analyzed conc. ± ASD	CSE
Rb	µg/g	87 ± 7	82.5 ± 0.4	0.4
Sr	µg/g	216 ± 6	217.1 ± 0.6	0.6
Y	µg/g	34 ± 5	38.9 ± 0.2	0.4
Zr	µg/g	524 ± 16	506.6 ± 1.4	1
Nb	µg/g	72 ± 6	69.4 ± 0.4	0.4
Mo	µg/g	2.7 ± 0.3	3.6 ± 0.2	0.6
Cd	µg/g	0.2 ± 0.1	0.2 ± 0.2	0.2
In	µg/g	*0.18*	0.4 ± 0.2	0.2
Sn	µg/g	9.5 ± 1.7	10.9 ± 0.4	0.4
Sb	µg/g	2.7 ± 0.4	3.5 ± 0.4	0.4
I	µg/g	1.6 ± 0.3	4.6 ± 0.6	0.4
Cs	µg/g	4.3 ± 0.8	3.8 ± 1.6	1
Ba	µg/g	760 ± 47	752 ± 2	3
La	µg/g	54 ± 3	63 ± 3	3
Ce	µg/g	109 ± 10	119 ± 3	3
Nd	µg/g	45 ± 5	26 ± 5	2
Sm	µg/g	8.5 ± 0.6	7.1 ± 1.2	1.8
Yb	µg/g	3.8 ± 0.6	5.9 ± 2.6	2.4
Hf	µg/g	13.6 ± 0.6	10.1 ± 0.8	1.8
Pb	µg/g	66 ± 6	61.1 ± 0.8	1.2
Bi	µg/g	3 ± 0.3	1.1 ± 0.4	0.2
Th	µg/g	12.4 ± 1.2	12.9 ± 0.4	0.6
U	µg/g	3 ± 0.4	3 ± 0.6	0.6

Conclusions

The SPECTRO XEPOS simultaneous XRF spectrometer provided a fast, accurate, and economic solution to analyze major, minor, and trace elements in sediment samples for bio-geochemistry applications.

Very high spectral resolution and exceptionally low limits of detection (LODs) were reported for most elements tested. Calibration based on well-characterized samples showed very good correlation for a wide range of elements

SPECTRO XEPOS performed with high repeatability and excellent precision, so that sample preparation and statistical counting formed the major part of any errors produced. And depending on a given application's range of elements and the required precision of analytical results, the analyzer's design allowed measurement time to be optimized.

Choosing an ED-XRF analyzer

ED-XRF technology keeps getting better and better. Today's most advanced instruments can provide a quantum leap in performance, even over earlier top-ranked models. Look for the following benefits:

High sensitivity and precision. In multi-element analysis of major, minor, and trace element concentrations, it's critical to maximize spectrometric sensitivity and precision. Example: the newest SPECTRO XEPOS analyzers combine exclusive new excitation technology with innovative detector and tube designs. These help deliver up to 10X greater sensitivity and 3X better precision than previous models. So users get fast, accurate analysis of a wide range of elements, from sodium to uranium.

Long-term stability. Most ED-XRF analyzers shut down their X-ray tube between measurements. Unfortunately, resulting temperature variations can negatively affect repeatability and accurate readings. To ensure stability, look for an instrument that maintains constant tube power.

Low detection limits. Lower limits of detection (LODs) improve performance with minor and trace element concentrations. The best new models combine high sensitivity with minimized backgrounds, achieving exceptionally low LODs for a wide range of elements.

Applications. Some XRF analyzers have strengths in the analysis of trace and minor elements, others are optimized for light elements. For this application, the complete range is important and the analyzer should be prepared to give accurate results for the full range of elements.

Lower costs. Today, an advanced ED-XRF analyzer such as SPECTRO XEPOS exhibits significantly lower costs — of initial investment and long-term ownership — than wavelength dispersive X-ray fluorescence (WD-XRF) spectrometers. Yet it generally provides comparable performance.

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