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XRF1089 - Analysis of hazardous heavy elements in soil and sediment using ZSX Primus IV

Introduction

Soil and sediment have a crucial role in our life as the foundation for agricultural crops and forests, and also by retaining water. When soil is polluted, it negatively impacts the ecosystem. Consequently, our health and the living environment suffer negative effects when we consume ground water and crops from polluted soil. To keep the environment clean, it is necessary to monitor soil and sediment.

For analysis of hazardous heavy elements in soil and sediment, X-ray fluorescence (XRF) spectrometry is used because of its simple sample preparation and short analysis time.

Soil and sediment contain a certain amount of organic material, which cannot be analyzed by XRF. Therefore, conventional matrix corrections, such as the theoretical alpha method, do not work effectively. In XRF analysis of soil and sediment, organic material causes significant error.

This application note demonstrates that a unique matrix correction, where the scatter ratio correction and the theoretical alpha correction are combined, can be applied to XRF analysis of heavy elements, including hazardous ones, in soil and sediment.

Instrument

The ZSX Primus IV and ZSX Primus III NEXT are tube-above sequential wavelength dispersive (WD) XRF spectrometers, which have high spectral resolution and high sensitivity from light to heavy elements. The instruments are designed to provide reliable analysis results and their flexibility provides versatility for a wide range of applications.

These spectrometers are equipped with a Rh target X-ray tube where the maximum tube power is 4 kW and 3 kW, respectively. The instruments also have a built-in intelligent auto sample changer (ASC). The ASC is upgradable to 48 or 96 samples.

The ZSX Primus IV and ZSX Primus III NEXT are optimized for powder sample analysis. The tube-above optics, variable vacuum speed and powder trap enable secure analysis of powder samples, and reduce maintenance by preventing pressed powder pellets from breaking apart and falling into the optics, and by protecting the vacuum pumps and magnetic valves from fine particles scattered from samples. The tube-above optics design also enables measurement of pressed powder samples without any binding agent. Pressing without binding agent simplifies sample preparation and reduces labor hours and the cost of binding agents.

The system software is designed for ease of use in routine analyses. The "Flowbar" in quantitative analysis guides users through calibration. The "Sample ID Table" and the "Program Operation" help operators carry out daily analysis.

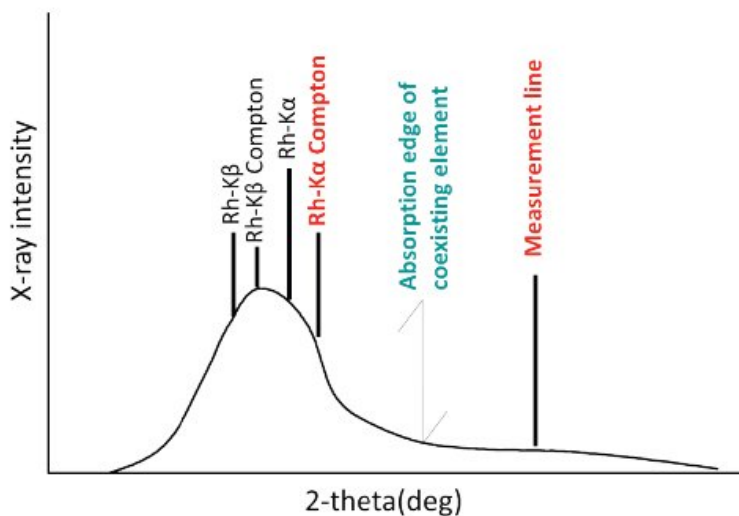


Figure 1: Schematic diagram showing positions of the measurement line, Rh Compton scatter and the absorption edge of an coexisting element.

Measurement conditions

The ZSX Primus IV was used in this application note. Measurement conditions are tabulated in Table 1. The measurement area was 30 mm in diameter and the path atmosphere was under vacuum.

Table 1: Measurement conditions.

Element	Cr	Mn	Fe	Co	Ni	Cu	Zn	As	Cd	Hg	Pb	Rh
Line	Kα	Kα	Kα	Kα	Kα	Kα	Kα	Kβ1	Kα	La	Lβ1	Kα-C
kV - mA	50-60	50-60	50-60	50-60	60-50	60-50	60-50	60-50	60-50	60-50	60-50	50-60
Primary beam filter	Al125	Al125	Al25	Al125	Al125	Al125	Al125	Ni40	Ni400	Ni40	Ni40	Al25
Soller slit	S2											
Analyzing crystal	LiF(220)											
Detector	SC											
Peak counting time (s)	60	10	10	50	40	20	20	40	80	100	40	20

BG counting time (s)	30 x2	10	10	50	20 x2	10 x2	20	40	40 x2	100	20 x2	-
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Sample and sample preparation

For calibration, 21 certified reference materials of soil and sediment from GSJ, USGS, NRC and NIST were used. All the reference materials, pre-dried, were pressed at 150 kN into PVC rings without binding agent.

Correction for calibration

Soil and sediment samples contain a certain amount of organic material. In addition, these samples show strong inhomogeneity, variation in particle size and mineral compositions. To compensate for errors caused by the organic material and the inhomogeneity of soil and sediment samples, the Compton scatter ratio method is used. This method is a conventional correction technique in XRF analysis, using the Compton scatter line as an internal standard, where the ratio of the X-ray intensity of an element line to the Compton scatter of the element of an X-ray tube target is used in quantitative analysis. However, if samples contain major element(s) with absorption edge(s) whose wavelength is between the wavelengths of the Compton scatter and the element line, the Compton scatter ratio method cannot work effectively (Figure 1). The "ZSX Guidance" software of ZSX Primus IV and Primus III NEXT has a unique correction method where the Compton ratio method and the theoretical alpha correction are combined. This program, the "Quant Scatter FP Method", improves accuracy of analysis for heavy elements in soil and sediment.

Figure 2 shows an example of applying the Quant Scatter FP Method to Zn. By applying the Compton scatter ratio, the calibration accuracy of Zn was improved to 80 ppm from 108 ppm without any correction. By applying the Quant Scatter FP Method, the accuracy was much improved to 25 ppm. The Quant Scatter FP Method was applied to all elements in this study except for Cd.

For the Cd analysis, the background ratio correction, where an intensity ratio of the peak to the background of the analysis line is used for XRF analysis, was applied. Since the mass absorption coefficient of an element line and its background can be regarded to be equivalent, the ratio of the peak intensity of the element line to the background intensity can compensate for the matrix effects.

In this application note, the background ratio correction was applied only for Cd. For the other elements, the Quant Scatter FP Method was applied.

Analysis results

Table 2 summarizes the calibration results and Figure 3 (on the next page) shows calibration curves of representative elements.

To demonstrate reproducibility, repeatability tests (10 runs) were carried out by running NIST SRM2711a. The test results are shown in Table 3.

The accuracy of calibration was calculated by the following formula:

$$Accuracy = \sqrt{\frac{\sum_i (C_i - \hat{C}_i)^2}{n-m}}$$

C_i : calculated value of standard sample
 \hat{C}_i : reference value of standard sample
 n : number of standard samples.
 m: degree of freedom (linear 2, quadratic 3)

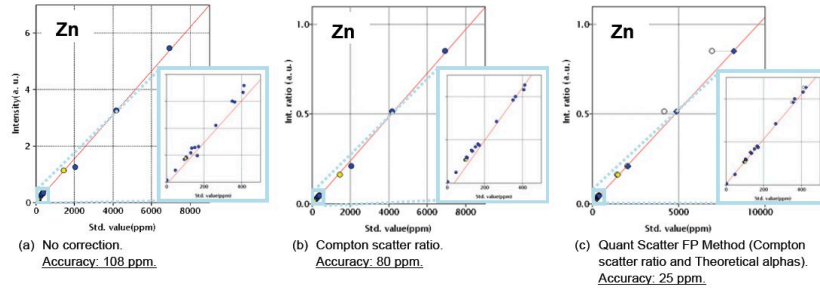


Figure 2: Calibration curves of zinc (Zn) for comparison between (a) no correction, (b) Compton scatter ratio and (c) Quant Scatter FP Method. Blue: point with correction applied, Yellow: corrected point for reference value, White: uncorrected point

Table 2: Calibration summary.

Element	Unit	Calibration range	Accuracy
Cr	ppm	22 - 500	3.8
Mn	ppm	51 - 2140	35
Fe	mass%	0.24 - 8.15	0.18
Co	ppm	0.7 - 226	2.2
Ni	ppm	2.2 - 311	3.5
Cu	ppm	2.3 - 3420	17
Zn	ppm	4.9 - 6952	25
As	ppm	0.8 - 1540	2.3
Cd	ppm	(0.02) - 54.1	0.6
Hg	ppm	(0.02) - 32.6	1.3
Pb	ppm	3.1 - 5532	36

Table 3: Repeatability test result.

Element	Unit	Average	Standard deviation	R.S.D.
Cr	ppm	92.4	3.01	3.3%
Mn	ppm	1001	19.	1.9%
Fe	mass%	3.53	0.004	0.12%
Co	ppm	18.5	0.93	5.1%

Ni	ppm	35.1	0.70	2.0%
Cu	ppm	179	1.3	0.72%
Zn	ppm	568	3.9	0.69%
As	ppm	130	2.8	2.2%
Cd	ppm	55.2	1.60	2.9%
Hg	ppm	7.5	0.69	9.1%
Pb	ppm	1735	4.0	0.23%

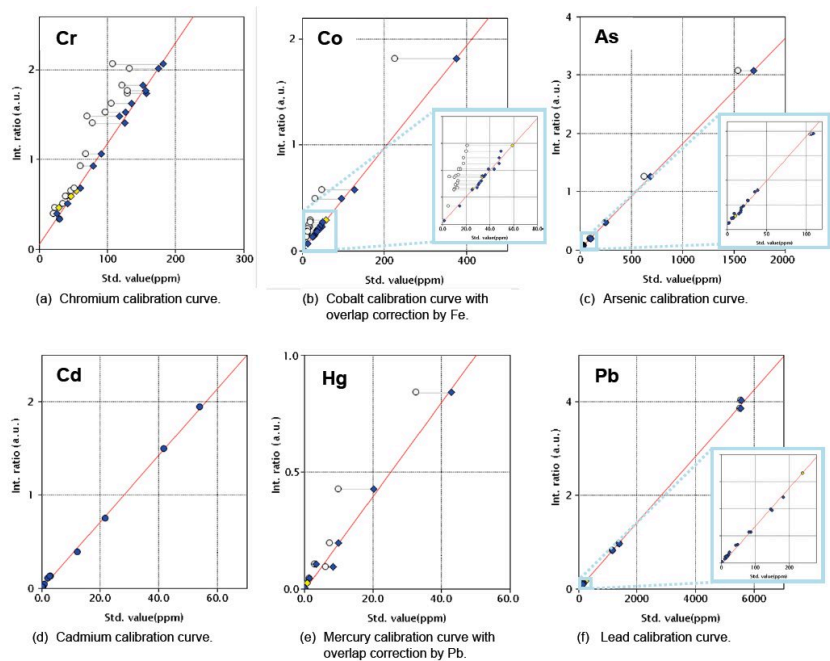


Figure 3: Calibration curves of representative elements. Blue: point with correction applied, Yellow: corrected point for reference value, White: uncorrected point

Conclusions

Heavy elements, including hazardous ones, in soil and sediment can be routinely analyzed on the ZSX Primus IV or ZSX Primus III NEXT with tube-above optics by pressing powder samples into pressed powder briquettes without any binding agent.

The ZSX Primus IV and ZSX Primus III NEXT have advantageous features for powder sample analysis; tube-above optics, variable vacuum speed and a powder trap. These features can reduce downtime, maintenance and operational cost.

A unique correction method, the Quant Scatter FP Method, where the Compton scatter ratio and the theoretical alpha correction are combined, improves calibration accuracy of the heavy elements in soil and sediment.

Related products



ZSX Primus III NEXT

Affordable, high-end, tube-above Industrial WDXRF for the analysis of solid samples



ZSX Primus IV

High power, tube above, sequential WDXRF spectrometer with new ZSX Guidance expert system software