LA-6869-MS

Informal Report

Special Distribution

Issued: June 1977

**Automated Energy-Dispersive X-Ray Determination of
Trace Elements in Stream Sediments**

J. M. Hansel
C. J. Martelli

los alamos
scientific laboratory
of the University of California
LOS ALAMOS, NEW MEXICO 87545

An Affirmative Action/Equal Opportunity Employer

UNITED STATES
ENERGY RESEARCH AND DEVELOPMENT ADMINISTRATION
CONTRACT W-7405-ENG. 36

This work was supported by the US Energy Research and Development Administration, Division of Uranium Resources and Enrichment. Program Code B048.

This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Energy Research and Development Administration, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights.

CONTENTS

LIST OF ILLUSTRATIONS	iv
LIST OF TABLES	iv
ABSTRACT	1
I. INTRODUCTION	1
II. PROCEDURE FOR ANALYZING SAMPLES	2
Sample Preparation	2
Equipment	2
Analysis of Samples	2
Analysis of Spectra	3
III. INVESTIGATIONS OF SAMPLE PREPARATION PARAMETERS	5
IV. EFFECTS OF DIVERSE IONS	5
V. RELIABILITY OF THE METHOD	5
Precision	5
Detection Limits	5
Accuracy	7
VI. POTENTIAL FUTURE WORK	8
ACKNOWLEDGMENTS	8
REFERENCE	8

NOTICE

This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Energy Research and Development Administration, nor any of their employees, nor any of their contractors, subcontractors, or their employees, make any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights.

MASTER

LIST OF ILLUSTRATIONS

1. X-Ray intensity as a function of sample weight.	6
--	---

LIST OF TABLES

I. Concentrations Calculated by the Line Intensity Method	4
II. Concentrations Calculated by the Mo Compton Ratio Method	4
III. Precision of the Method	7
IV. Experimental Detection Limits	7

AUTOMATED ENERGY-DISPERSIVE X-RAY DETERMINATION OF TRACE ELEMENTS IN STREAM SEDIMENTS

by

J. M. Hansel and C. J. Martell

ABSTRACT

Nickel, copper, tungsten, lead, bismuth, niobium, silver, cadmium, and tin are determined in stream sediments using a computer-controlled energy-dispersive x-ray fluorescence system. The system consists of an automatic 20-position sample changer, a silicon lithium-drifted detector, a pulsed molybdenum transmission-target x-ray tube, a multichannel analyzer, and a minicomputer. Samples are analyzed as minus 325-mesh powders. A computer program positions the samples, unfolds overlapping peaks, determines peak intensities for each element, and calculates the ratio of the intensity of each peak to that of the molybdenum $K\alpha$ Compton peak. Concentrations of each element are then calculated using equations obtained by analyzing prepared standards. Detection limits range from 5 ppm for silver, cadmium, lead, and bismuth to 20 ppm for niobium. The relative standard is 10% or less at the 100-ppm level and 20% at the 20-ppm level. Samples can be analyzed at the rate of sixty per day.

I. INTRODUCTION

As part of the nationwide Hydrogeochemical and Stream Sediment Reconnaissance of the National Uranium Resource Evaluation Program being conducted by the Energy Research and Development Administration, the concentrations of several trace elements are being determined in waters and stream sediments. An analytical method was needed to determine nine of these elements, including nickel, copper, tungsten, lead, bismuth, niobium, silver, cadmium, and tin in the sediments, to complement neutron activation analysis methods. Requirements for the method were that it should be rapid, inexpensive, and provide good precision and low detection limits. An automated energy-dispersive x-ray fluorescence method was chosen for these analyses.

The stated requirements necessitated compromising the optimal excitation parameters for the nine elements and analyzing each sample only once using the compromised set of excitation parameters. Multiple readings could improve detection limits and precision slightly, but not enough to justify the increased analysis time.

II. PROCEDURE FOR ANALYZING SAMPLES

Sample Preparation

Three 10-gram samples are simultaneously ground for 6 min in a Spex Shatter-box rotary swing-mill grinder using hardened steel grinding containers. This grinding produces a powder 95% of which passes 325 mesh, a sufficiently small particle size for good x-ray analyses. Analysis of the containers showed very low nickel and copper content, and the only contaminant added to the samples upon grinding was a small amount of iron which was not one of the elements of interest. Six grams of the ground sample are transferred to a 3.2-cm-diam polypropylene sample cell which is covered with 0.006-mm-thick Mylar. The cell is inverted and tapped on a smooth surface to ensure compaction of the powder against the Mylar.

Equipment

Automatic sample changer and detector. A Nuclear Semiconductor Spectrace 440 automatic 20-position sample changer and a Si(Li) detector were satisfactory.

Data analysis system. Consists of a multichannel analyzer, a push-button control panel, a tape transport for magnetic tape cassettes, and a dedicated minicomputer. A Tracor Northern NS-880 data analysis system with computer software on magnetic tape cassettes and a PDP-11/05 computer with 24K of memory are being used and are satisfactory.

X-Ray tube and pulsed power supply. A molybdenum transmission-target x-ray tube and a Watkins-Johnson power supply controlled by a Nuclear Semiconductor pulse controller are used. The pulsing system deactivates the tube when the amplifier is busy and reactivates it when the amplifier is free to process more data. This pulsing is done on a microsecond scale and reduces analysis time considerably.

Operating conditions

Excitation potential	50 kV
Current	0.15 mA
Filter (between x-ray tube and sample)	0.177-mm Mo
Live counting time	350 sec
Energy range (Fe K α to Sn K α)	6-26 keV

Analysis of Samples

The analysis procedure uses the system capability that allows two spectra to be stored simultaneously in the memory of the multichannel analyzer (MCA). Each spectrum is stored in a 500-channel block designated as first- or second-half memory of the MCA and may be accessed like any other computer data. Separate operations may be performed on each spectrum simultaneously.

1. Twenty samples are loaded into the sample changer, and the equipment is set for automatic operation under computer control.
2. A spectrum of the first sample is acquired in the second-half memory of the MCA.
3. This spectrum is moved into the first-half memory of the MCA.
4. The next sample is moved into position, and acquisition of a spectrum is begun in the second-half memory of the MCA.
5. The spectrum of the first sample stored in the first-half memory of the MCA is analyzed.
6. The results are printed.
7. When acquisition of the spectrum begun in Step 4 is complete, the program returns to Step 3 to repeat the cycle.
8. The above steps are continued until all 20 samples are analyzed.

An automatic shutdown option, if enabled, turns off the x-ray tube at the end of the run. This allows an analysis to run past normal working hours with automatic shutdown. Analysis time for the 20 samples is slightly more than 3 h. Using both halves of the MCA memory simultaneously substantially reduces the analysis time because a significant amount of computer time sharing is taking place.

Analysis of Spectra

1. Using the Tracor software program, the sample spectrum is fitted by a multiple, least squares, fitting routine to 17 pure element reference spectra stored in the computer's memory. In addition to the nine elements of interest, pure element reference spectra of all other elements present in the sample must be included in the fit. This routine deconvolutes overlapping peaks and returns intensities of x-ray peaks for each element. By using this program, all but the most severe overlap problems are eliminated. The only severe overlap is that of the small niobium peaks by the large molybdenum Compton peaks which causes the niobium detection limit to be abnormally high.
2. The ratio of the peak intensity for each element to the intensity of the molybdenum $K\alpha$ Compton peak is then calculated. This fast and simple method to correct for matrix effects depends upon increases in mass absorption coefficient and decreases in peak intensities as the average atomic number of the sample increases.¹ The inelastically scattered molybdenum x rays (Compton peaks) also decrease in intensity as the average atomic number increases and serve as good internal reference peaks because they are affected the same as the x rays from the sample. To check the effectiveness of the molybdenum Compton ratio method in correcting for matrix changes, samples were prepared which contained fixed concentrations of the nine elements and different concentrations of iron. Iron was chosen because it is the heaviest major component expected to be present in sediments. Concentrations were first calculated using only the peak intensities of the elemental x rays (Table I). The concentration values for all elements

TABLE I
CONCENTRATIONS CALCULATED BY THE LINE INTENSITY METHOD

Element	Concentration, ppm			
	No Fe	5% Fe	8% Fe	10% Fe
Ni	120	91	69	56
Cu	120	89	79	63
W	130	76	61	55
Pb	120	82	56	44
Bi	120	82	69	60
Nb	130	107	89	86
Ag	110	90	81	70
Cd	110	90	76	74
Sn	125	70	65	52

decreased markedly as the iron concentration increased due to absorption of the x rays by the iron. Concentrations were then calculated using the same data, except that the molybdenum Compton ratio method was used (Table II). The values are much better, and the method works well even in the presence of a large amount of iron.

TABLE II
CONCENTRATIONS CALCULATED BY THE Mo COMPTON RATIO METHOD

Element	Concentration, ppm			
	No Fe	5% Fe	8% Fe	10% Fe
Ni	120	124	124	125
Cu	120	111	125	121
W	130	116	101	123
Pb	120	111	110	118
Bi	115	104	102	106
Nb	130	133	140	146
Ag	110	111	110	115
Cd	110	114	110	123
Sn	125	92	110	113

3. Using the molybdenum Compton ratios, the concentration of each element is calculated from a curve prepared from standards.

III. INVESTIGATIONS OF SAMPLE PREPARATION PARAMETERS

A sample must be of sufficient thickness to prevent passage of x rays completely through it. When the sample thickness is such that a further increase in thickness results in no further increase in a desired signal, it is said that the sample is of infinite thickness. To select a weight which provided a sample of infinite thickness, a plot was made of tin $K\alpha$ x-ray intensity versus sample weight (Fig. 1). The tin $K\alpha$ x-ray was used because it is the highest energy x ray of interest. The curve is relatively flat from approximately 5 grams up; therefore, a 6-gram sample size was chosen.

Pelletizing the sample was tried, but the x-ray intensity was increased by only a small amount and was not considered to be a sufficient improvement for the time involved. Also, the samples were high in silica content and produced very fragile pellets.

IV. EFFECTS OF DIVERSE IONS

Spectral interference is almost eliminated by using the least squares fitting program. As stated previously, niobium is the only element seriously affected. For small quantities of niobium, there is overlap of the niobium peak by the molybdenum Compton peak, making the method less sensitive for determining niobium. If large quantities of iron are present, the 65K-count capacity of the Fe $K\alpha$ peak channels is exceeded. The channel contents overflow to zero and begin to accumulate again, producing a peak within a peak, thereby completely disrupting the fitting procedure. To prevent this problem, the computer program checks for such a condition and stops the counting before peak overflow occurs. This is only necessary in about 8% of the samples.

V. RELIABILITY OF THE METHOD

Precision

The precision of the method (Table III), expressed as percent relative standard deviation, is based upon 10 determinations each at the 20-ppm and 100-ppm levels. The samples were prepared by adding known amounts of each element to ground sand from a local arroyo and were analyzed using the analysis procedure. The results show that the relative standard deviations range from 2 to 10 percent at the 100-ppm level and are poorer, as expected, at the lower concentrations.

Detection Limits

The detection limits, defined as three times the standard deviation for measuring a blank, were determined from ten measurements of the blank (Table IV). Theoretical detection limits also were calculated and were found to agree in most cases with the measured values. The abnormally high value for niobium is due to the molybdenum Compton interference, as mentioned earlier. The limits for nickel, copper, and tungsten are higher than would have resulted with a lower excitation voltage. However, optimizing conditions for these three elements lowered their limits only about 5 ppm. Therefore, little capability has been sacrificed by using the 50-kV excitation potential. The detection limit for tin is higher than those for silver and cadmium because the tin x ray is

Fig. 1.

X-Ray intensity as a function of sample weight.

TABLE III
PRECISION OF THE METHOD

<u>Element</u>	<u>Relative Standard Deviation, % at</u>	
	<u>20-ppm Level</u>	<u>100-ppm Level</u>
Ni	38	8
Cu	27	8
W	25	10
Pb	10	4
Bi	9	3
Nb	27	7
Ag	9	2
Cd	8	2
Sn	14	4

TABLE IV
EXPERIMENTAL DETECTION LIMITS

<u>Element</u>	<u>Detection Limit, ppm</u>
Ni	15
Cu	10
W	15
Pb	5
Bi	5
Nb	20
Ag	5
Cd	5
Sn	10

superimposed upon the beginning edge of the continuum from the x-ray tube. This produces a higher background and thus, a higher detection limit.

Accuracy

Certified stream sediment standards were not available to check the accuracy of the method, but some United States Geological Survey mineral standards were available. Most of the elements were present at levels below the detection limits of the method. Measured nickel, copper, and lead values were within the range of the method, and the concentrations found agreed reasonably well with the recommended values.

VI. POTENTIAL FUTURE WORK

Stream sediment standards, when available, will be purchased and analyzed to further check the accuracy for determining all elements. In the absence of standards, previously analyzed samples will be analyzed using an independent method, and the values compared to define better the true values. The computer program will be modified to run more efficiently, thereby shortening analysis time, and a few new elements of interest will be determined.

ACKNOWLEDGMENTS

The authors thank E. A. Hakkila for many helpful suggestions during the development of the method and G. R. Waterbury for help in preparing the manuscript.

REFERENCE

1. R. C. Reynolds, "Matrix Corrections in Trace Element Analysis by X-Ray Fluorescence: Estimation of the Mass Absorption Coefficient by Compton Scattering," *American Mineralogist* 48, 1133 (1963).