CONF-910862--4

PNL-SA--19812

Reci DE91 018473

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MASTER

August, 1991

Presented at the
Pacific-International Congress on X-Ray
Analytical Methods
August 12-16, 1991
Honolulu, Hawaii

Work supported by
the U.S. Department of Energy
under Contract DE-AC06-76RLO 1830

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PNL-SA-19812

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ABSTRACT

A method has been developed to simultaneously compute matrix corrections from a composite spectrum of multi-target energy-dispersive (EDXRF) and multi-crystal wavelength-dispersive (WDXRF) x-ray fluorescence systems. A serial line installed between the WDXRF and EDXRF spectrometers via a PDP 11/34a computer allows acquired wavelength data to be digitally transformed into an energy spectrum. The low-energy x-ray information from the WDXRF unit is then coupled with the backscatter coherent/incoherent information from the EDXRF unit, enabling enhanced quantitative analysis for low-atomic-number (low-Z) elements. The peak resolution obtainable from the WDXRF spectra often removes the necessity for peak-overlap corrections.

Backscatter intensities obtained from the EDXRF unit are used to provide information on total sample mass and to correct for matrix effects. The resulting backscatter fundamental-parameter (BFP) calculations generally provide an accurate analysis of samples without prior knowledge of the sample matrix. Such an approach is particularly useful for samples in which quantities of carbon, oxygen, and other low-Z constituents cannot be explicitly determined.

Regions of interest (ROI) are created by the computer code "PREP" and processed by the BFP code "MSAP" an extension of the "SAP3" computer program for quantitative multielement analysis by energy-dispersive x-ray fluorescence.[1]

INTRODUCTION

Some typical requirements for a BFP analysis are that all backscatter must originate from the sample, that the sample must be reasonably homogeneous, and that the coherent and incoherent backscatter peaks must be resolvable. Spectral peaks with no associated discrete coherent/incoherent backscatter peaks, such as those arising from WDXRF and from Ti fluorescence in EDXRF, are candidates for BFP analysis through formation of a composite spectrum.

The BFP code "SAP3" has been used with success in evaluating multi-target EDXRF spectra[2] to determine matrix correction, sample mass, and elemental concentrations. Figures 1a and 1b illustrate the methodology involved in the composite dual-spectra approach in which 2 EDXRF spectra are combined that have been acquired from the same sample but that have different excitation sources, Ti and Zr. Since Ti has no resolvable coherent-incoherent backscatter peaks, "SAP3" efficiently employs the data in BFP calculations using only the backscatter peaks from Zr. The combined results take advantage of features which are common to both analyses: identical sample thickness and identical matrix composition, resulting in identical x-ray absorption characteristics. Based on the success of the composite dual-spectra approach, the BFP technique was extended to a composite multi-spectra approach in which incoherent and coherent backscatter intensities from a single excitation source (Zr K_α) define matrix corrections for elements determined by WDXRF, using 4 crystals, and by EDXRF, using 3 or more secondary targets.

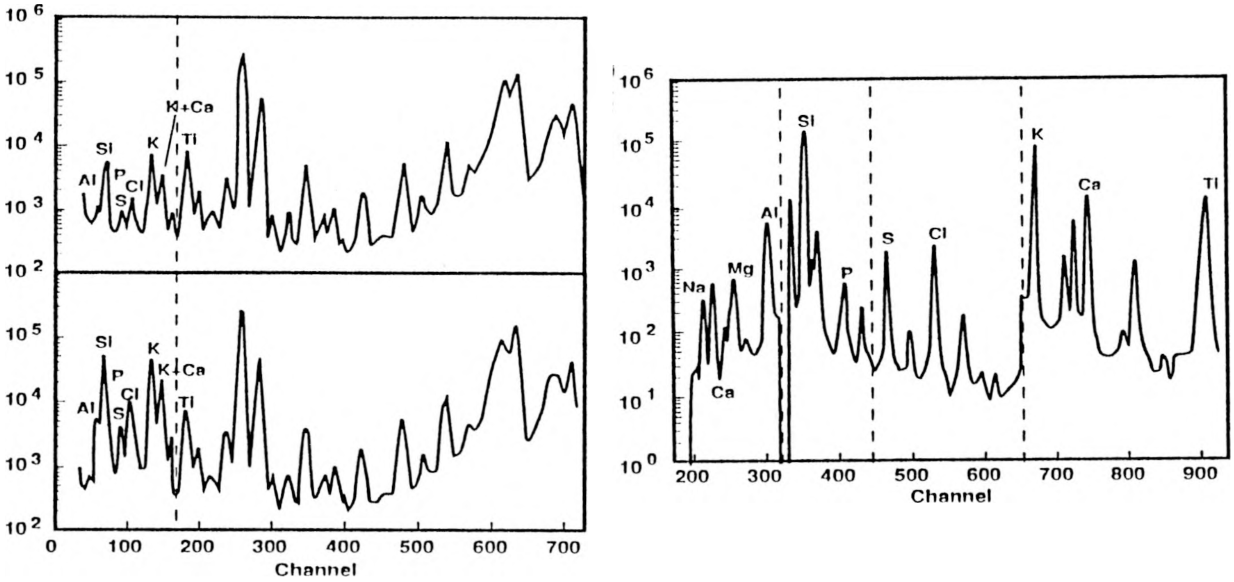

Figure 1. a) EDXRF spectrum of MESS-1 acquired under Zr secondary-source excitation (0.025 keV/channel). b) Dual spectrum formed by combining the spectrum in 1a) with the EDXRF spectrum acquired under Ti secondary-source excitation. c) WDXRF spectrum of MESS-1 acquired using four dispersion crystals: TAP, PET, Ge, LiF. The wavelength data has been digitally transformed to form a high-resolution energy spectrum (0.005 keV/channel).

The extended approach is intended for direct, multielement analysis of samples without similar standards and is based on the previously reported BFP method[1,2,3] for performing matrix corrections. Observed elemental masses (per unit area) are first estimated from characteristic emission intensities. Then the scatter contributions from the masses to the backscatter intensities are determined. These contributions are subtracted from the scatter intensities, and the difference is used to characterize the unobserved, light-element (low-Z) component of the sample (H, C, N, O, etc.) Two representative light elements are chosen from low-Z scatter intensity ratios, and their masses are estimated by relating intensities to scatter cross sections. Matrix corrections for self-absorption and enhancements are then computed from both light- and heavy-element masses and are applied to emission and scatter intensities for each element. The process of light-element selection and matrix correction is repeated with the corrected intensities until no further significant changes are obtained. Elemental concentrations and total sample mass are then computed from the corrected light- and heavy-element masses.

The BFP program "MSAP" was originally intended for EDXRF analyses employing Ti, Zr, Ag, and Gd targets. Although "MSAP" was partially developed in late

1983, it was never fully implemented, due, in part, to the success and versatility of the "SAP3" code. The "SAP3" approach, with the exception of the Ti-Zr composite spectrum, employs backscatter intensities from the actual secondary source providing the excitation energy. The "MSAP" code uses the backscatter intensities only from the Zr spectrum and operates against the ROI file prepared by the program "PREP" using a library, MULTSP.LIB, which provides the parameters to set gain and integrate peak areas. The ROI file is processed by "MSAP," using MULTSP.LIB, to provide matrix corrections and to determine corrected element concentrations. The reemergence of the code "MSAP" resulted from the acquisition of a wavelength spectrometer. Rate meter (2θ) scans demonstrate the exceptional peak-resolution and intensities for low-Z elements when compared to EDXRF, as shown by comparing Figure 1c to 1a. The wavelength spectrometer was originally acquired for stand-alone development; however, the success of the "SAP3" dual-spectrum approach encouraged a limited "MSAP"-BFP evaluation by combining EDXRF spectra with a pseudo-energy spectrum composed of digitally transformed wavelength spectra.

The "MSAP" approach operates similarly to the dual-spectrum approach of "SAP3" in that two backscatter peaks from one analysis (Zr target) are used in the matrix corrections for all analyses. Also, elemental masses from observed characteristic peaks in all spectra are used to define scattering contributions to the backscatter peaks of the Zr secondary target. The main difference between single- and multisource fluorescence is the use of different excitation energies in computing the matrix corrections for characteristic emission peaks excited by targets other than Zr. The "MSAP" approach, like that of dual spectra, is of particular interest in extending the BFP method to element peaks that would not normally be candidates for BFP analysis.

EXPERIMENTAL

This paper evaluates a limited "MSAP" application of multi-crystal, multi-target, ROI-spectrum BFP matrix correction methodology with the analysis of four geological standard reference materials: USGS rock (BCR-1), USGS rock (G-2),[4] NRCC marine sediment (MESS-1) and NRCC marine sediment (BCSS-1).[5] Four dispersive crystals (PET, TAP, Ge, and LiF) are used for analysis of the light elements Na, Mg, Al, Si, P, S, Cl, K and Ca. The Ti peak is also acquired to set gain. Secondary targets for the EDXRF contributions are Zr, Ag, and Gd.

The samples are analyzed as unweighed, self-supporting pressed pellets. The dimensions of the prepared samples are 3.18 cm in diameter with an approximate thickness of 62 mg per cm^2. The samples are ground in a high density alumina mortar and pestle to a size of approximately 300 mesh. The resultant powder is pressed in a hardened carbon-steel die at 25000 kg. The prepared samples are placed in the four-position sample changer of the WDXRF excitation system and the sample chamber is placed under vacuum for spectrum acquisition. The samples are removed from the WDXRF system, mounted on 35-mm slides, and placed in the sample chamber of the EDXRF system under vacuum for excitation and spectrum acquisition.

EDXRF excitation utilizes Ti K_α/K_β (used in the "SAP3" comparison), Zr K_α/K_β, Ag K_α/K_β, and Gd K_α/K_β x rays from secondary sources excited by a tungsten x-ray tube. Acquisition is under control of the PNL-developed codes "XRF" and "MCA" using the parameters provided in Table 1. The x-ray detector is a 30-mm^2 Si(Li) diode with a resolution of 180 eV full-width at half maximum (FWHM) at 6.4 keV. A multielement, thin-film sensitivity curve[1,3] was used as the primary elemental calibration. The Zr backscatter peaks are both calibrated with sensitivity factors (intensity per unit mass per unit scatter cross section) as described elsewhere.[1].

Table 1. EDXRF Acquisition Parameters

Secondary Source	Tube High Voltage (kV)	Tube Current (mA)	Acquisition Time (s)
Ti	40	10	375
Zr	40	10	3000
Gd	60	10	750
Ag	45	10	2000

WDXRF excitation uses a Cr x-ray tube operating at 30 kV and 20 mA. The detector is a gas flow proportional counter. The acquisition from each dispersion crystal is at a 2Θ scan rate of 0.05 with a readout setting of 2 s. Acquisition parameters are provided in Table 2. A complete thin-film calibration was not performed due to time limitations so that much of the calibration curve is based upon the USGS BCR-1 standard. Some thin-film standards were processed to evaluate higher order overlaps, such as third-order Ca on Mg. The 2Θ versus intensity data is transfered via serial line using the PNL code "RDO" to create a temporary 2Θ spectrum on the storage disk of the dedicated EDXRF computer. Each temporary spectrum is processed by the PNL code "DNO," which converts the 2Θ versus intensity spectrum to an energy-versus-intensity spectrum at a user-selected gain.

Table 2. WDXRF Acquisition Parameters

Analyzer Crystal	Detector High Voltage (kV)	Discriminator Setting (E_ℓ)	ΔE	2Θ Scan
TAP	1666	0.25	1.35	60° - 34°
PET	1554	0.25	1.35	120° - 55°
Ge	1542	0.20	1.60	145° - 50°
LiF	1464	0.20	1.45	140° - 72°

The library MULTSP.LIB used by the peak analysis program "PREP" and the BFP program "MSAP" was originally developed to process four different secondary excitation sources. To facilitate data processing, a composite spectrum is formed using the WDXRF spectra. The resulting multicrystal spectrum is used in place of the spectrum normally obtained by analyzing the sample using a Ti secondary source. The splicing program "WXA" reads the four WDXRF spectra from disk and outputs selected regions to a single spectrum representing the desired contributions from each crystal. The "TST" code reads the user-specified energy spectrum from disk and directs the peak analysis program "PREP" to use the library MULTSP.LIB to form a ROI file based on the associated excitation energy. The resulting ROI file incorporates 1) number of counts observed in each element peak and its associated background integral, 2) live time, 3) real time, 4) tube current and voltage, and 5) values representing the coherent and incoherent scatter for both K_α and K_β excitation peaks. Scatter cross sections contained in the library for observed and unobserved elements are for Zr excitation, since only the Zr backscatter intensities are used in computing the BFP matrix corrections. The Zr K_β coherent/incoherent ROI are used for matrix definition to achieve slightly better resolution of the scatter intensities than is available for the Zr K_α coherent/incoherent ROI. All scatter cross sections, photoelectric cross sections, and jump ratios are from McMaster et al.[6] and fluorescent yields are from Bambynek et al.[7]

RESULTS AND DISCUSSION

Results for the rock and soils samples are presented in Table 3 in terms of analytical element concentration from "MSAP" and "SAP3" for comparison with the reference concentrations. The results for an unoptimized analysis are encouraging. Many of the heavier elements from the Gd target are below detection level. However, the low-Z elements obtained by wavelength dispersion, (Na, Al, P, S, K, and Cl) are intense and adequately resolved. Mg has a large third-order Ca interference and requires severe overlap corrections. Most elemental concentrations, however, agree within the statistical error of the peak analysis and the error associated with the reference material. Some notable exceptions to agreement are Si on the soil samples for both "MSAP" and "SAP3" and elements determined by "MSAP" using Ag and Gd excitation. The low Si values in the soil samples is probably explained by heterogeneity: examination of the samples under 5-power magnification reveals small reflective particles, probably associated with mica. The bias in Ag- and Gd-excited elements for "MSAP" is presently undetermined. The As value in the BCR-1 sample is attributed to another experiment not connected with this study and should be compared with the "SAP3" data only.

In summary, the performance for the WDXRF analysis is favorable and certainly demonstrates improved low-Z analysis over the limited range of this application. Thickness calculations over the small range evaluated are satisfactory. The EDXRF analysis based solely on the incoherent and coherent backscatter intensities from Zr did not perform as well as "SAP3" analyses using the additional backscatter information obtained when using Ag and Gd targets, as was expected. More evaluation is required for the technique (or variations of the technique) to be implemented routinely, including extending the analysis to significant weight variation of the sample material and to the analytical determination of tissue samples[3] and metals.[8]

ACKNOWLEDGMENT

The authors express appreciation to K. K. Nielson for implementing major portions of the "MSAP" code, to D. P. Brown for developing the electronic data transfer hardware, and to J. M. Deal for assisting in the review of the manuscript. Appreciation is also expressed to the PNL Analytical Chemistry Laboratory (XRF Center) for financial support. This work was supported by the U.S. Department of Energy under Contract DE-AC06-76RLO 1830. Pacific Northwest Laboratory is operated for the DOE by Battelle Memorial Institute.

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Table 3. Summary of MSAP and SAP3 Results for Rock and Soils Samples with Reference Concentrations.

REFERENCE SAMPLE	Na %	Mg %	Al %	Si %	P %	S ppm	Cl ppm	K %	Ca %	Ti ppm	V ppm	Cr ppm	Mn ppm	Fe %
USGS BCR-1 MSAP-BFP	2.5	2.05	7.65	25.8	0.21	507	105	1.47	4.96	1.33	386	<34	1441	9.5
USGS BCR-1 SAP3-BFP			8.41	26.2	<0.07	<200	<90	1.42	4.92	1.33	376	<33	1397	9.2
Ref. Conc.	2.5	2.09	7.20	25.5	0.17	570	99	1.41	4.95	1.32	399	7.6	1400	9.4
NRCC MESS1 MSAP-BFP	1.8	0.83	6.00	28.6	604	7125	8235	1.80	0.51	0.47	72	74	482	3.0
NRCC MESS1 SAP3-BFP			6.58	29.6	<500	8190	10740	1.75	0.48	0.49	67	67	486	3.0
Ref. Conc.	1.9	0.86	5.84	31.5	630	7200	8200	1.86	0.48	0.54	72.4	71	513	3.1
NRCC BCESS-1 MSAP-BFP	1.9	1.29	6.04	28.1	756	7096	10540	1.80	0.55	0.39	43	138	217	3.3
NRCC BCESS-1 SAP3-BFP			6.37	29.1	<470	4380	12550	1.65	0.50	0.45	105	139	255	3.6
Ref. Conc.	2.0	1.47	6.26	30.9	672	3600	11200	1.80	0.54	0.44	93.4	123	229	3.3
USGS G-2 MSAP-BFP	3.0	0.45	7.76	33.0	462	134	123	3.71	1.51	0.30	<50	<18	252	2.0
USGS G-2 SAP3-BFP			7.74	31.6	<500	<130	<90	3.26	1.42	0.31	<49	<19	252	1.9
Ref. Conc.	3.1	0.46	8.10	32.3	640	250	99	3.74	1.43	0.30	35.4	7	260	1.9

REFERENCE SAMPLE	Ni ppm	Cu ppm	Zn ppm	Ga ppm	Pb ppm	As ppm	Br ppm	Th ppm	Rb ppm	Sr ppm	Y ppm	Zr ppm	Nb ppm	Ba ppm	La ppm	Ce ppm
USGS BCR-1 MSAP-BFP	14	19	119	20	13	26.3	<.90	3.6	46.8	352	38	202	11	676	28	52
USGS BCR-1 SAP3-BFP	23	20	121	21	12	26.0	<1.0		47.1	328	38	190	13	673	<19	67
Ref. Conc.	16	18	120	20	18	0.79	0.15	6.0	46.6	330	37	190	14	675	26	54
NRCC MESS1 MSAP-BFP	29	24	168	11	37	9.1	54.4	3.9	91.7	82.9	33	524	14	233	29	60
NRCC MESS1 SAP3-BFP	32	26	178	12	35	10.6	93.7		93.7	87.3	39	582	17	361	32	74
Ref. Conc.	30	25	191		34	10.6				(89)						
NRCC BCESS-1 MSAP-BFP	59	18	101	9.9	24	10.4	75	3.6	72.0	110	20	250	14	252	25	54
NRCC BCESS-1 SAP3-BFP	65	22	117	12	23	12.1	101		85.2	99	25	244	12	291	<20	61
Ref. Conc.	55	19	119		23	11.1				(96)						
USGS G-2 MSAP-BFP	6.8	12	87	22	37	<1.6	<.64	14	173	430	8.8	291	8.9	1444	51	126
USGS G-2 SAP3-BFP	6.5	12	89	23	34	<1.6	<.78		174	458	11	320	10	1813	72	155
Ref. Conc.	5.1	12	85	22	31		0.3	12	168	479	12	300	14	1870	96	150