RESEARCH NOTE

ENERGY DISPERSIVE X-RAY FLUORESCENCE ANALYSIS TECHNIQUE FOR GEOLOGICAL, BIOLOGICAL AND ENVIRONMENTAL SAMPLES

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Abstract

Energy Dispersive X-Ray fluorescence (EDXRF) technique for the analysis of geological, biological and environmental samples is described. The technique has been applied in the analysis of 10 (geological, biological, environmental) standard reference materials. The accuracy and precision of the technique were attested to by the good agreement between our measured results and the certified values of these standards. The measured and the certified values were generally within 5% of each other except for a few cases that were within 15% of each other for the geological samples.

1. Introduction

Qualitative and quantitative determination of elements in given samples are very important tasks in geological, mineralogical, environmental, medical, industrial and other fields (Ertugrul *et al*., 1996). Accurate and precise determination of major, minor and trace elements in mineral ores is very important in their geochemical studies (Ossaka *et al*., 1994). In the food industry, it is known that a knowledge of the chemical composition of foods is essential in most quantitative studies of human nutrition and in dietary treatment of diseases (McCance, 1960). Also elemental characterisation of environmental samples - soil, water and aerosols, is very crucial in pollution monitoring and control.

With the large number of samples involved in the various fields requiring elemental analysis, there is a need for a fast, reliable and multi-elemental technique for sample analysis. The Energy Dispersive X-Ray Fluorescence (EDXRF) technique is one such technique. It is non-destructive and can be used for the analysis of a wide variety of samples (Johnson *et al*., 1996; Leenanupan and Srichom, 1996; Nwachukwu *et al*., 2000; Obiajunwa, 2001). The EDXRF technique is capable of measuring elemental concentrations from trace levels of parts per million (ppm) up to 100% levels for major components. Solid samples for EDXRF analysis, in general, need little preparation. They only need to be presented in a homogeneous and reproducible form to the spectrometer (Obiajunwa, 2001).

In the present work, we demonstrate the capability of the EDXRF spectrometer to give accurate and reliable analysis of geological, biological and environmental samples.

2. Experimental

Samples

The samples analysed in this work consisted of (i) six geological standards, namely: NBS 278 (obsidian), BE-N (basalt), Mica-Fe (biotite), Mica-Mg (phlogopite), AC-E (granite) and GSR5 (shale); (ii) one environmental standard - MAG-1 (marine mud), obtained from the National Institute of Standards and Technology (NIST); (iii) three biological standards - CRM 062 (olive leaves), CRM 063 (natural skim milk), both from the European Community Bureau of Reference Standards, and A-11 (milk standard) from the International Atomic Energy Agency (I.A.E.A). These standards were pressed into thick pellets of 13 mm diameter in Spec-Caps (Obenauf, 1991) with no binders.

Analysis

The elemental analysis of the samples was performed using the Energy Dispersive X-Ray Fluorescence (EDXRF) spectrometer set-up at the Centre for Energy Research and Development, Obafemi Awolowo University, Ile-Ife. The spectrometer consists of a Siemens FKO-04 tube with Mo anode, a Kristalloflex 710H X-ray Generator, a Canberra series 7300 Si(Li) detector (resolution of 165eV at 5.9keV), a Canberra Model 1510 Integrated Signal Processor, and a Canberra S 100 MCA card interfaced to a 486 IBM/PC. The equipment runs under QXAS (Quantitative X-ray Analysis System) (IAEA, 1993) which includes facilities for data acquisition, spectrum analysis and interpretation and quantitative analysis. Each pellet was irradiated for 20 minutes at fixed tube operating conditions of 25kV and 6mA. The unfiltered $Mo\text{-}K_{\alpha,\beta}$ excitation allows determination of elements with characteristic K- or L- lines in the energy range 3.3 - 16 keV. A parameterless smooth-filter model in the AXIL program of the QXAS package was used for fitting the spectra over the energy region of interest. The AXIL program was also used to obtain the quantitative data on the samples, using the "Direct Comparison of Count rates" procedure. This procedure very much reduces the matrix effects when standards of similar composition to the analysed samples are used for the program implementation. The following standards were used of the quantitative analyses – AD2000 (Obsidian), G2 (Granite),

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GSR3 (Basalt), from NIST, and IAEA-V-10 (Hay powder), from the International Atomic Energy Agency, and BCR 151 (contaminated milk powder) from the European Community Bureau of Reference Standards.

3. Results and Discussion

Figures 1a-1c show typical XRF spectra for a geological (shale) sample, an environmental (marine mud) sample and a biological (olive leaves) sample respectively. The continuous background lying under the characteristic x-ray lines is an inherent feature of the photon excitation. It is due mainly to the Compton scattering of x-rays in the target and in the detector (Benyaich *et al.*, 1997).

The results of the EDXRF analysis for the geological standards and the certified values are presented in Table 1, while those of the environmental and biological standards and the certified values are presented in Table 2. All data are the results of an average of three measurements on each sample with a relative standard deviation of less than 10%.

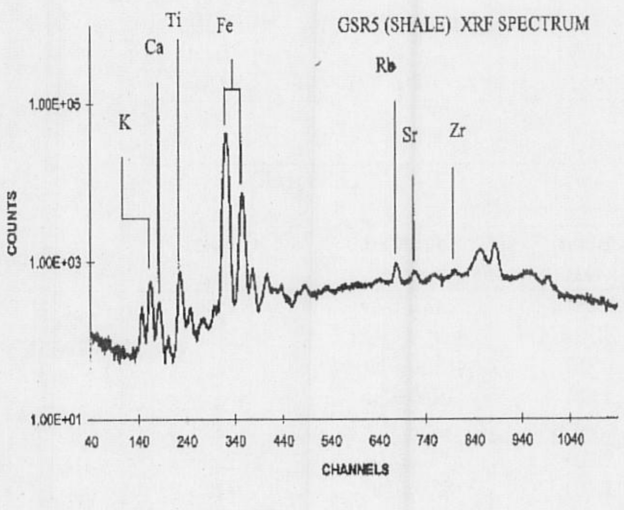

Figure 1a: XRF spectrum of GSR5 (shale) sample

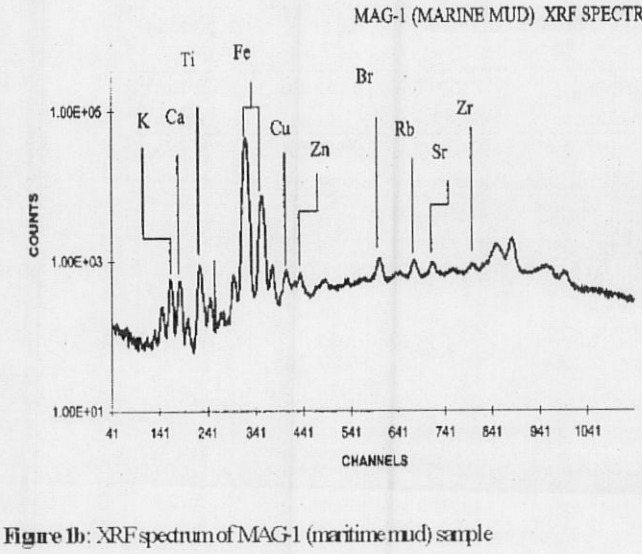

Figure 1b: XRF spectrum of MAG-1 (maritime mud) sample

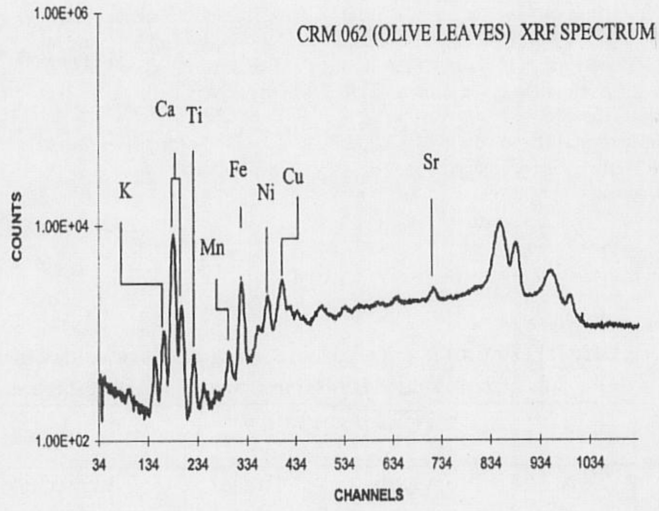

Figure 1c: XRF spectrum of CRM062 (olive leaves) sample.

The measured results are in good agreement with the certified values (Govindaraju, 1994; BCR, 1992; IAEA, 1989). With the assured accuracy of the experimental values obtained from this EDXRF spectrometer, the system can be used on a routine basis for the analysis of geological, biological and environmental samples.

4. Conclusion

The EDXRF set-up of the Centre for Energy Research and Development, (CERD), Obafemi Awolowo University, Ile-Ife, has been used for the elemental analysis of geological, biological and environmental samples. The EDXRF technique is fast, reliable, multi-elemental and non-destructive. The concentrations of major, minor and trace elements in ten standard reference samples were determined. The measured elemental concentrations in the samples were in very good agreement with the certified values. The measured and the certified values were generally within 5% of each other except for a few cases that were within 15% of each other for the geological samples.

REFERENCES

Benyaich, F., Makhtari, A., Torrisi, L. and Foti, G., 1997. PIXE and XRF comparison for application to sediments analysis, Nucl. Instr. and Meth. B 132 481.

Community Bureau of Reference (BCR), 1992. Reference Materials, Brussels.

Ertugrul, M., Kobya, M. and Dogan, O., 1996. Radioisotope x-ray fluorescence analysis of some elements in fly ash of Afsin-Elbistan power plants, J. Radioanal. Nucl. Chem. 203 119-123.

Govindaraju, K. (ed.), 1994. Geostandards Newsletter, Vol. 18

International Atomic Energy Agency (IAEA), 1993. QXAS (Quantitative X-Ray Analysis System) Users Manual. Vienna, Austria.

International Atomic Energy Agency (IAEA), Information sheet for Reference Material A-11, Milk Powder. Vienna, October 1989.

Johnson, A., Lalor, G.C., Robotham, H. and Vutchkor, M.K., 1996. J. Radioanal. Nucl. Chem. 209 101.

Leenanupan, V. and Srichom, K., 1996. Energy dispersive x-ray fluorescence analysis of airborne particulate matter, J. Radioanal. Nucl. Chem. 207 137-144.

McCance, R.A., 1960. *The Composition of Foods*, Her Majesty's Stationary Office, London.

Nwachukwu, J.I., Obiajunwa, E.I. and Obioh, I.B., 2000. Elemental Analysis of Kerogens from the Niger Delta, Nigeria; In Anil K. Garg, V. Banerjie, S. N. Swamy, P. Dwivedi (eds.). Petroleum Geochemistry and Exploration in the Afro-Asian Region. BRPC New Delhi, India, pp. 139-145.

Obenauf, R.H. (ed.), 1991. SPEX handbook of sample preparation and handling, 3rd edition, p.95.

Obiajunwa, E.I., 2001. Analysis of some Nigerian solid mineral ores by energy dispersive x-ray fluorescence spectroscopy, Nucl. Instr. and Meth. B 184 437-440.

Ossaka, T., Kekagawa, K., Oi, T. and Mukaida, M., 1994. J. Radioanal. Nucl. Chem. 183 235-244.

Table 1: EDXRF results for the geological standards and their certified values. Concentrations of elements are given in µg/g except for those of major elements in %. Errors are due to counting statistics.

	NBS 278 (obsidian)		BE-N (basalt)		Mica-Fe (biotite)	
Element	Analysed value	Certified value	Analysed value	Certified value	Analysed value	Certified value
K	2.73±0.12%	2.76%	1.3± 0.4%	1.154%	7.22±0.87%	7.26%
Ca	5774.0±200.0	5620.0	11.08± 0.55%	11.8%	3550.0±500.0	3070.0
Ti	1154.0±102.0	1170.0	1.65± 0.15%	1.564%	1.65± 0.60%	1.499%
Mn	274±16.0	322.2	1547.0±60.0	1549.0	2905.0±165.0	2711.0
Fe	1.14±0.05%	1.141%	8.04±1.02%	8.98%	16.8± 2.0%	17.94%
Zn	51.0±12.0	44.0	138.0±14.5	120.0	1105.0±60.0	1300.0
Rb	101.0±10.0	102.0	45.0±7.5	47.0	2220.0±170.0	2200.0
Sr	56.0±10.0	50.8	1365.0±60.0	1370.0		
Zr	265.0±30.0	232.0	254.0±26.0	256.0	793.0±55.0	800.0

Table 1 (Contd.)

	Mica-Mg(phlogophite)		AC-E (granite)		GSR5 (shale)	
Element	Analysed value	Certified value	Analysed value	Certified value	Analysed value	Certified value
K	8.23± 0.87%	8.301%	3.75± 0.15%	3.727%	3.37± 0.25%	3.453%
Ca	629.0±50.0	572.0	2329.0±450.0	2430.0	4894.0±900.0	4288.0
Ti	1.02± 0.13%	0.977%	625.0±40.0	659.0	4151.0±110.0	3956.0
Mn	2055.0±150.0	2014.0	437.0±20.0	449.0	180.0±50.0	155.0
Fe	6.46±0.55%	6.616%	1.82± 0.05%	1.769%	5.15± 0.5%	4.68%
Zn	293.0±25.0	290.0	222.0±35.0	224.0	57.0±10.0	55.0
Rb	1302.0±105.0	1300.0	126.0±20.0	152.0	85.0±10.0	90.0
Sr	32.0± 4.5	27.0			110.0 ±20.0	96.0
Zr	23.0±5.0	20.0	774.0±30.0	780.0		

Table 2: EDXRF results for the environmental and biological standards and their certified values. Concentrations of elements are given in µg/g except for those of major elements in %. Errors are due counting statistics.

	MAG-1 (marine mud)		CRM 062 (olive leaves)		CRM 063 (natural skimmilk)		A-11 (IAEA milk powder)	
Element	Analysed value	Certified value	Analysed value	Certified value	Analysed value	Certified value	Analysed value	Certified value
K	2.86±0.25%	2.947%	3194.0±150.0	3070.0	1.76±0.056%	1.78%	1.69±0.040%	1.72%
Ca	9820.0±115.0	9791.0	1.67±0.20%	1.75%	1.26±0.036%	1.26%	1.29±0.040%	1.29%
Ti	4540.0±70.0	4501.0	276.0±40.5	239.8				
Mn	740.0±50.0	759.0	57.0±5.0	57.0	ND	0.226	ND	0.259
Fe	4.68±0.30%	4.756%	293.0±25.0	281.5	2.0±0.15	2.06	3.4±0.30	3.65
Zn	125.0±20.0	130.0	25.0±5.0	16.0	43.0±3.80	42.0		
Rb	154.0±12.0	149.0					ND	0.378
Sr	148.0±12.0	146.0	120.0±10.0				39.0±2.45	38.9
Zr	120.0±10.0	126.0					31.0±1.80	30.8

ND: Not determined