

TXRF Technique in Trace Level Analysis of Environmental Samples

F.S. Olise*, O.K. Owoade and H.B. Olaniyi

Environmental Research Laboratory
Department of Physics, Obafemi Awolowo University, Ile-Ife, Nigeria
✉ felix_rsh@yahoo.co.uk

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Abstract: Total Reflection X-Ray Fluorescence (TXRF) technique capability in the multi-elemental analysis of samples of diverse matrices is reported. This technique has been used in the simultaneous assay of geological, environmental and biological samples. The TXRF technique having an advantage over the conventional Energy Dispersive X-Ray Fluorescence (EDXRF) technique in detecting elements at trace concentrations, 10 ppb, is demonstrated. The IAEA Soil 7 reference standard was analysed to attest to the accuracy and precision of the technique. The measured results and the reference or certified values of the reference standard were in good agreement. For most analysed elements, the precision in this work was better than 1.20%.

Key words: TXRF, multi-elemental, diverse matrices, accuracy, precision.

Introduction

The importance of qualitative and quantitative elemental characterization of samples of various matrices in various fields has been emphasized (Ertugrul et al., 1996; Owoade et al., 2004). Accuracy and precision of procedure and technique are very important in the elemental assay of samples. This is necessary in the geochemical studies of mineral ores (Ossaka et al., 1994), quantitative studies of human nutrition and in dietary treatment of diseases (McCance, 1960). The pollution of our environment—soil, water and air—brings one form of illness or the other to us and the concentrations of these environmental pollutants causing or aggravating these illnesses may just need to be at trace levels. Therefore adequate characterization of environmental samples is needed in order to have reliable pollution monitoring and control measures in place.

One of the qualitative requirements of a study is the adequacy and representativeness of the data. To achieve

this, large samples are involved, implying that fast and reliable techniques capable of multi-elemental analysis of these samples are required. The analytical infrastructure that has so far been used in obtaining information on most environmental samples in Nigeria are Atomic absorption spectroscopy (AAS), wave dispersive and energy dispersive x-ray fluorescence (WDXRF and EDXRF) techniques (Adejumo, 1994; Ogunsola, 1993; Oluyemi, 1997; Ikamaise, 2000; Nwachukwu et al., 2000; Obiajunwa, 2001; Olisemeke, 2002). The shortcomings of these techniques range from slowness and high degree of contamination in AAS to high detection limits and inability to analyze liquid samples in WDXRF and EDXRF. The TXRF, a variety of EDXRF technique has been demonstrated to be better than the mentioned techniques in trace level elemental concentrations measurements (Prange and Knochel, 1985; Prange et al., 1987; Bennun et al., 2002). The application of TXRF have covered estuarine and marine water quality management and research, air pollution studies, mineralogical investigations, medicine, etc. and

* Corresponding Author

detection limits up to 100 ppb, significantly lower than obtained for solid sample XRF spectra analysed have been achieved (Bennun et al., 2002).

Solid samples and even some liquid ones like sewage and marine water needs simple but careful preparation prior to TXRF analysis. This is then homogeneously presented to the spectrometer (Olise, 2004; Owoade et al., 2004). The instrumentation for TXRF as well as its principle of operation has been reported elsewhere (Andreas, 1989; Klockenkampe, 1997).

In this work, TXRF technique capability in giving reliable and accurate analysis of samples is demonstrated. Its low detection limit (DL) characteristic, giving rise to better trace analytical capability based on similar work carried out in the same laboratory, Environmental Research Laboratory (ERL), is reported.

Experimental

Samples

The solid samples that have so far been analysed in this laboratory (ERL) are rock, soil and food ranging from seeds to vegetables. Rock samples were first washed with double distilled water and subsequently cut into smaller pieces. The rock and soil samples were homogenized and quartered to obtain a representative portion. The rock samples in this form and the dried pulverized soil and food samples were homogenized in a 5% nitric acid conditioned mortar and pestle. The digestion of the homogenized samples was carried out according to Ogner et al. (1991). Sub-samples of 0.2 g were weighed into 125 ml Teflon bomb and 4 ml of a 3:1 mixture of ultra-pure HNO_3 and HF, and HNO_3 and H_2O_2 added for soil and food samples respectively. The Teflon bombs were then heated in a microwave oven at 300 W, 450 W and 600 W, for 7 min. at each level. The solutions were then analysed after cooling.

Aerosols collected on Whatman and Nuclepore filters was digested in similar way to soil samples except that the acid mixture was in the ratio 2:1 of HNO_3 and H_2O_2 . When filters with heavy sand loadings are suspected, HF instead of H_2O_2 was used.

A good degree of digestion was also achieved when samples with the acid mixtures in plastic containers were heated in water baths at 70°C for periods ranging from 10 minutes to one hour depending on the matrix.

Fruit juice and light water samples were sometimes analysed directly when nonexistence of large particle suspensions capable of causing scattering of x-rays is

evident. Other water samples were prepared for analysis by APDC pre-concentration method. The sample pH is tested and if necessary adjusted to between 3 and 4 with a drop by drop addition of nitric acid. A 1% APDC solution was prepared by adding 1.0 g of APDC powder to 100 ml of ultra pure water. A 200 ml of the solution was then pipetted into the water sample and thoroughly mixed and allowed to settle for one hour at room temperature. An approximate 200 μl of Cd standard (1000 ppm) giving 1.0 ppm in 200 ml of sample was used to coagulate the suspended particulates. A 0.22 μm pore size Millipore filter was used for filtration of the particulates. The particulates on the filter were digested in 1.0 ml conc. HNO_3 and the digestate sucked into a glass tube by a vacuum pump. A 0.25 to 0.5 ml of H_2O_2 was used to rinse the digestate off the filters.

All samples were internally standardized with 5.0 ppm Ga. A 5.0 μl of samples were pipetted on a pre-cleaned quartz glass reflector and dried under infrared lamp at such distances where sample burning is avoided.

Analysis

The TXRF spectrometer consists of an *Ital Structures-IS2215/20* fine-focus tube with Mo anode, a *Ital Structures Compact 3K5* X-ray Generator, a Canberra series *SL 80175* Si(Li) detector (resolution of 175 eV at 5.9 KeV) and a Canberra Model INK-2K INSPECTOR 2000 Integrated Signal Processor interfaced to a computer.

The equipment runs under Quantitative X-ray Analysis System (QXAS) (IAEA, 1993) which includes facilities for data acquisition, spectrum analysis and interpretation and quantitative analysis. Dried drops of samples on carriers were irradiated for 1000 sec at fixed tube operating conditions of 40 KeV and 20 mA. 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. Calibration of the system was carried out using the counts and concentrations of known 10 element standards analysed under same conditions with the samples.

A parameterless smooth-filter model in the AXIL programme of the QXAS package was used for fitting the spectra over the energy region of interest. The AXIL programme was also used to obtain the quantitative data on the samples, using the "Regression of Count rate Vs. Concentration" procedure.

This procedure designed for TXRF thin film samples, which are spiked with a standard (an element of known

concentration) enabled the ratio of the respective fluorescence intensities to lead to acceptable precision. A typical sample, each, of matrices representing rock, soil, water, food and aerosols as well as the reference standard IAEA Soil-7 is presented.

Results and Discussion

Figures 1a and 1b show typical XRF spectra of soil and food samples respectively (Obiajunwa, 2004) while Figure 1c shows that of an aerosol sample (Ali and Bacsó, 1996). 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). Figures 2a and 2b show typical TXRF spectra of food and aerosol samples respectively. The comparisons between spectra, particularly for similar matrices, show remarkable difference in the background. The very low background achieved in the TXRF analysis is as a result of little interaction of x-ray with the sample holder since irradiation of samples was at about 0.1° . This led to a remarkable achievement in the detection of elements at trace levels as evident in the compared EDXRF and TXRF detection limits (Table 1).

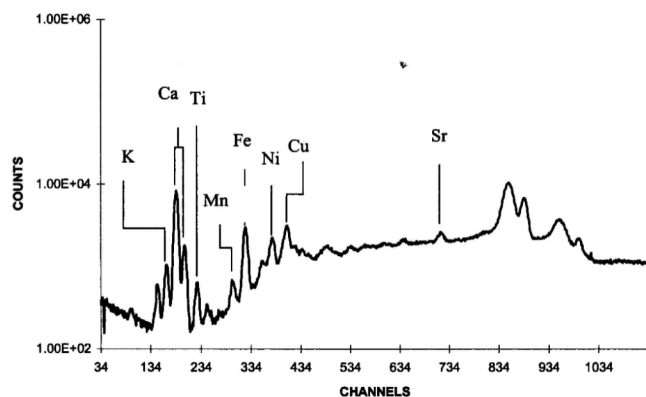


Figure 1a: Typical EDXRF spectrum of food sample.

The TXRF technique's accuracy in the analysis of samples is shown in the result of Soil-7 reference standard

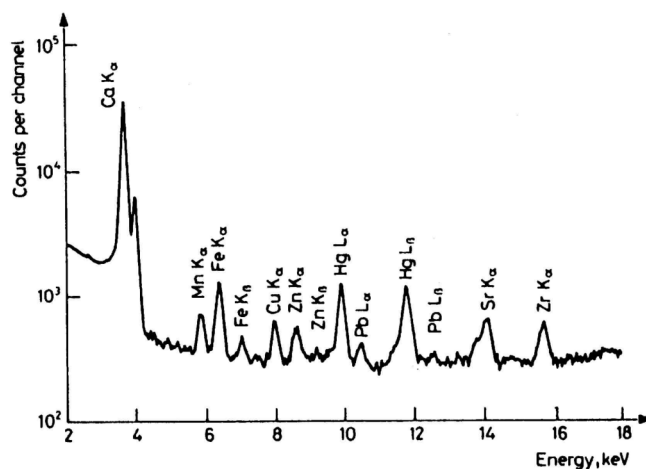


Figure 1b: Typical EDXRF spectrum of aerosol sample.

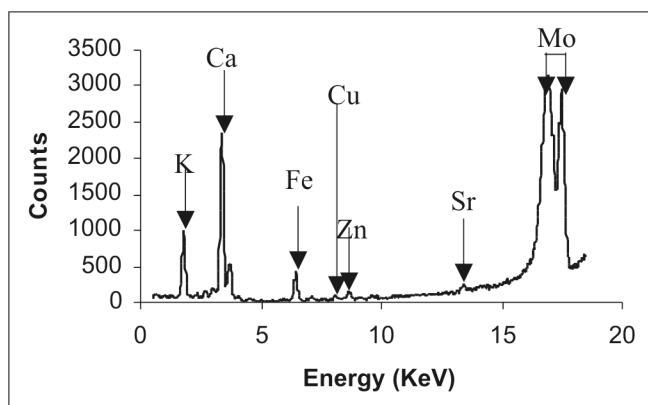


Figure 2a: Typical TXRF spectrum of food sample.

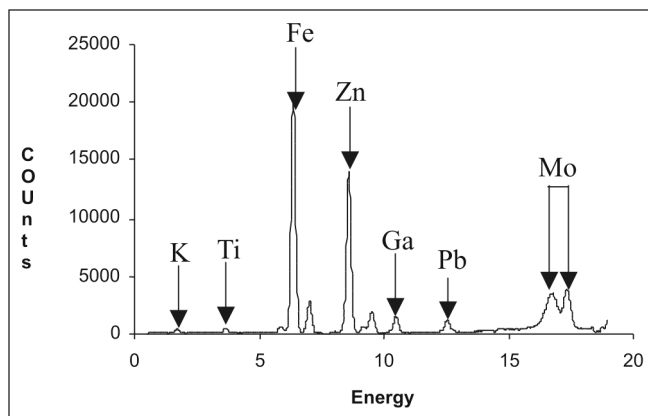


Figure 2b: Typical TXRF spectrum of aerosol sample.

Table 1: Detection Limits ($\mu\text{g/g}$) Obtained for Some Elements Detected in Air Particulate

Elements	K	Ca	Ti	V	Co	Cr	Mn	Fe	Ni	Cu	Zn	Se	Br	Sr	Y	Pb
EDXRF	22	9.4	7.3	9.2	6.8	5.4	3.8	3.5	3.2	6.3	0.3	6.7	7.7	4.3	4.8	13.7
TXRF	0.25	0.4	2.7	0.14	0.07	0.09	0.11	0.19	0.07	0.04	0.05	0.03	0.23	0.09	0.06	0.16

(Table 2). The results are within the 95% Confidence Interval recommended.

Table 2: IAEA Soil 7 Analysis Result

<i>Element</i>	<i>Recommended value (µg/g)</i>	<i>95% confidence interval (µg/g)</i>	<i>Obtained values (µg/g)</i>
Ti	3000	2600 – 3700	2700
V	66	59 – 73	57
Cr	60	49 – 74	53
Mn	631	604 – 650	700
Fe	25700	25200 – 26300	26800
Ni	26	21 – 37	22
Cu	11	9 – 13	10
Zn	104	101 – 113	108
As	13.4	12.5 – 14.2	15
Rb	51	47 – 56	66

Conclusion

The reliability of TXRF technique in giving accurate data on the analysis of samples of various matrices has been demonstrated. The fantastic lower detection limit as compared with the conventional EDXRF would be of help in the analysis of samples with trace levels of analytes especially ambient air aerosols with little contaminants resulting from few hours of sampling or low particulate load.

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