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Short communication

PRECISION MEASUREMENTS WITH THE TOTAL REFLECTION X-RAY FLUORESCENCE SYSTEM IN DAR ES SALAAM

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ABSTRACT: Total Reflection X-Ray Fluorescence (TXRF) analysis has been developed at the Dar es Salaam University, Tanzania. The precision and accuracy were checked using samples of certified and reference materials. We have used the method to analyze aerosol samples.

Key words/phrases: Aerosol, Energy Dispersive X-Ray Fluorescence (EDXRF), Thin Film, Total Reflection X-Ray Fluorescence, TXRF

INTRODUCTION

Investigations of sources of air contaminants in the city were carried out using X-Ray fluorescence analysis. It is the first time Total Reflection X-Ray Fluorescence (TRXRF) analysis was introduced in extension to already existing ordinary Energy Dispersive X-Ray Fluorescence analysis (EDXRF). After design and assembling of the TRXRF system, calibration, precision and accuracy were determined. Aerosol samples were analyzed to check the capability. In this paper we discuss the results.

The TRXRF method is well explained by Van Grieken and Markowicz (1993) and Aiginger and Waubrauschek (1974). Photons from the tube go through a fine double slit walls to produce a line focus. The reflector is adjusted to a small angle with the beam to produce total reflection. The cut-off energy for a quartz reflector is given by $32/\phi$ mrad where ϕ is the glancing angle. The sample is deposited as thin film on the reflector and is adjusted so that the conditions are satisfied. As a result of this the detection of the radiation from the sample is optimised and therefore enhances the detection limit of the spectrometer.

EXPERIMENTAL

For sampling a Sierra Impactor model 244 was used to fractionate of two sizes particles greater and less than 15 μm. We have sampled for 24 hours and the results presented are for samples from Tanzania Oxygen Limited with Coarse and fine particles, respectively.

The samples were digested by concentrated nitric acid to put them in a liquid form. A liquid sample of 5 μℓ was deposited on a quartz reflector. It is left to dry and leave a thin film on the Si reflector ready for TRXRF measurements.

A solution was prepared from elements of K, Ca, Ti, V, Mn, Fe, Ni, Cu, Zn, Br, Rb, Sr, Y, Zr, Pb and Cd with concentration of 1000 ppm each (Fig. 1). This source was used for calibration of the system for analysis of higher concentration analysis. We also prepared a sample for smaller concentrations with V-(1 ppm), Mn-(0.2 ppm), Fe-(1 ppm), Ni-(1 ppm), Zn-(1 ppm), Se-(1 ppm), Sr-(1 ppm), Y-(0.5 ppm), Sc-(5 ppm), Cu-(1 ppm), Pb-(10 ppm).

The TRXRF set-up is composed of an X-Ray tube with an Ag anode operating from a Kristaloflex Siemens power supply. In this experiment 45kV and 15mA were used. The tube is attached to a TRXRF module with a reflector and sample-reflecting backing. The X-Rays from the sample are detected by a Si(Li) detector vertically oriented biased at 500V. Signals arrive at amplifier Canberra 2026 connected to Canberra ADC 8701 and PC with MCA board. For data taking and analysis the Canberra S100 software is used.

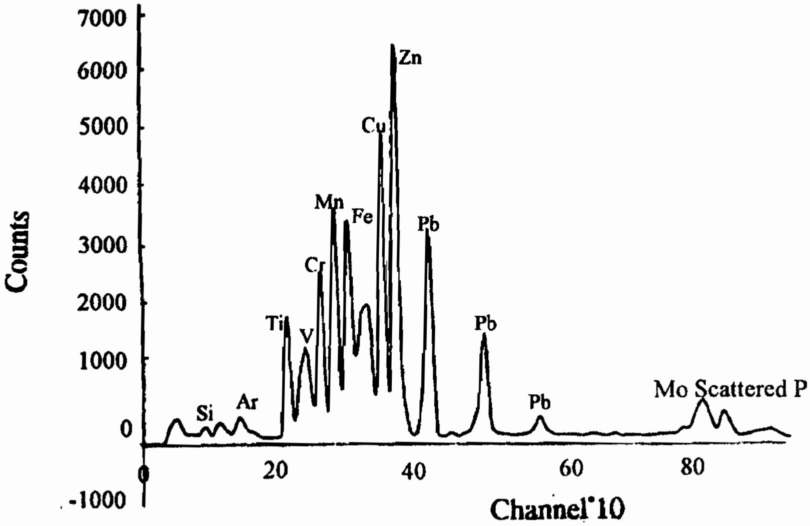

Fig. 1. Typical TRXRF spectra.

RESULTS AND ANALYSIS

The blank-quartz plate must be free from contaminants unless uncleaned it may result in element traces. The blank-quartz spectrum looks like a straight horizontal line from 1 KeV to 20 KeV very close to the Ag line.

Precision was measured by exciting a sample for 1000 seconds and the peak counts were obtained for elements for Ca, Ti, Mn, Fe, Cu, Zn and Pb for four successive measurements.

The accuracy was determined using certified reference materials Nb-ore, OKA-1: Zn-Pb-Sn-Ag ore, Mp-2: Zn-Sn-Cu-Pb ore, Mp-1a: W-Mo ore, KC-1a: prepared by the Canadian Centre for Mineral and Energy Technology. The inaccuracy was less than 5% (Tables 1–4). Typical TRXRF spectra of the standard material is presented in Fig. 1.

Table 1. Zn-Pb-Sn-Ag ore KC-1a

Element	Recommended value (%)	Experimental value (%)
Zn	34.65 ±0.15	33.66±0.17
Pb	2.24±0.03	1.6±0.06
Cu	0.629±0.015	0.59±0.02
Sn	0.61±0.02	0.50±0.002
Ag	0.167±0.002	0.18±0.002
Other values		
S	27.5	
Fe	10.9	10.76±0.055
Si	10.4	

Table 2. W-Mo ore MP-2.

Element	Recommended value (%)	Experimental value (%)
W	0.65±0.020	0.67±0.01
Mo	0.281±0.01	0.27±0.017
Bi	0.245±0.007	
Sn	0.043±0.002	0.038±0.001
Approximate Composition		
Fe	3.7	3.6±0.2
Ca	2.7	2.6±0.01
Zn	0.4	0.4±0.22
Cu	0.9	0.8±0.05
Pb	0.04	0.04±0.005

Table 3. Nb ore OKA-1

Element Nb Methods	Consensus value 0.37 Mean value (%)	95% C.I. ±0.1 No of determination
XRF	0.37	125
Calorimetry	0.37	91
D.C Plasma Emission	0.38	20
Gravimetry	0.38	10
Atomic Emission	0.36	17
Atomic absorption	0.39	4
Element	TRXRF Experimental value	
Nb	0.37	5
Sr	0.59	5

C.I., Confidence interval – errors less than 5%.

Table 4. Reference Zn-Sn-Cu-Pb ore Mp-1a.

Element	Recommended value (%) 95% C.I	TRXRF Exp. value (%)
Zn	19.02±0.10	18.66±0.88
Pb	4.33±0.03	4.00±0.26
Cu	1.45±0.01	1.15±0.05
Sn	1.25±0.04	1.20±0.31
W	0.04±0.005	<400 ppm
Ag	69.7±2.2 ppm	69.6±18 ppm

In Fig. 2, measurements of aerosol samples collected in an industrial area, namely Tanzania Oxygen Limited are presented. The results for fine and coarse particles were determined. The high composition comes from Mn, Fe, Ni, Cu and Zn for fine particles which are derived from the dust origin. Pb, Sr, Zr, K, Ca, Ti and V apart from soil sources come from the burning fuel from cars and the neighbouring soap factory. The coarse particles mainly carry Fe, Co and Ca.

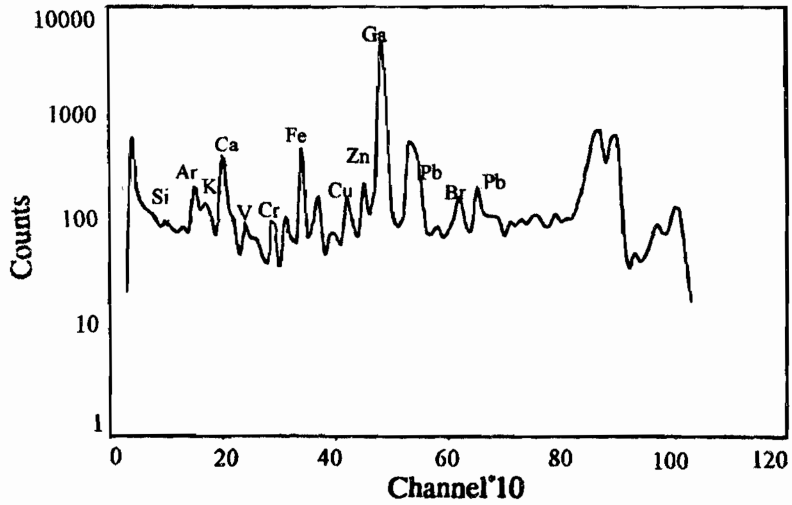

Fig. 2. Typical spectra of aerosol measurement.

CONCLUSION

A TRXRF system was tested and found to be excellent for analysing aerosol, biological and geological samples. The results especially provide useful information about rigorous environmental problems.

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