X-RAY SPECTROMETRY
X-Ray Spectrom. 2006; **35**: 40–41
Published online 21 February 2005 in Wiley InterScience (www.interscience.wiley.com). DOI: 10.1002/xrs.812

X-ray fluorescence spectrometry in Dar es Salaam

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Received 20 September 2004; Accepted 14 December 2004

Energy-dispersive x-ray fluorescence (EDXRF) analysis has been established at the University of Dar es Salaam, Faculty of Science, Department of Physics. Calibration was conducted using thin films from Micromatter (USA) for secondary target XRF. We report on the performance of the spectrometer including the detection limits attained, which range from 0.01 to 10 ng cm^{-2} using collimators of 6 and 8 mm diameter under excitation conditions of 50 kV, 35 mA. The accuracy of the measurements was checked using IAEA SOIL-7 and NIST 3087a Certified Reference Materials. The experimental values differed by <5% from the certified values. The total reflection x-ray fluorescence (TXRF) facility added as a module to the existing XRF system provides detection limits between 0.1 and 100 pg for most of the elements measured.

INTRODUCTION

X-ray fluorescence (XRF) analysis has been in operation in Dar es Salaam since 1979. Previous work has included measurements of photon cross-sections for different materials,[1] trace analysis of water for pollution studies,[2] aerosol trace analysis,[3] geological rock analysis looking for concentrations of tin[4] and serum analysis of malnourished children.[5] Since that time, efforts have continuously been made to refine the method and improve the detection limits to cover as low a concentration as possible in different types of samples. The detection limits ranged from 10 μg cm^{-2} in 1979 to 10 ng cm^{-2} in 2000 for energy-dispersive (ED) XRF. Recently, a total reflection (T) XRF module manufactured under the auspices of the IAEA by P. Wobrauschek of the Atomic Institute, Vienna, Austria, was added as a related technique to the existing EDXRF. The modification resulted in a detection limit of 10 pg at a spot size of a 5 μl liquid sample after drying. In TXRF, the passage of x-rays through slits and reflectors is conducted so as to obtain a total reflection condition. This is used to excite the sample without introducing a bremsstrahlung background in the sample spectra. The detection limit of TXRF is also reported in this paper in addition to that of EDXRF.

Each component of the spectrometer was received as individual items and therefore the instrument had to be assembled and optimized. The calibration of the EDXRF system was performed using thin homogeneous standards manufactured and supplied by Micromatter (USA).[6,7]

EXPERIMENTAL

Secondary target EDXRF and the total reflection excitation TXRF mode using an Si(Li) detector were used.

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The EDXRF experiment

The EDXRF set-up consisting of a Siemens FK60 x-ray tube with four operated electromagnetically windows was mounted vertically. A Kristalloflex 710H generator and the Canberra SL 30 180 Si(Li) detector completed the system. The PC QXAS software for spectra evaluation from the IAEA was used.[8,9]

The TXRF experiment

The TXRF facility includes most of the main equipment used in the EDXRF set-up with a TXRF module and a sample holder attached to the x-ray tube. The reflected beam, in a total reflection condition, is incident on a sample carrier, which is a reflecting surface at critical condition. The characteristic x-rays from the sample are detected by the Si(Li) detector and associated electronics. Calibration was conducted using liquid standards deposited as thin films on quartz plates as explained elsewhere.[10,11]

RESULTS AND DISCUSSION

The sensitivity K_i for an element i is calculated in the calibration as $K_i = I_i/(A_c C_i)$, where I_i is obtained from irradiation of standard material and C_i is the concentration of element i. K lines are used for determining the sensitivity of elements up to Nb (atomic number 41) and L x-rays for higher atomic number elements. Two collimators were used of 6 and 8 mm aperture at the beryllium window. The elemental sensitivities were determined experimentally using these two collimators.[11] For the collimator with a 6 mm aperture, the sensitivity curves for the K and L lines show that the narrow 6 mm collimator gives lower sensitivity than the 8 mm collimator.

The detection limits achieved by the EDXRF spectrometer in Fig. 1 for both collimators range from 0.01 to 10 ng cm^{-2}. The accuracy measurements were conducted using standard materials. IAEA SOIL-7 Certified Reference Material was analysed as pellets and absorption corrections were made;

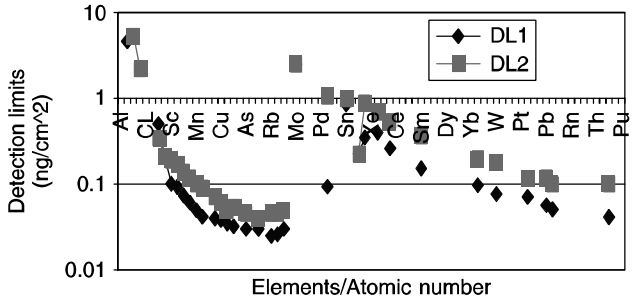

Figure 1. Detection limit curve using the 8 mm (DL 1) and 6 mm (DL 2) collimators for elements on Nuclepore filters for a total spectrum count of 700 000. The tube parameters were 50 kV, 35 mA and with a measurement time of 3000 s.

NIST 3087a Certified Reference Material was analysed as thin-film samples. Errors in the results are due to counting statistics and the experimental values are in agreement with the certified values with a difference of <5%. The calibration was conducted using thin films from Micromatter and the detection limits were obtained from the background counts when irradiating a blank Nuclepore filter.

The detection limit curves for both collimators appear to have the same shapes for the K and L lines, but different values as illustrated in Fig. 1. For the 8 mm collimator the detection limits range from 0.01 to 10 ng cm^{-2} for the K lines of elements up to $Z = 40$ and from 0.05 to 5 ng cm^{-2} for the elements above $Z = 30$. The 6 mm diameter collimator was similar with the difference that for the L lines the detection limit of the 6 mm collimator cut at $Z = 40$ whereas that of the 8 mm cut at $Z = 50$. In both collimators the tube parameters were 50 kV, 35 mA with a total spectrum count of 700 000.

On increasing the anode voltage the intensity of the scattered radiation also increases, which results in a higher background.[3,5] After consideration of several voltages and currents, a compromise between the highest count rate and the lowest detection limits was obtained and the 50 kV, 35 mA excitation conditions were chosen. However, the experiment was flexible in the use of other voltage and current parameters, depending on the requirements of the sample and the performance of the spectrometer.

The sensitivities for TXRF were measured using an Ag and an Mo anode. Single and compound elements in liquid form were used with an internal standard dropped as a 2–5 µl deposit on the quartz plate followed by x-ray excitation after drying.[12]

The detection limits determined for TXRF are shown in Fig. 2 for both the Ag and Mo anode x-ray tubes. In the case of the Ag x-ray tube, the detection limits range from 0.15 to about 100 pg for elements above Na in atomic number. The excitation range for the Ag anode is slightly wider than

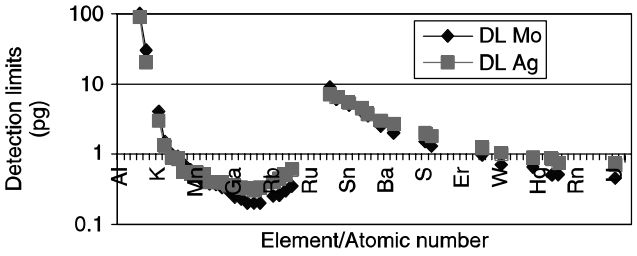

Figure 2. Detection limits using the Ag and Mo anodes in TXRF with a measurement time of 2000 s.

for the Mo anode tube. However, the Mo tube has detection limits in the range from 0.1 to 100 pg. The excitation efficiency is high when the excitation energy is just above the binding energy of a particular element. The detection limits presented are based on thin-film measurements of liquid standards in all cases.

CONCLUSIONS

An XRF analysis system based on both EDXRF and TXRF components was implemented. After a series of calibrations using 6 and 8 mm diameter collimators, the detection limits found were of the order of 10 ng cm^{-2} for EDXRF and 10 pg for TXRF.

Acknowledgements

The equipment used in this work was facilitated by the IAEA, Vienna, for which we are grateful. SIDA (Sweden) and the University of Dar es Salaam (Tanzania) supported the first author's participation at the Berlin X-ray Spectrometry Conference 2002.

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