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Analytical Note

Improvements in energy dispersive X-ray fluorescence detection limits with thin specimens deposited on thin transparent adhesive tape supports☆

Buddhadev Kanrar, Kaushik Sanyal, N.L. Misra *, S.K. Aggarwal

Fuel Chemistry Division, Bhabha Atomic Research Centre, Mumbai 400 085, India

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ABSTRACT

The elemental detection limits observed in total reflection X-ray fluorescence analysis (TXRF) are better compared to that of energy dispersive X-ray fluorescence (EDXRF) by approximately three orders of magnitude (in pg level) mainly due to efficient excitation geometry and special features of total reflection of X-rays. Also, the matrix effects are negligible and the thin film approximation is valid for all types of specimens. The detection limits in EDXRF can be improved using thin specimens deposited on thin sample supports so that scattering and thereby background are reduced. In the present study, the detection limits in EDXRF could be improved to ng–pg level for different elements using thin specimens of the samples deposited on thin transparent adhesive tape supports. The EDXRF analytical results were in very good agreement with those of TXRF. The EDXRF detection limit achieved using this approach for Cr was found to be 1050 pg compared to 320 pg obtained in TXRF. For Y these values were found to be 320 and 168 pg respectively. The EDXRF detection limits achieved in the present work have given a new EDXRF analysis methodology for sample analysis with detection limits comparable to TXRF using a simple instrumentation.

1. Introduction

X-ray fluorescence (XRF) is a well established non-destructive multi elemental analytical technique [1,2]. Though the technique is well established for major element determinations, it could not compete with the other well established trace elemental analytical techniques e.g. inductively coupled plasma–mass spectrometry (ICP-MS), inductively coupled plasma–optical emission spectrometry (ICP-OES), neutron activation analysis (NAA), etc. in terms of detection limits [3]. Generally, the detection limits achieved in XRF are in μg level. The main reasons for the comparatively higher detection limits in XRF are high background produced due to the penetration of the X-rays inside the sample/sample support and a comparatively longer distance between the sample and detector [4]. In addition, matrix matched standards are essential in XRF because of the appreciable matrix effects [1,2]. It is difficult to get matrix matched standards for different samples. The above disadvantages of the XRF have been taken care in total reflection X-ray fluorescence (TXRF) spectrometry [1,2,5] which is comparatively a new variant of energy dispersive X-ray fluorescence (EDXRF). In TXRF, the X-rays fall at an angle less than the critical angle at a flat polished sample support on which a thin specimen is placed for analysis. The incident X-rays are totally reflected from the support. Since the critical angel is near to 0.1°, the detector can be placed very near to the sample support [6]. In addition the background is reduced as the X-rays scarcely penetrate in to the supporting reflector and thereby scatter is reduced. Further, a special feature based on the physical phenomenon is the double excitation of the sample in TXRF leading to an almost doubling of the fluorescence intensity in comparison to conventional excitation in EDXRF [1,4]. These factors improve the detection limits in TXRF by almost three orders of magnitude compared to those achievable in EDXRF. In addition, since the sample specimen thickness is in nm level, matrix effects are almost negligible and there is no need of matrix matched standards. These factors make TXRF not only comparable but superior in certain respects compared to other well established trace element analytical techniques. However, maintaining TXRF geometry is very difficult as the critical angle is very small and it is very difficult to get a parallel beam falling at an angle less than the critical angle on the sample support/specimen in the case the pre adjusted conditions were lost for some reasons. If a thin specimen of the sample is made on a thin sample support and a monochromatic or a narrow band of X-rays is allowed to excite this thin specimen using EDXRF geometry, there shall be very less scattering and thus considerable decrease in background. Using such EDXRF geometry of thin specimens the detection limits in EDXRF can be improved significantly. Some preliminary

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* Corresponding author. Tel.: +91 22 25594565; fax: +91 22 25505151.
E-mail addresses: nlmisra@barc.gov.in, nlmisra@yahoo.com (N.L. Misra).

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work on improvements of detection limits using thin film of gold deposited on Rigaku, Japan made thin "Ultra-carry" carriers is already reported in literature [7]. The authors have studied the variation of signal to background ratio with takeoff angle in EDXRF and grazing exit X-ray fluorescence (GE-XRF) geometries. They extended this work for Ti solution (1.016 mg/mL) deposited on ultra-carry carriers [7]. Later similar study exploring the possibility of wavelength dispersive X-ray fluorescence (WDXRF) trace determination of Zn and some hazardous elements in river water using 500 μL of preconcentrated samples deposited on ultra-carry supports was performed [8]. Similarly, reduction in background and improvements of detection limits are reported in literature with polarized X-ray sources also but these have not been used for routine analysis [9,10]. In the present work, studies have been made to improve the detection limit in EDXRF using thin specimens deposited on thin sample supports viz. thin transparent adhesive tapes or Mylar films of a few micron thickness. The study has been made with an aim to apply such development for routine sample analysis by EDXRF with detection limits comparable to those of TXRF but with simple instrumentation.

2. Experimental

2.1. Sample preparation

Eight non-interfering multielement solutions were prepared by mixing Merck single element standard solutions of the elements Mn, Ni, Ga, Se and Y having elemental concentrations of 1000 μg/mL and diluting appropriately with 1.5% high purity HNO_3 solutions in milli-Q water to get elemental concentrations of 0.78, 1.56, 3.12, 6.25, 12.5, 25, 50 and 100 μg/mL respectively. Similarly interfering multi elemental solutions were prepared by mixing and diluting Merck single element standard solutions of the elements Cr, Mn, Co, Ni, Ga, Se and Y having same concentrations as the solutions containing non-interfering elements. To countercheck the results in the presence of several interfering elements, MERCK ICP multi-element standard solution IV was diluted with 1.5% HNO_3 in milli-Q water to get solutions with elemental concentration levels of 0.25, 0.50, 1, 2, 5 10, 25, 50, and 100 μg/mL. For EDXRF measurements, aliquots of 10–100 μL of each sample solution were deposited, by drying, on three thin supports made of approximately 25 μm thick transparent adhesive tapes spread over a 30 mm internal diameter, 40 mm outer diameter and 2 mm thick aluminum discs. The size of the residues obtained after drying the aliquots was in the range of 3 mm to 6 mm. For the solutions having elemental concentration <2 μg/mL, 100 μL aliquots were deposited whereas for the rest of the solutions, 10 μL aliquots were deposited. For TXRF measurements, 10 μL aliquots of the solutions were deposited on polished quartz sample supports and dried. TXRF measurements were also made on three separate specimens for each sample solution.

2.2. Instrumentation

The EDXRF spectra of the specimens were measured in air atmosphere using a Jordon Valley, Israel, Ex-3600 TEC spectrometer. The specimens were excited by Rh anode X-ray tube and Rh filter was used to reduce the background. Tube voltage and currents used were 40 kV and 500 μA, respectively. The diameter of the X-ray beam falling on the specimens was approximately 7 mm. The X-rays were detected using a Si-PIN diode detector having a resolution of 140 eV (FWHM) at 5.9 keV (Mn Kα). The measurement time was 1000 s live. The TXRF spectra of the specimens were measured in air atmosphere with monochromatic Mo K_α (17.47 keV) excitation obtained using W–C multilayer. Tube voltage and currents used were 40 kV and 20 mA respectively. The X-rays were detected using a Si (Li) detector having a resolution of 139 eV (FWHM) at 5.9 keV (Mn Kα). Measurement time for each TXRF spectrum was 500 s live for the analysis whereas it was 1000 s for calculation of detection limits. The details of the instrument are provided in our other publication [11]. The EDXRF spectra were processed using the IAEA QXAS software after format conversion. The relative sensitivities of the elements were determined using multielement solutions having elemental concentrations of 1.56 and 6.25 μg/mL. Using these sensitivity values, EDXRF spectra of all the samples were processed to obtain the elemental concentrations.

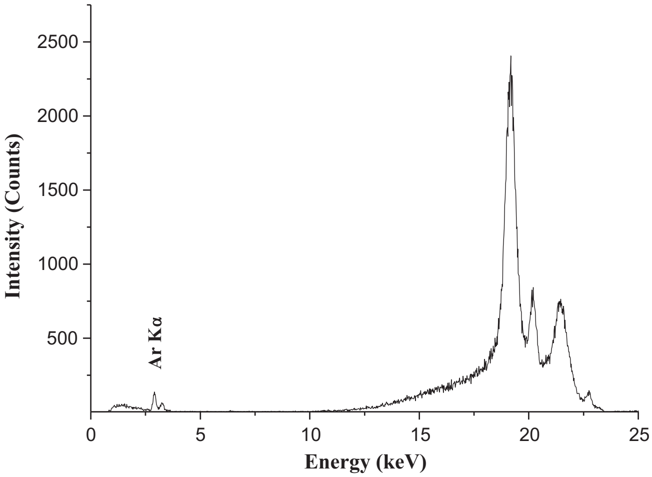

Fig. 1. EDXRF spectrum of a blank transparent adhesive tape obtained using Rh X-ray tube excitation source and Rh filter.

3. Results and discussion

Aliquots of the solutions containing non-interfering elements were deposited on different sample supports viz. quartz, absorbent sheet, Mylar film and transparent adhesive tape and their EDXRF spectra were measured. The EDXRF spectra of these specimens revealed that Mylar film of 4 μm thickness and the transparent adhesive tape are better in terms of signal to noise ratio compared to other specimen supports. The Mylar and transparent adhesive tape supports gave minimum scattering of the X-rays and hence minimum background. Since the transparent adhesive tape supports are easily available and these gave similar result as Mylar films, these supports were used for subsequent studies. In addition, the transparent adhesive tape was found free from any contamination as seen from its EDXRF spectrum shown in Fig. 1. Due to the reduction in the unwanted background in the EDXRF spectra, the detection limits should improve drastically when

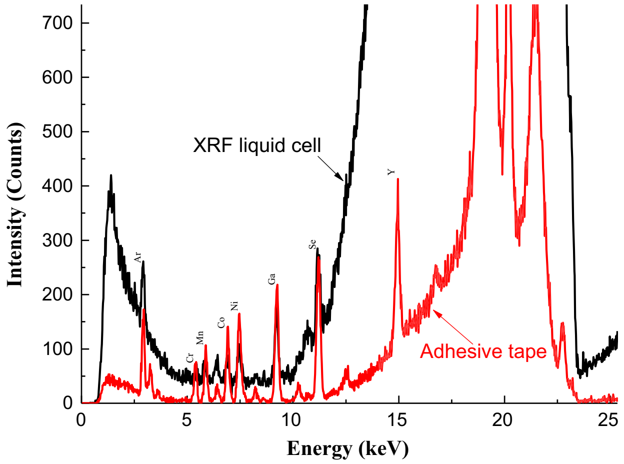

Fig. 2. A comparison of EDXRF spectra of MES with elemental concentrations of 3.1 μg/mL. Aliquot of 10 μL was deposited on transparent adhesive tape support whereas 1 mL of sample solution was taken directly in a sample cup with 4 μm thick Mylar window.