

MONTE CARLO CALCULATION FOR CALIBRATION FUNCTIONS IN TOTAL REFLECTION X-RAY FLUORESCENCE SPECTROMETRY*

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ABSTRACT

Simulation approach includes such processes as photon emissions from X-ray tube with a spectral distribution, total reflection on the sample support, photoelectric effect in thin layer sample, as well as characteristic line absorption and detection. The calculation results are in agreement with experimental ones.

Keywords Total reflection X-ray fluorescence analysis, Calibration function, Monte Carlo simulation

1 INTRODUCTION

Total reflection X-ray fluorescence (TXRF) analysis significantly improves detection limit, and can be widely applied to a variety of materials^[1]. Calibration is a necessary step to the quantification analysis, and usually established in TXRF by repeated measurements to standard solutions with various concentrations that it will be changed when either experimental hardware or a sensitive part of the software is varied. In this paper a method for Monte Carlo simulation of calibration functions is presented. Some experimental measurements are also performed for comparing with simulation results.

2 APPARATUS AND TECHNIQUES

A total reflection X-ray fluorescence system is shown in Fig.1. Its detailed description was given in Ref.[2]. The angle accuracy of this system is better than 0.08 mrad.

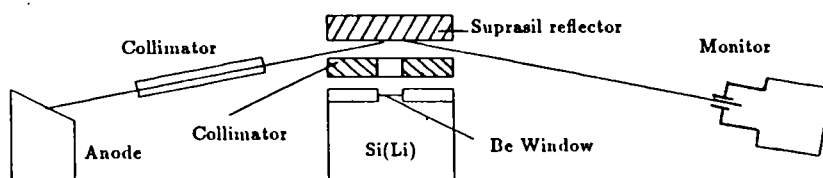


Fig.1 Schematic drawing of TXRF system

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The X-ray source (Rh-target) is operated at 24 kV and 20 mA. The high-energy part of the primary radiation is cut off by a 50 μm Mo foil. A 80 mm² Si(Li) detector is mounted about 1.5 mm from the suprasil (quartz) reflector. Its FWHM for 5.89 keV is 170 eV. The intensity of the reflected beam is measured by an X-ray monitor positioned at 155 cm beyond the centre of the reflector. The angular divergence of the primary X-ray beam is 0.5 mrad.

The standard aqueous sample containing both analytical elements and yttrium as an internal standard is pipetted onto a suprasil reflector. The use of an internal standard is essential, as this minimizes errors due to the specimen's inhomogeneity, instrument fluctuation, and pipetting.

3 MONTE CARLO APPROACH

A Monte Carlo model for an X-ray system excited by discrete energy photons was described by Gardner *et al.*^[3]. A series of weight factors obtained in a large number of random walks are associated with such processes as source emission, X-ray interactions with the sample, and characteristic line production and detection.

In the present case photons emitted from X-ray tube have a spectral distribution in which characteristic lines of the target are usually superimposed on a continuum. In order to evaluate the photon population distribution with respect to photon energies, the value of maximum energy (E_0) corresponding to the target excitation voltage was evenly divided into 1024 intervals, i.e. the energy width of each interval ΔE is $E_0/1024$. According to Tertian and Broll [4], the number of photons within i th energy interval ($E_i, E_i + \Delta E$) in continuum can be given in the expression

$$N(E_i) \propto (E_0/E_i - 1)^q E_i^2 \exp(-Q' \mu_{A,E_i}^n) \exp(-\mu_{Be,E_i} \rho_{Be} d) \quad (1)$$

where q, n and Q' are empirical parameters depending on the target and the excitation conditions. μ_{A,E_i} and μ_{Be,E_i} are mass absorption coefficients at the energy E_i for the target and the tube window, respectively. ρ_{Be} is window density, and d window thickness. The weight factor of the photon emission from the tube with energy interval ($E_i, E_i + \Delta E$) is expressed by

$$W_o(E_i) = N(E_i) / \sum_{j=1}^{1024} N(E_j) \quad (2)$$

Besides the continuum, the characteristic lines of the target usually affect the emission weight factors at certain discrete energies as well. Pella *et al.*^[5] derived the expression for the ratio of the characteristic line to the continuum intensity, with which emission weight factors at characteristic energies can be corrected. The photon energy was randomly selected from 0 to E_0 in the simulation. When the energy was less than the absorption edge of analytical element, this event was considered as an unsuccessful ones. The weight factor of source photons intersecting the sample area was evaluated analogous to that described previously^[6].

The incident angle of the exciting radiation in TXRF is only a few minutes of arc, the relative angular spread is usually less than a few percent. We assume that the measuring sample forms a thin layer on the reflector, the diameter of the sample is so small that it can be fully covered by incident collimation beam, and this beam is totally reflected by the suprasil. In this case an average effective length (L) of the primary X-ray interaction in the sample can approximately be used to describe the sample depth of the fluorescence processes induced by both the incident and the reflected beams. The weight factor appropriate to forcing an interaction to occur within the average effective length and to produce the desired characteristic X-ray may be written as [6]

$$W_4 = \omega W(1 - 1/r)\tau_i \rho L \quad (3)$$

where ω and W are the fluorescence yield and weight fraction of the desired element, respectively, r jump ratio of the element, and τ_i its photoelectric absorption coefficient for the exciting radiation of energy E_i , ρ sample density. The values of ω , r , and τ_i were obtained from the formulae and the subroutine[7]. The characteristic X-rays produced from the sample interaction is absorbed and detected by the detector. The weight factor appropriate to this case has been introduced by Gardner *et al*[3].

The product of all the weight factors pertinent to each successful history was averaged with all previous histories to obtain the average fluorescence probability for both the analytical element and internal standard one. The calibration function—relative fluorescence intensity vs atomic number—can be introduced from the ratio of the fluorescence probability of the analytical element to that of the internal standard after completing a large of random walks.

4 RESULTS AND DISCUSSION

The primary radiation from a Rh target (24 kV excitation) was totally reflected on the suprasil surface with adjusting the incident angle. Empirical parameters used for calculating the continuum distribution have been given by Tertian and Broll[4] as follows $q = 1.10$, $n = 0.7$, $Q' = 0.0161$. The ratio of the target characteristic line to the underlying continuum intensity at the characteristic energy has been described in detail by Pella *et al*. [5].

The simulation was performed for both the analytical element and the internal standard (yttrium) simultaneously, each calculation was based on 5000 histories. The relative fluorescence (K -line) probabilities (P_x/P_T) of analytical elements with respect to yttrium calculated by the simulation model are shown in Fig.2. TXRF measurements were also completed for some elements with standard aqueous samples containing the internal yttrium. The measured fluorescence intensities for both analytical elements and yttrium were normalized for their concentrations, and the results of relative fluorescence intensities to yttrium are also shown in Fig.2. The agreement between the model and experimental values is reasonably good. Owing to errors in evaluations of the fluorescence

parameters and absorption coefficients, the relative deviation in the simulated probability is about 8%.

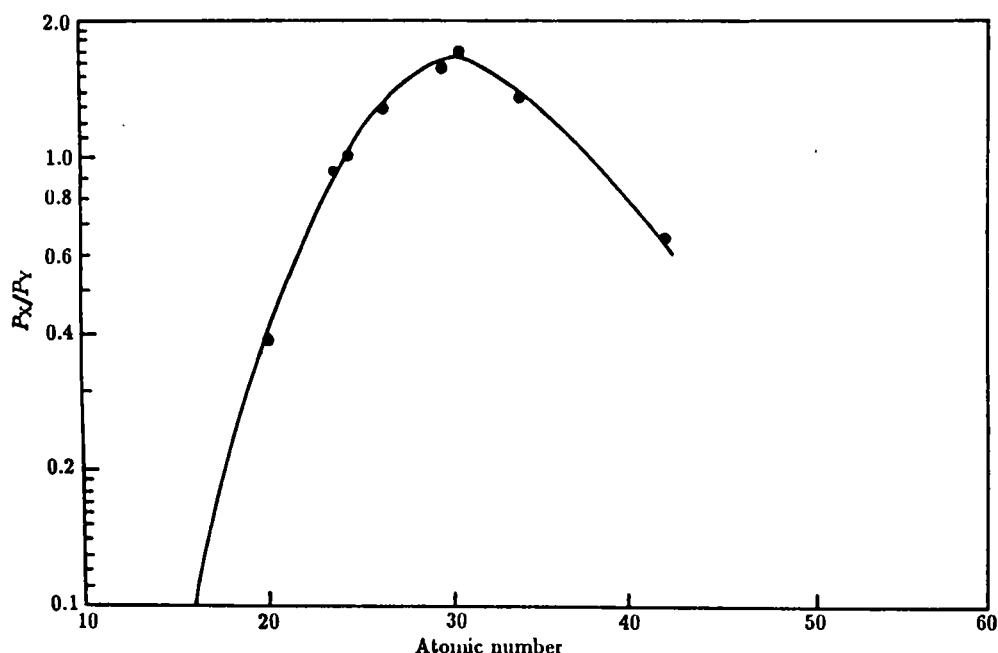


Fig.2 Dependence of relative fluorescence probability on atomic number in TXRF analysis for Rh-excitation K lines

● Data from experiment,—Data from the model

It will be noticed that the method presented here has not accounted for the corrections for matrix absorption and enhancement effects of the fluorescence radiations, as these corrections in thin layer sample analysis can be neglected.

5 CONCLUSIONS

The calibration function for a TXRF analysis system was derived using both the simulation model and the experimental method. Good agreement between the simulated and the experimental values was obtained.

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