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COMPARISON OF X-RAY EMISSION ANALYSIS SENSITIVITY UNDER VARIOUS TECHNIQUES OF EXCITATION IN BIOLOGICAL AND ENVIRONMENTAL STUDIES

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The analytical performance of different X-ray emission elemental analysis techniques is compared for two applications. Synchrotron radiation X-ray fluorescence [SRXRF] with tunable monochromated excitation gives a lower detection limit than PIXE for dried biological samples. The superiority of SRXRF is most pronounced for elements with $Z > 30$. Experimental indications are given that SRXRF can be more sensitive than electron-probe X-ray microanalysis for small-volume or individual-particle analysis of environmental samples for elements with $Z > 40$

1. Introduction

Since EDS detection of X-rays is possible with sufficient resolution, various X-ray emission analytical methods became popular in the field of environmental and biological applications. Due to the attractive aspects of X-ray fluorescence, i.e. relative simplicity, low cost, nondestructive and multielemental nature as well as quasi-uniform sensitivity, a great number of sample types could be conveniently analysed with reasonable sensitivity and accuracy.

The limitations of the method when low concentrations or small amounts have to be analysed became obvious. The physical reason lies in the low count-rate capability of Si(Li) detectors (1–5 kcounts/s) in the interesting energy region (6–40 keV), the low ionization cross sections and, for elements with atomic number $Z < 20$, the low fluorescence yield and detection efficiency. By photon excitation the photoelectric cross section is small compared to charged-particle excitation, and to find an optimal X-ray source in the required energy region is not always simple.

Since the pioneering work of Sparks [1], the using of the advantages of synchrotron radiation – high brilliance, low beam divergence, high polarization – resulted in a revolutionary improvement of sensitivity. Soon several stations for SRXRF trace-element analysis were constructed in the USA [2,3], Asia [4,5] and Europe [6,7], using "white" or monochromatic excitation with narrower or wider bandpass.

Comparison of bulk analysis with other modes of excitation [8] and the effect of experimental conditions [9] were already given. The purpose of this paper is to compare the analytical performance of different excitation modes applied to trace analysis of biological and environmental samples in a sense of sensitivity and lower limit of detection.

2. Experimental

Radioisotope-induced X-ray fluorescence was measured using a 300 MBq ^{109}Cd annular source; the radiation was detected by a Canberra Si(Li) detector of 3 mm thickness and 30 mm^2 sensitive area. Proton beam of 3 MeV energy was generated with the 5 MeV Van de Graaff accelerator of the Central Research Institute for Physics in Budapest, Hungary. The details of the PIXE setup were published elsewhere [10]. The final beam spot on the target had a diameter of about 2 mm; beam currents were only a few nA to avoid deadtime difficulties and also to prevent samples from radiation damages. Scanning electron microscope experiments were done on a JEOL JSM-840 scanning electron microscope equipped with an EG&G Ortec 5000 energy-dispersive X-ray spectrometer system. At 25 and 35 kV acceleration voltages, 0.3–1 nA electron current was used for fly-ash samples.

Synchrotron radiation experiments were carried out in Novosibirsk, using the VEPP-3 machine of 2 GeV energy, equipped with a wiggler of 2 T maximum magnetic field. The experimental station was 9 m away from a tangent point of the storage ring (see ref. [11]). The synchrotron radiation produced was pathing through a pyrolitic graphite monochromator with 1° (FWHM) mosaic spread. A 5 mm thick Ortec Si(Li) detector of 30 mm^2 was alligned 90° to the exciting beam; a 15 mm long alkonite collimator of 2 mm diameter shielded the

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peripheral region of the detector. The coefficient of linear polarization was 0.95. Monochromator and detection angles were changed by computer control; the solid angle of the sample viewed by the detector was 1.3×10^{-9} sr. With the above setup the excitation energy could be tuned from 10 to 40 keV. Off-line spectral deconvolution was carried out on an IBM AT compatible PC [12].

A dried animal blood standard of the IAEA was mixed with 20% high-purity carbon and pressed into 10 mg/cm^2 thick pellets of 13 mm diameter. Pd and Se internal standards were also added to the sample.

Thin homogeneous fly-ash samples were prepared by suspending 100 mg of the sample in inert liquid and filtering through a Nuclepore filter with 0.4 μm pore size. The resulting sample thickness was 5–10 mg/cm^2.

Fly-ash particles were sieved and the fraction having a diameter of 200–300 μm, coated by 5 nm carbon, was taken for individual particle analysis.

3. Results and discussion

Dried blood samples that are typical biological samples have a high organic content. The strongly scattering part of the low-Z elements are heavily loading the detector at conventional X-ray excitation. Among X-ray emission techniques, PIXE is considered to be best suited for such samples. Fig. 1a–c shows X-ray emission spectra of certified reference freeze-dried animal blood A-13. In fig. 1 a typical thick-target PIXE spectrum can be seen where the Pd K_α lines at 21 keV are hardly observable. Detection limits for 1000 s counting time are shown in fig. 2, calculated as concentrations giving the same K_α intensity as three times the square root of the background under the peak.

Detection limits obtained by synchrotron radiation excitation are lower for elements with $Z > 25$, but the superiority in analytical performance of SRXRF is more obvious for elements having absorption edges closer to the excitation energy. Best sensitivity can be achieved for transition metals, for which both the fluorescence yield and the photoelectric cross sections are high. At higher excitation energies the appearance of a double Compton scatter peak (the 30–32 keV energy region in fig. 1c) hampers the full exploration of the energy band.

In environmental chemical research there is a demand for spectroscopic methods that are efficient in trace analysis, but very often only analysis from a small sample volume is necessary. The ability to perform chemical analysis of individual particles became recently of great importance for recognizing emission sources of particulate air or water pollution. Electron-probe X-ray microanalysis (EPXMA) is most frequently applied in this context. However, trace concentrations are hardly possible to determine; for higher Z (> 25) the limit of determination is above 0.1 wt.%.

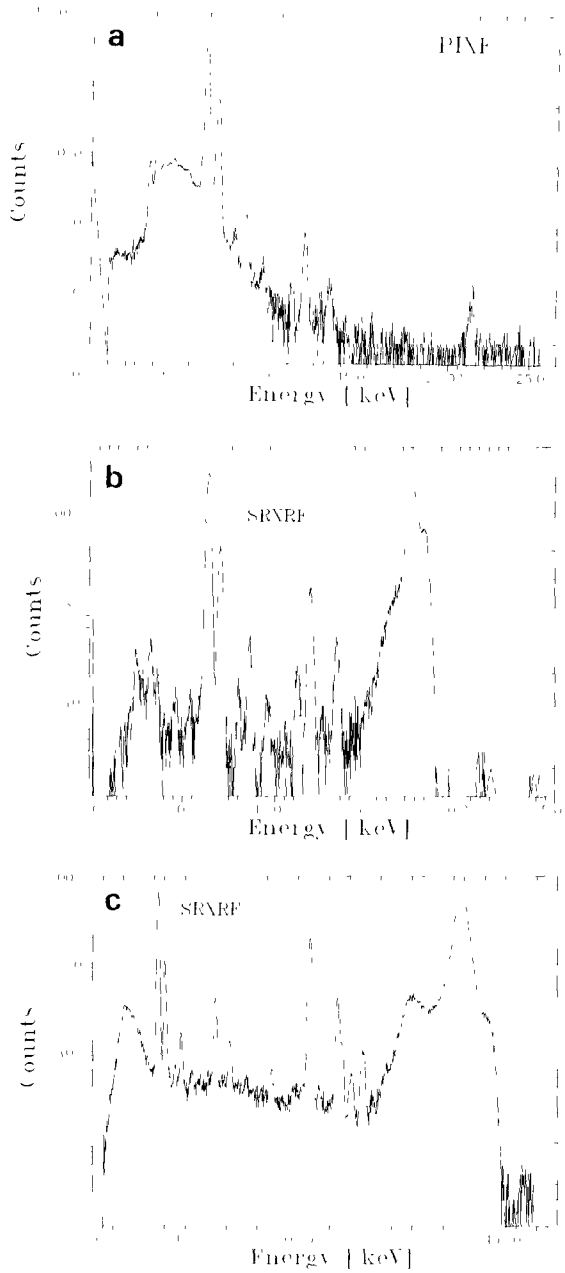

Fig. 1 X-ray emission spectra of freeze-dried animal blood: (a) PIXE by 3 MeV proton energy, counting time 900 s; (b) SRXRF at 18 keV excitation, counting time 100 s; (c) SRXRF at 39 keV excitation, counting time 300 s.

Using a synchrotron radiation (X-ray) beam, photoelectric cross sections are higher compared to electron beam excitation and energy deposition is far inferior compared to any charged-particle excitation. A synchrotron causes less radiation damage, and migration of elements in the excited volume can be avoided as well.

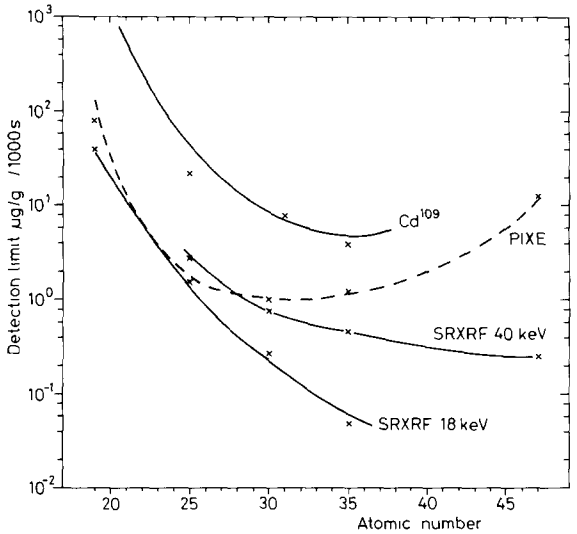

Fig. 2. The lower limit of detection in animal blood by various excitation modes for 1000 s counting time.

A NBS standard reference fly-ash sample was measured by SRXRF in order to determine the sensitivity of several elements for a 5 mg/cm^2 homogeneous thickness sample placed in a 2 mm diameter synchrotron radiation beam.

Sensitivity values for EPXMA analysis of 200 μm diameter fly-ash particles were roughly estimated in a similar way. Approximate concentration values were determined by standardless ZAF method and the excited volume was supposed to be 10 μm^3 on the average [13] with a 2.6 g/cm^3 density. The current was adjusted to obtain about 2000 imp/s for each measurement.

Table 1 shows the sensitivities of elements in fly ash in terms of cps/ng for SRXRF and EPXMA using different incident beam energies. Since individual fly-ash particles are very inhomogeneous, values obtained for EPXMA are informational. It can be concluded from the table that, using proper collimation of the exciting beam [14], SRXRF could be an ideal analytical method for individual-particle or microvolume trace analysis of environmental samples such as silicates, rocks, ashes, coal, etc., for elements with $Z > 40$. EPXMA measurements were carried out at 35 kV accelerating voltage as well, but elements heavier than Y were not detected in the ash for 1000 s counting times.

Table 1
Sensitivity [cps/ng] of EPXMA and SRXRF for elements of a fly-ash sample

	EPXMA 25 kV	SRXRF	
		15 keV	40 keV
Al–Fe	10^5–10^4	10^{-2}– 5	10^{-3}– 1
Zn–Y	10^2–10^3	20 –200	15 – 80
Zr–Ba	not detectable	not detectable	150–200

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