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Synchrotron Radiation Excited Fluorescence Micro-Analysis Using a New Imaging Technique

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Introduction

The great importance and large field of applications the x-ray fluorescence analysis (XFA) found in the last decade are due to its extraordinary qualities. It is a very flexible method, it is nondestructive, fast and requires only a very simple sample preparation. It is not necessary to perform the analysis in vacuum, so samples containing volatile components pose no problem (e.g., biological and medical samples).

The penetration depth of x-rays ranges from a few μm up to several 100 μm and is thus much greater than that of electrons (used to excite the sample with scanning electron microscopy). The analyzed volume of the sample thus increases and

results in a high sensitivity of the method. Additionally, x-rays cause much less radiation damage than corpuscular beams [1].

Using synchrotron radiation as a very powerful primary x-ray source, the sensitivity of the method is very high and is comparably good for all elements having $Z \geq 18$ [2,3]. Figure 1 shows the detection limits for synchrotron radiation excited x-ray fluorescence analysis (SYXFA). A 1 mg/cm² multielement sample was measured for 300 s using a beam diameter of 0.5 mm. The solid line indicates the detection limits measured using a white beam, the dotted line those using a graphite monochromator adjusted to eliminate the As-K α /Pb-L α interference.

The main advantages of applying synchrotron light as the primary radiation source in XFA could be summarized as follows:

- The high photon flux makes filtering, monochromatizing and masking of the primary beam feasible.
- A very broad continuous white spectrum allows simultaneous multi-elemental analysis featuring very good limits of detection (absolute $\geq 10^{-13}$ g, relative ≥ 0.1 $\mu\text{g/g}$).
- Synchrotron radiation is linearly polarized in the storage-ring plane, thus improving the signal-to-noise ratio significantly.
- The source size is very small and the synchrotron beam is very well collimated, so a high spatial resolution is achievable (see later).
- Since the properties of synchrotron radiation are calculable, the evaluation of the measured data becomes easier and more reliable.

We are applying SYXFA to help solving different analytic problems that hardly could be approached with other methods. For example, we analyzed cosmic dust particles smaller than 10 μm in diameter to find out their composition. A second example is the analysis of the printing ink on very precious documents, including the 42-line bible by Gutenberg.

X-Ray Imaging

SYXFA becomes even more interesting if one succeeds in combining spatial resolving analysis with the high sensitivity of the method.

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X-ray imaging has experienced a renaissance in the last few years; microscopic details of specimens can now be imaged [4], but unfortunately only with soft x-rays. Zone plates show a low effective transmission (typically 10%) even in the soft x-ray region; for energies above 1 keV they are no longer applicable.

Reflecting optics also suffer from various difficulties; for use in microscopy, such optics are extremely complicated to make, since very high accuracies are required. The otherwise most promising multilayer reflection optics act as a relatively narrow band-pass filter and work only for a single defined x-ray energy.

We are therefore going another way to reach the goal of achieving high resolution imaging and still maintaining a good signal-to-noise ratio; using coded imaging techniques we are increasing the interaction area of the incident beam with the sample (fig. 2) [5-7]. Line-scanning increases the interaction area by the linear dimension of the measured image, and area-scanning enables us to irradiate up to 50% of the sample.

Line-scanning requires a linear and a rotational motion; the set of data-points measured at a given rotation angle is called a "profile." Figure 3 shows schematically the process of back-projecting the measured data [8]; the profiles have to be filtered prior to their backprojection in order to avoid reconstruction errors [9]. Since each data-point contains information about several sample-pixels, the loss of some data-points has very little influence on the resulting image.

An estimation of the relative errors in the reconstructed image is given in figure 4 (the signal area is defined as the percentage of the sample area contributing to the signal; 0/1-contrast was assumed).

The experimental set-up is outlined in figure 5. Several steps reduce the scattered radiation; the total-reflecting mirror is used to cut off x-rays that are too hard. The slit-aperture (No. 4 in fig. 5) is made very accurately and has a width down to 2 μm . The alignment of the rotation axis of the sample has to be adjusted very carefully with respect to the synchrotron-beam axis. Both axes have to be parallel better than a few tenths of an arc minute.

Figure 6 compares an image measured by line-scanning to another measured by conventional point-scanning. In both cases the sample was measured under the same conditions (geometry, measuring time, filtering, parameters of electronics and accelerator).

Discussion

By applying the line-scanning technique to scan the sample, it was possible to reach spatial resolutions down to 3 μm with SYXFA, still being able to measure trace elements. Nevertheless, this is a very demanding technique. A synchrotron radiation laboratory is necessary, a computer is needed to decode (backproject) the measured data, and a very tricky alignment of the experiment has to be performed.

Considering the fascinating properties of this SYXFA-microprobe, many interesting fields of applications promise interesting results, e.g., aerosols, pigments of printing-ink on historic documents or oil paints on canvas, blood particles, diffusion processes and structured multilayers (e.g., electronic circuits).

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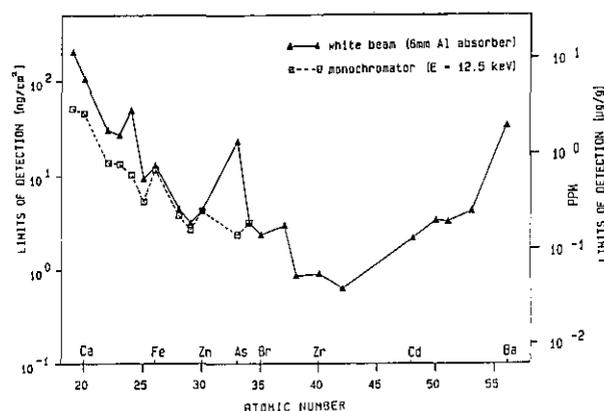


Figure 1. Detection limits for SYXFA [2].

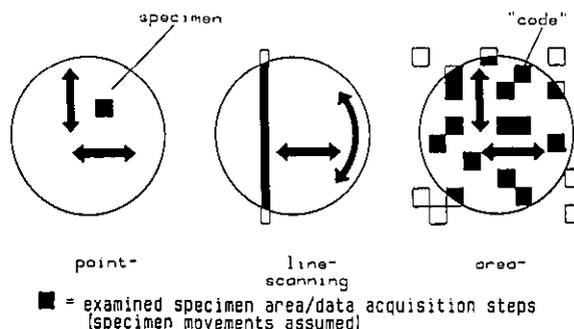


Figure 2. Different methods of x-ray scanning [7].

Accuracy in Trace Analysis

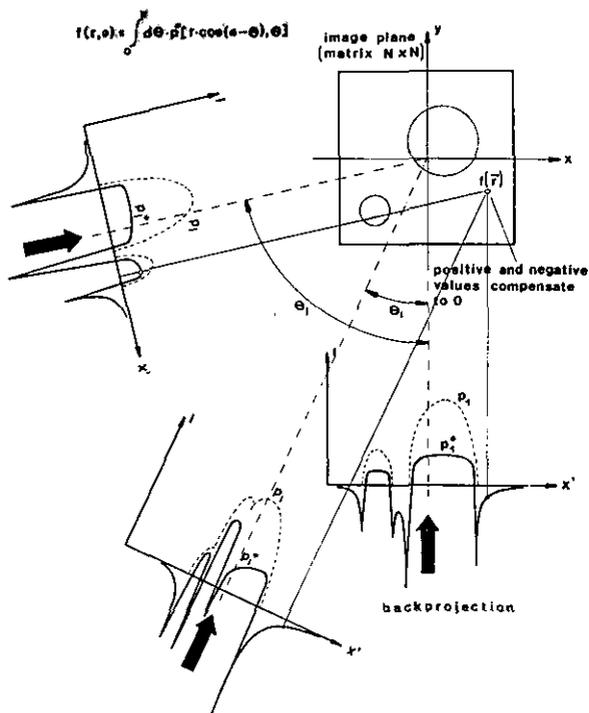


Figure 3. Filtered backprojection [8].

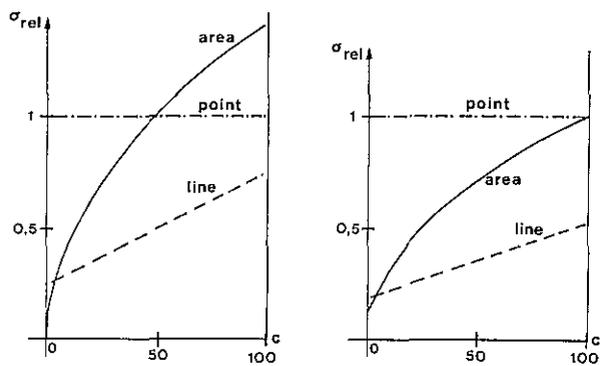


Figure 4. Estimated errors (σ_{rel}) in reconstructed images versus signal area ($c, \%$) for different scanning methods (for the right plot the presence of a constant background was assumed).

LINE-SCANNING

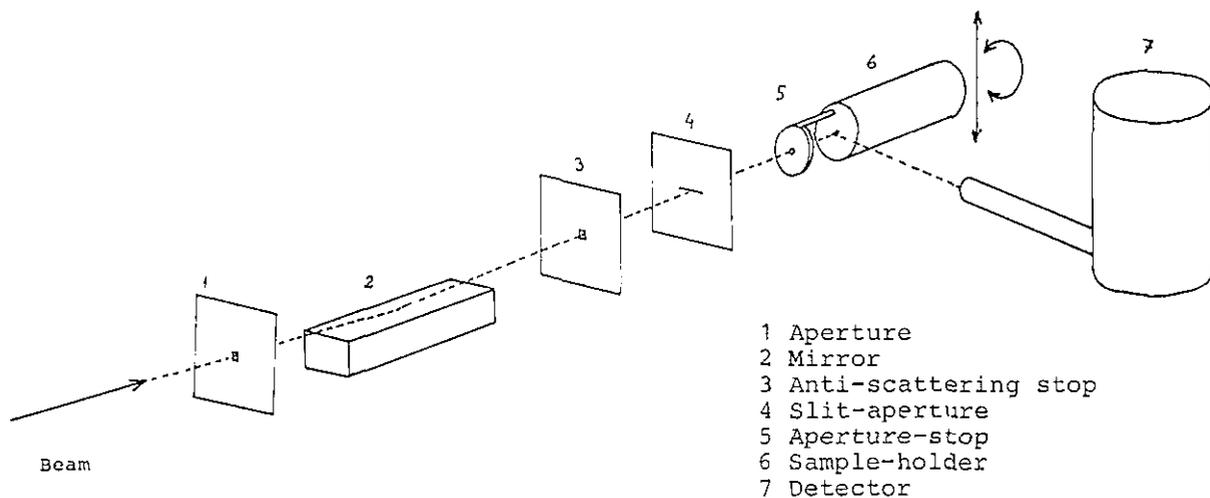


Figure 5. Experimental setup.

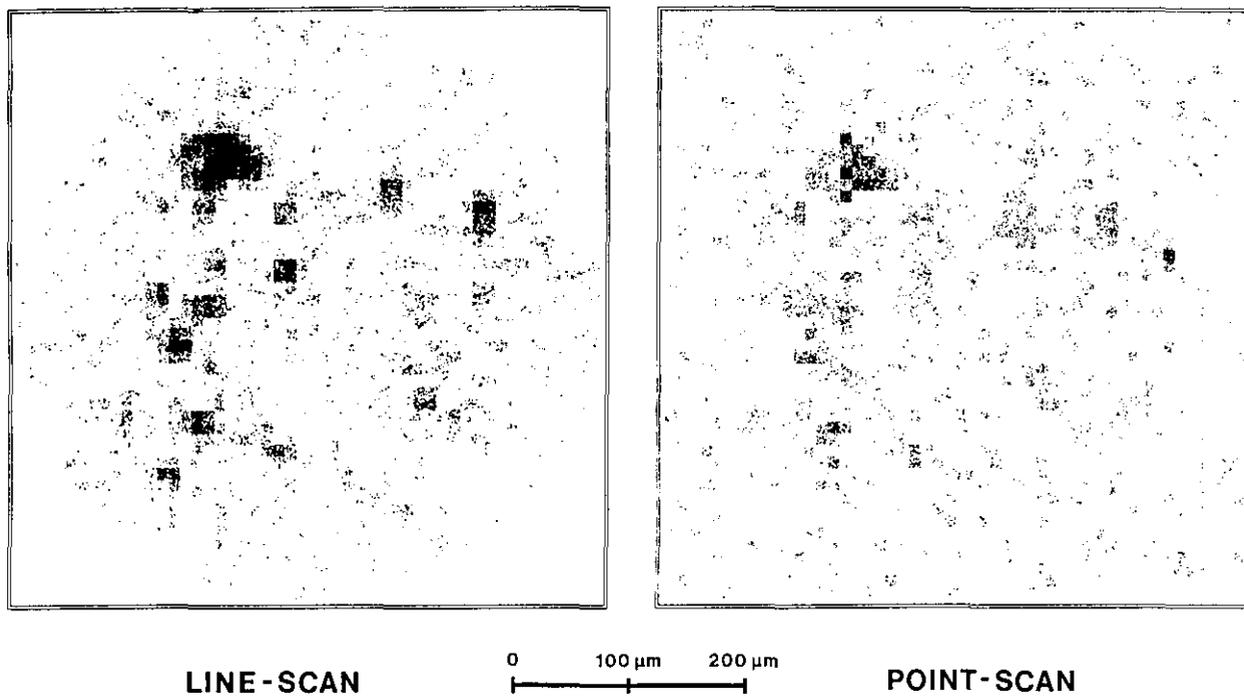


Figure 6. Comparison: line- and point-scanning (experimental; Sn grains in organic polymer matrix).

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*Direct Solids Analysis Using Sputter
Initiated Resonance Ionization
Spectroscopy (SIRIS)*

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Direct, determination of trace chemical species in solids is a fundamental analytical problem. The need to measure trace and ultra-trace concentrations of species in solids requires a method that is free of matrix effects and can be carried out with minimal contamination. Sputter Initiated Resonance Ionization Spectroscopy (SIRIS) is such a method, allowing a minimum of chemical pretreatment, the chief source of contamination, and providing a highly selective and sensitive measure-

ment of essentially any element. SIRIS is an ultra-sensitive analysis technique which uses an energetic ion beam to sputter a solid sample and Resonance Ionization Spectroscopy (RIS) to selectively and efficiently ionize neutral atoms of the element of interest in the atomized cloud. RIS and SIRIS have been adequately described elsewhere [1]. A primary advantage of SIRIS technology is the potential to reduce or eliminate the matrix effect in direct solids analysis by utilizing the predominant neutral population produced by primary ion bombardment. Since the origination of the patented SIRIS technology in 1981, numerous matrix types have been analyzed for a variety of elements. We have found that for metals, semiconductors, and alloys, trace elements can be quantitated interference-free over a broad range of concentrations by using a single point calibration. Complex matrices, such as biological or geological specimens, generally require internal standardization with separated isotopes.

We have reported [1] sensitivities for SIRIS as low as 2×10^{-9} (atom fraction) and demonstrated linearity down to the ppm level with aluminum, vanadium, boron, copper, silicon, and selenium in standard steel samples from the National Bureau of Standards. The SIRIS measurements showed good linearity with certified values, and the relative signals from the different elements were in good agreement with the standard values.

The principal results to be reported here come from using SIRIS to investigate the spatial distribution of trace elements in specially fabricated crystals or devices. Since the ion beam is pulsed (at 30 Hz and with 1 microsecond duration) during a measurement, only about an equivalent monolayer of material is sputtered away, and the analysis pertains strictly to the surface. However, use of the unpulsed beam can remove material rapidly (ion milling), and thus provide a profile of the element being measured with depth into the sample.

Figure 1 shows a SIRIS depth profile measurement of silicon-29 implanted into gallium arsenide. The SIRIS measurements were normalized to the known peak concentration of 5×10^{18} atoms/cm³ and the depth scale was calibrated by measuring the sputtered crater with a Dektak profilometer. The profile is compared to LSS theory [2] and shows good agreement at depths near the peak concentration. At larger depths the agreement is poorer, the measurement showing higher concentrations than predicted by theory. This has been explained by Shepherd [3] to be the result of