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PRESENT STATUS OF X-RAY FLUORESCENCE ANALYSIS OF TRACE ELEMENTS USING SYNCHROTRON RADIATION

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INTRODUCTION

Whenever physicists develop a new machine it seems that chemists try and make an analytical tool out of it, and sometimes with great success. This has also happened with the application of Synchrotron Radiation (S.R.) to X-ray fluorescence analysis. Since the pioneer work of C. Sparks at Stanford (1) a little more than ten years ago this technique was tested in most Synchrotron Radiations centers and we wish to give a general view of the present status in this field.

By now there is a growing need, in every human field of activity, for the determination and characterization of elements at trace concentration, that is below one part per million by weight. For qualitative as well as quantitative analysis X-ray fluorescence is often used as a signature of elemental composition. Coupled with other techniques it will soon be able to give interesting chemical information, even at low concentration, thanks to the intense and perfectly well adapted Synchrotron Radiation sources.

PRINCIPLE OF X-RAY FLUORESCENCE ANALYSIS

In principle X-ray fluorescence analysis is a very simple technique. A given sample is placed in a chamber. A beam strikes this sample in order to create inner-shell vacancies and a detector records the X-ray fluorescence spectrum.

This is a qualitative method of analysis as each X-ray line is characteristic of a given element (or should be). It is also quantitative since the number of recorded X-ray is proportional to the concentration of the emitting element. Moreover it is quite universal except for very light elements (Z<12) because of their too low fluorescence yield and uneasy to detect characteristic X-ray lines. Another general and quite interesting feature is that it is often a non destructive analytical method.

The variety of beams (photons, electrons, heavy charged particles ranging from proton to uranium) and of detectors now available gave rise to many different combinations, each owner claiming his to be the best. In fact, as long as we are only concerned with the identification of a particular element at the lowest concentration possible, physical reasons should help and decide which really is the best arrangement.

SEARCH FOR SENSITIVITY USING SYNCHROTRON-RADIATION

General considerations

Whatever the experimental set up will be we shall end with an X-ray spectrum. For high sensitivity we want the peak area of a given X-ray line to be the largest as possible. Unfortunately many other radiative processes of interaction occur with the whole sample, in competition with X-ray fluorescence of the searched trace elements. Consequently the fluorescence peak always sits on a continuous background that should be minimum.

One can then calculate minimum detectable limits (M.D.L.) by comparing the fluorescence intensity (S) with the square root of the background (B). Statistical consi-
The article discusses the use of X-ray fluorescence for identifying elements. It introduces a formula to calculate the minimum detectable limit (M.D.L.) for a given element, which depends on the ratio of quantities such as fluorescence cross section, background production cross section, number of incident particles, and overall detector efficiency. The formula is:

$$\frac{S}{\sqrt{B}} \approx \frac{N_Z \sigma_{FZ} I_0 \Sigma}{\sqrt{N_T \sigma_B I_0 \Sigma}}$$

where:
- $N_Z$ = number of atoms of element Z and of the whole sample per cm$^2$
- $\sigma_{FZ}$ = fluorescence cross section for element Z
- $\sigma_B$ = background production cross section
- $I_0$ = number of incident particles on the sample
- $\Sigma$ = overall detector efficiency.

The M.D.L. are obtained by resolving:

$$\frac{N_Z \sigma_{FZ}}{\sqrt{N_T \sigma_B I_0 \Sigma}} \geq \text{given number.}$$

This equation will help discuss the interest of S.R. excited X-ray fluorescence over other particles.

### Target and detector influence

The first and last term of equation 2 are independent of the choice of the exciting beam. We shall only mention that the sample backing should be as thin as possible to keep $N_T$ small. Care must also be taken that the elemental constitution or the structure of this backing can be of significant importance on the background intensity.

It appears also that the detector overall efficiency is of primary interest and should be large. For this reason most experimental set up now use Si(Li) detectors to record the fluorescence spectrum.

### High intensity and its drawback

Intensity (we mean the number of incident projectile) should be very high as M.D.L. only improves with its square root. The choice of the beam enters then into consideration and we must wonder wether or not the sample will support without any damage the desired high intensity.

Charged particles would seem to have the favor because their beam are usually well collimated and moreover they can be rather easily focused on small samples (we are not speaking about microprobes). Technically intensity of the order of a $\mu$A can be obtained on small areas, that means $10^{12}$ to $10^{13}$ projectiles per second. Conventional X-ray sources cannot compete but because of its intense beam of very low angular divergence S.R. becomes a perfect tool.

When considering the sample ability to support such high flux S.R. becomes even more interesting. In Table 1 we have reported the calculated energy (in keV) left in various 1 $\mu$m thick targets when one characteristic X-ray line is produced by different projectiles of different energies. The interest of monochromatic photons is obvious and can be easily understood. The photon which has not interacted passes through the sample without leaving any energy whereas a charged particle looses its energy during its showing down in a quite short range wether or not it has created a useful inner-shell vacancy.
Table 1

<table>
<thead>
<tr>
<th>Projectile Energy (KeV)</th>
<th>Photon 5</th>
<th>Photon 20</th>
<th>Electron 20</th>
<th>Electron 50</th>
<th>Proton 3000</th>
<th>Proton 5000</th>
</tr>
</thead>
<tbody>
<tr>
<td>Target</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Al(K)</td>
<td>5</td>
<td>50</td>
<td></td>
<td></td>
<td>170</td>
<td></td>
</tr>
<tr>
<td>Cu(K)</td>
<td>14</td>
<td>1900</td>
<td>830</td>
<td></td>
<td>31000</td>
<td>10000</td>
</tr>
<tr>
<td>Au(L3)</td>
<td>13</td>
<td>1700</td>
<td>910</td>
<td></td>
<td>71000</td>
<td>21000</td>
</tr>
</tbody>
</table>

Energy left (in keV) in different lum thick targets by various projectiles for the production of one characteristic X-ray.

Fluorescence cross section

This is another interesting point for photon excitation. Photoionization cross sections are usually large, much larger than inner-shell ionization cross sections by charged particles of usual energy for fluorescence analysis. Moreover for a given energy the photoionization cross section scales like $Z^4$ whereas inner-shell ionization probability drops very rapidly, nearly as $Z^{-4}$. Remembering the universal abundance of elements drops by more than 12 orders of magnitude between hydrogen and uranium this behavior of the photoionization cross section is most interesting in trace element analysis.

This appears even more strikingly when considering the thick target X-ray yield. For a suitable chosen energy no more than 3 or 4 incident photons are necessary to get one Kα line of nearly any element whereas 100 to 10 000 charged particles are needed for the same result.

Background and its origin

Finally the background under the considered fluorescence peak should be as low as possible. In order to see whether this background can be reduced or not we must find its origin. For this discussion we shall refer to figure 1 representing the result of calculations from Jaklevic (2). The X-ray fluorescence of a same sample consisting of 250 ng cm$^{-2}$ of elements Al, S, Ca, Fe, Cu, Br deposited on a 25 mg cm$^{-2}$ carbon backing (that is a 10 ppm concentration) is recorded with a Si(Li) detector of 200 eV energy resolution. Excitation is done by electron protons and continuous X-ray spectrum (like that of S.R. or W anode X-ray tube).

For electrons (Figure 1b) one only sees a continuous background and in this case M.D.L. should be set more likely around 100 ppm. This background is due to the bremsstrahlung accompanying the slowing down of the incident electrons as well as the ejected electrons during collisions. It cannot be avoided but in principle minimized when using lower energy electrons (but ionization cross sections will also decrease) and samples with low Z matrix.

The spectrum obtained under 3 MeV protons excitation (Figure 1a) is much more interesting as X-ray peaks also appear and one can say that for elements Fe to Br (in this example) M.D.L. could be as low as 1 ppm. This increase in sensitivity is mainly due to a drastic reduction in background shape and overall intensity. Bremsstrahlung due to the slowing down of the proton becomes negligible because of its $m^{-2}$ dependence and the contribution of the ejected electrons is quite low since they usually are ejected with very small kinetic energy.

The last spectrum (Figure 1c) for photoexcitation, do show characteristic peaks but 10 ppm seems a limit. In this case the continuous background is due to the
scattering (Rayleigh and Compton) of the incident beams on the sample. Of course the scattering cross sections are usually much smaller than photoionization cross sections but there are so many more atoms in the sample than the ones we are interested in that this background contributes to the great major part of the count rate when looking at trace elements.

Figure 1. X-ray fluorescence spectrum of a 10 ppm sample under various excitations (from Ref.2).

The situation changes drastically when using monochromatic photons as it appears from figure 1d. In this case the scattered events are reduced to a sharp peak which energy is of course higher than that of the fluorescent lines to be observed. Then the background is only due to the low energy tail of the total absorption peak observed with every Si(Li) detector. Of course the signal is reduced but not as much as one could fear. Because of the \(E^{-3}\) dependence of the photoionization cross section it appears that most fluorescence events arise from those photons whose energy is just above the considered absorption edge while the others mostly contribute to scattering events and thus to the background. Then monochromatization ends up with much lower M.D.L.

Such monochromatic beam (or near monochromatic) can be obtained with properly filtered X-ray tubes. But S.R has many unique characteristics that allow to take full advantage of this very intense beam:

(i) the low divergence of the beam, which is of the same order as the diffraction pattern of perfect crystals, allows for a very efficient monochromatization;

(ii) the high degree of horizontal polarization leads to a further reduction in scattering if the detector is placed in the plane of polarization and at 90° of the incident beam;
(iii) the continuous energy that can be optimized considering the element to be studied and the matrix constitution.

EXAMPLES

A more complete relation than equation 1 allows the calculation of M.D.L. This is a useless calculation as the results strongly depend on the machine used because the energy spectrum of S.R. spreads more or less in the high energy X-ray range and that the real beam divergence, its polarization and the electron source size changes drastically from a machine to another and even sometimes from a beam line to another. All these factors greatly affect the number of photons that can strike a given sample as well as the intensity of the unwanted scattered radiation.

In the following we shall present some typical results as a guide to get an idea of the power and promises of this technique.

Experimental set-ups

Different experimental set-ups have already been used in the various S.R. centers.

The simplest one consists of a set of slits that can define a very small aperture in the direct beam. Such a device is currently in use in Brookhaven (3) and because of the beam quality M.D.L. at the ppm level on very small samples are routinely reached. S. Sutton (4) has pointed out that under white beam excitation Bragg peaks are most likely to appear, mixed with the fluorescence spectrum, if microcrystals are present in the sample (as in geological samples). Such a phenomenon becomes quite improbable under monochromatic excitation and the observed spectrum will usually be free of such dangerous interferences. Nevertheless these Bragg peaks could happen to be of a certain aid to get some interesting structural information of the sample.

Most of the other facilities use monochromatic excitation. The monochromator can consist of two parallel perfect crystals, often of the "channel cut" type. This is well adapted for the study of large samples, up to a few cm², and very useful to get representative average quantitative results.

Curved crystals are also widely used. They allow an interesting focusing of the beam in the horizontal plane with a few tenfold increase on the incident flux on the sample. This geometry is very interesting for the study of small samples, up to a few mm². Quite often mosaic crystals are then used to improve further the number of incident photons but with the drawback of a larger band pass.

Because of the high beam quality reached with new machines, especially the incredible gain in source brilliance (photons mrad⁻¹ mm⁻² s⁻¹) more sophisticated arrangement are on the verge to be used. These new generation facilities will often include multilayer devices for pre-monochromatization and/or focusing reflecting mirrors associated with sophisticated monochromators to get rid of harmonics in the monochromatic beam, etc... The final goal in these investigations is to build a scanning microprobe which could compete very well with what is currently obtained with electrons and protons.

To our knowledge every facility uses Si(Li) detectors to record the fluorescence spectrum.

Typical spectrum

Figure 2 shows a typical spectrum obtained at LURE-DCI (in Orsay). The sample is a 1g cellulose matrix with 1 ppm elements from V to Zn. The detector (Si(Li) of 26 mm² area) is located 20 cm apart from the sample, the incident beam intensity has been attenuated by a 0.5 mm thick aluminium filter and nevertheless the exposure time is only of 100 s. The running conditions for the beam was 1.72 GeV and 200 mA. The characteristic peaks corresponding to the Ka lines of these elements show up nicely indicating a well under the ppm level M.D.L. But the most apparent feature is the huge peak due to scattering processes. Had it not existed the detector could have been set much closer from the sample with a resulting important increase in fluorescence radiation.
intensity and a consecutive reduction in M.D.L.

Figure 2. Typical spectrum of 1 ppm V ... Zn in 1 g cellulose matrix (see text for details).

This spectrum shows clearly that M.D.L. are in fact imposed by the inability of Si(Li) detectors and of the whole associated electronic to keep an acceptable energy resolution under high count rate. Although slight improvements can be expected with new machines because of a reduction in Rayleigh scattering, new detector devices must be thought off.

Improvements can be also obtained when using ultra thin samples deposited on totally reflecting backing such as quartz or ultrapure silicon, as pointed out by W.L. Dorn (5). This leads to difficult sample preparation which cannot apply to any kind of specimen. There seems to be also some problems in getting reliable quantitative results with this geometry.

Anyhow it is hopeless to observe trace elements at a sub ppm level if fluorescent major elements are present at the same time in the sample as long as Si(Li) detectors are to be used. A new device, trying to conciliate the advantages of Si(Li) detectors (namely a multielement analysis with high efficiency) and those of wavelength dispersive systems (high resolution to avoid most of the energy interferences between many characteristic X-ray lines), has been tested at LURE with some success. It associates a flat mosaic crystal with a position sensitive detector. The principle is shown in figure 3. We see how such a crystal can refocus the fluorescence spectrum emitted from a point source at characteristic points according to the wavelength. Simple geometrical considerations show that a photon of wavelength \( \lambda \) leaving a point source with an angle \( \alpha \) in regard to the central ray (we mean the one reaching the crystal surface with the proper Bragg angle), may find inside the mosaic crystal a microcrystal just tilted enough so that Bragg conditions are met. This photon will be refocused on a point, symmetric of the point source. For a small mosaic spread \( \Delta \theta_{\text{max}} \) is typically of the order of 1°) and further small in regard of the Bragg angle the image size can be calculated to be

\[
\Delta x = \frac{2D}{\tan \theta_B} \frac{\alpha^2}{\sin^2 \theta_B}
\]
where \( D \) is the distance between the point source and the crystal plane. This means a first order focusing in \( \alpha \) which confers a high transmission to the system. This transmission competes quite well with the usual solid angle that can be found when using Si(Li) detectors.

![Diagram](image)

Figure 3. New detector device for X-ray fluorescence analysis.
1- graphite mosaic crystal. 2- Position sensitive detector. 3- Slits (see text for details).

If a position sensitive detector is placed at the focus and perpendicular to the central ray we see that a large range of Bragg angle can be covered at the same time. Then a multielement analysis (for neighbour element) is still possible. Moreover slits in front of the detector can prevent unwanted wavelengths to reach the detector. This is interesting to get rid of the scattered radiation but also of the fluorescence of major elements and avoid unnecessary saturation of the detector.

We present the spectrum of a spherule of extraterrestrial matter about 300 \( \mu \)m diameter observed with a Si(Li) detector (figure 4b) under the same conditions. Saturation from the scattered radiation and from the fluorescence of Fe and Ni was avoided and we can observe with high resolution characteristic lines due to Ge and Ga which are only at the 2 ppm level.

M.D.L. of a few ppb have been measured with this device as is attested from Fig.5 which shows a calibration curve obtained with a series of Co standards ranging from 20 ppb to 1 ppm in a 1 g cellulose matrix.

**CONCLUSIONS**

X-ray fluorescence analysis induced by S.R. offers already unbeatable M.D.L., even on bulk samples, compared with other fluorescence techniques using X-ray tubes, protons or electrons. Due to the penetrating power of the photon this technique is perfectly adapted to the study of medium or high \( Z \) elements in low \( Z \) matrix. In conjunction with the low energy left in the sample it becomes an ideal mean of investigation for biological samples.

This technique is still under improvements. Just like PIXE and its association with R.B.S. and N.R.A. which did not become operational until the disponibility of solid state detectors, synchrotron X-ray fluorescence analysis needs new detectors and real
Figure 4. X-ray fluorescence spectrum of an extraterrestrial spherule.
a) Si(Li) detectors. b) graphite mosaic crystal plus position sensitive detector.

Figure 5. Calibration curve for cobalt in the 10-1000 ppb range.
X-ray range optics to take full benefit of synchrotron radiation promises. This is a common need with many other research fields and it should help keep optimism.

Finally, X-ray fluorescence should be more widely associated with other fields of research. For example, in conjunction with XANES and EXAFS very interesting characterizations of trace elements should be possible with the intense flux of new S.R. machines.

REFERENCES
5 W.L. Dorn, A. Knöchel: ESRF Sup 1 and 2 European Science Foundation. Strasbourg (May 1979)