Specific features of XRF techniques using capillary lenses and synchrotron radiation

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Plan

- X-ray fluorescence analysis excited with synchrotron radiation (SRXRF)
- SR-TXRF
- μ-XRF spectrometers
- Preparation of samples
- Classical analytical methods
- Some mistakes of application these methods
- Conclusion
INTRODUCTION

This report gives the brief characteristic of special features of the application of variants of the X-ray fluorescence analysis (XRF) such as X-ray fluorescence analysis excited with synchrotron radiation (SRXRF) and XRF using capillary x-ray optics.
The brilliance of X-ray sources

- 1st generation
- 2nd generation
- 3rd generation
- Free electron laser?

Brilliance (photons/s/mrad²/mm²,10.1% bandwidth)

Year: 1900, 1950, 2000

Fixed tube, Rotating anode
Synchrotron radiation sources, location

1st generation SR sources – 11
Japan - 11
USA - 10
Russia - 6
Germany – 6
France – 4
China – 3
Sweden – 3
Brazil - 2
Denmark – 2
India - 2
Italy - 2
UK – 2
Ukraine - 2

2nd generation SR sources – 24
CCd* - 5

3rd generation SR sources – 10
CCd* - 10
CCd* - constructed, constructing and designing
Annual number of articles on SR-XRF
TRENDS

- Monochromatization of primary synchrotron radiation
- The combination of TXRF with the synchrotron sources of radiation, in particular with the sources of the third generation – SR-TXRF, Ch. Streli, 2001
- Application wavelength-dispersive spectrometers, K. Sakurai et al.
- Application of capillary lens.
XRF spectrum of NIST SRM 2690 (coal fly ash, several tens of micrograms, K. Sakurai et al, 2001)
Differences between SRXRF and conventional XRF

1. The shape of the spectral distribution of the exciting radiation
2. Difference between the components of the X-ray background
3. Phenomena of the Raman scattering
4. X-ray beams of very small sizes entail the problem of inhomogeneity
Angular flux of SR from bending magnets for some storage rings, M. Watanabe, 2004
Shape of the spectrum (Hasylab, DORIS III ring)
The modeled profile of the resonant X-ray Raman scattering including detector broadening is shown (-), as well as the Gaussian fits for the Al signal (- -). The sum of the Gaussian fit and the Raman profile is shown as a solid line.

K. Baur et. al., 2001
Annual number of articles on micro-XRF
Schema of the μ-XRF set-up of the University of Antwerp, K. Janssens et al., 1996
XRF spectrometer “Focus M”

Energy dispersion XRF spectrometer (Institute for Röntgen Optics, Moscow) include:

- Polycapillary lens, focal spot may be from 50 μm up to 300 μm
- Air cooled tube with Mo-anode and sharp focus, 50 W
- Detector Amptek, USA; 150 eV energy resolution at 5.9 keV; may be arranged at the distance of ~ 10 mm from the investigated area on a sample
- Three-coordinate sample stage
- Optical microscope (magnification from 15 to 60) for the x-ray beam’s adjustment

Sample with sides of 16 x 16 mm
µEDX-1400, Shimadzu

The focus spot down to 50 μm
EAGLE III μ-Probe

- Monocapillary lens with focal spot 300 μm.
- Polycapillary lens with focal spot from 20 μm up to 40 μm.
- Anode – Rh, Mo, W.
- Coordinate movable table with step 1.5 μm.
1 – X-ray tube; 2 – polycapillary lens; 3 – drift chamber detector; 4 – X-ray tube power supply; 5 – zoom microscopy; 6 – optical CCD camera; 7 – sample position.
Мобильный µ-XRF спектрометр ArtTAX, Германия
Schematic layout of the Hasylab μ-SRXRF spectrometer
Kanngisser, 2003

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Siberian Branch of Russian Academy of Sciences, Irkutsk, Russia
Despite the substantially larger size of beam in comparison with the electron-probe microanalysis the use of the above-mentioned modifications of the spectrometers, is of important advantage. This advantage is that there is no need for vacuum into a sample chamber. Also, such an advantage is especially important in studying biological samples. To these facts it should be added the greater depth of radiation penetration inside the sample, the lower level of background and, therefore, the better values for detection limits.
<table>
<thead>
<tr>
<th>Material</th>
<th>Effective depth of analysis in μm of K lines x-ray in C-matrix (Rh anode, 40 kV)</th>
<th>Effective volume of analysis in case conventional XRF (cm³)</th>
<th>Effective volume of analysis in case SRXRF (cm³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al</td>
<td>11.1</td>
<td>0.005</td>
<td>0.0003</td>
</tr>
<tr>
<td>Si</td>
<td>33.5</td>
<td>0.016</td>
<td>0.001</td>
</tr>
<tr>
<td>Ca</td>
<td>176</td>
<td>0.086</td>
<td>0.004</td>
</tr>
<tr>
<td>Fe</td>
<td>720</td>
<td>0.35</td>
<td>0.023</td>
</tr>
</tbody>
</table>
Dependence between spectrum intensity and Mo-anode thickness for through-target X-ray tube; B.I. Kitov, 2002

1- massive anode, 2 – 20 µm, 3 – 100 µm.
Transmission bands for Kumakhov capillary half-lens; N.S Ibraimov et al., 2002
Reconstructed XR spectrum from Teflon scattering data, Afanasiev I.B. et.al., 2005
Classical analytical methods

1. External standard;
2. Internal standard;
3. Background standard;
4. Addition method;
5. Substrate method;
6. Regression methods;
7. Lachance - Trail method;
8. Rasberry - Heinrich method;
9. Semiempirical equations of relationship;
10. Theoretical correction method;
11. Fundamental parameter method.
Over the recent past years, few innovative ideas in XRF methodology have been proposed. The main tendency was refinement of the classical analytical methods:
The fundamental parameters calibration procedure

\[ \begin{align*}
I_s &= G_F \frac{\varepsilon(E_i)}{\sin(\psi)} \int_{E_{ab}^{KL}}^{E_{max}} w_i \tau_i(E_0) \frac{r_{KL} - 1}{r_{KL}} \omega_{KL} \tau_f A(E_0, E_i) I_0(E_0) dE_0 \\
I_R &= G_R \varepsilon(E_0) A_R(E_0, E_0) I(E_0) \sum_j \frac{N_0}{A_j} \omega_j \sigma_{R,j} \\
I_C &= G_C \varepsilon(E_C) A_C(E_0, E_C) I(E_0) \sum_j \frac{N_0}{A_j} \omega_j \sigma_{C,j}
\end{align*} \] 

\[ G_F = a + b c^E \]

R. Padilla et al, XRS, 2005
Objective reasons

1. The specialization.
2. The tendency increasing the number of publications.
3. The some authors ignore the publications.
4. Some authors ignore the recommendations for the use of the classical XRF techniques, developed by other researchers.

The result is usually that was called as "the invention of the bicycle".
J.D. Angelo et al., XRS, 2002

\[
\ln \left[ \frac{I_{l}^{q}(\lambda)}{I_{k}^{s}(\lambda)} \right] = \ln \left[ \frac{I_{l}^{q}(\lambda)}{I_{k}^{s}(\lambda)} \right] + \left[ \mu_{film}(\lambda_{k}^{s}) - \mu_{film}(\lambda_{l}^{q}) \right] \csc \phi_{2} \rho z
\]
Classical analytical methods

1. External standard;
2. Internal standard;
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In studying the sediments with SRXRF the authors of the paper [Goldberg E.L., et al., NIM. 2005] used Ca as the element of comparison in internal standard method after the successful determination of its content.

Our theoretical estimations show, that the errors in the determination of the concentrations of elements from Ni to Mo can reach 20-50% depending on the range of changes in contents of some elements in studied samples.

Unfortunately, the authors don’t present the ranges of the contents of the separate elements in the studied samples. It is typical omission!
The publication by V.B. Baryshev V.B. et al. [Analytical testing of the SRXRF experimental station // NIM. 2001. Sect. A 470. P. 426–430.] is of interest. In a number of cases the values of relative standard deviations $S_r$, characterizing the reproducibility of results of the determination of chemical elements for the certified reference material of the soil SCHT-3, exceeded 20% (Sc – 34%, Cr – 77%, Co – 24%, Ga – 83%, Se – 230%, Rb – 38%).
In conclusion I would like to remind of the statement of Tyas {~ 1965-1967}, the meaning of which can be conveyed with the following words “Never before we could obtain obviously false results to such a high accuracy!”

I consider and I rest assured that one can avoid this situation in the XXI century.
Conclusion

So, the very good detection limits were obtained for the considered versions of XRF. The further extension of the combined application of SRXRF and SRTXRF is possible. The improvement of the detection limits is possible after the detailed study of background sources, related to processes in detectors. The need for the improvement of a methodical support is also evident.