THE ANALYTICAL POSSIBILITIES OF A PORTABLE TXRF-SPECTROMETER

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ABSTRACT

A portable TXRF-spectrometer on the base of a 40 W metal ceramic Mo X-ray tube and a Si-PIN-Diode detector has been developed. The advantages and disadvantages of several optical arrangements and different types of detectors for such a portable TXRF-spectrometer will be described and discussed. In the present device the excitation radiation has been monochromatized (17.5 keV) by a one stage Ni/C multilayer monochromator module. The absolute detection limits for this TXRF-spectrometer are in the lower pg level. These results will be compared with actual detection limits in real samples with different matrices. The combination of a low power X-ray tube with a Si-PIN diode detector provides a portable TXRF-system with a suitable detection power for a wide range of application.

INTRODUCTION

The analytical performance of a TXRF-spectrometer strongly depends on the excitation source. Today TXRF is a method based on stationary technique with X-ray tubes in the kW power range and with liquid nitrogen cooled X-ray detectors. Consequently, the use of highly intensive synchrotron radiation sources for TXRF was a logical development. But for a lot of analytical tasks in art history, environmental analysis and archaeology a TXRF-spectrometer near the analysed object is of great interest. For this reason our development went into the opposite direction in 1996. The interesting question for us was: what type of TXRF spectrometer – which analytical performance is possible with a low power X-ray tube and a thermoelectrically cooled X-ray detector. Additional motivations for the development of such a device are:

1. An experience made by the users very often was that MDL from fg to pg were not always necessary - the main advantages are the capability of micro- and trace analysis and the great variety of applications.
2. Another fact is that for a lot of applications a single excitation with Mo-K-radiation is sufficient.
3. The development of a portable spectrometer independent of any special supply like liquid nitrogen or cooling water.
4. The development of a device low in price is of big interest.

One important fact is that the requirements on the detector for such portable systems can be fulfilled by novel types of those devices only for a few years.
This document was presented at the Denver X-ray Conference (DXC) on Applications of X-ray Analysis.

Sponsored by the International Centre for Diffraction Data (ICDD).

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DESIGN

What are the requirements and limitations in the design of a portable TXRF-system? In fact the design of the excitation unit is the main problem of optimisation. A small divergence and a small bandwidth necessary for the total reflection limit and the reduction of background mean a considerable loss of intensity. This is a well known problem in the design of XRF-arrangements. For a portable system the resulting optimisation can only be a compromise between several parameters with opposite properties.

![Figure 1: Set up of the spectrometer](image1)

![Figure 2: Effect of monochromatisation](image2)

![Figure 3: Portable TXRF-spectrometer](image3)

**Specification**

- **Tube:** Metal-Ceramic, Mo, 40W air cooled, 1.2 x 0.1 focus
- **Optics:** Multilayer module, Ni/C, 17.5 keV reflec. 80 %
- **Detector:** Si-PIN diode, 7 mm², FWHM 195 eV
- **Carrier:** 30 mm Quartz disk
- **Size:** 420 x 590 x 300 mm³
- **Weight:** 35 kg
- **Power:** Complete system 180 W
Figure 1 shows the schematic drawing of the arrangement and the most important components of
the spectrometer.

The excitation source is a 40 W metal ceramic Mo-tube with a focal length of 1.2 mm and a focal
width of 100 µm. The tube works with a grounded cathode and air cooling. The main advantage
of this type is the compact design with a short distance between the target and the tube window of
about 15 mm. The grounded cathode means a small and cheap HV-generator.

The main element of the beam adapting unit is a one stage Ni/C-multilayer monochromator with
a reflectivity for the Mo-K line higher than 80 %. The module is adaptable to the energy of
interest - beginning from the total reflection mode up to the Bragg reflection of the multilayer.

Normally, the monochromator has been adjusted and fixed for the Mo-K line. Figure 2 shows the
effect of monochromatization. In comparison with a cut off reflector the background is reduced at
least an order of magnitude.

Today several types of thermoelectrically cooled X-ray detectors for portable systems are
available. The most suitable types are the Silicon Drift Detector (SDD) [1] and the Si-PIN diode.

There are examples of a new generation of X-ray detectors. Both detectors have advantages and
disadvantages. The main advantages of a Silicon Drift Detector are the very good resolution of
150 eV and the maximum count rate of several ten thousand cps. Disadvantages are the small
sensitive area, the low efficiency for high energy photons and a relatively long warm up time.

In comparison to the Silicon Drift Detector the sensitive area of the PIN-diode is a bigger one. For
low count rates (20 µs shaping time) the resolution is a good one (190 eV). The main advantage
is that the detector is really suitable for a portable spectrometer. For this reason we have selected
a 7 mm² Si-PIN diode detector. Figure 3 shows the device. The complete system in this config-
uration needs only 180 W power.

ELEMENT RANGE AND DETECTION LIMITS

Figure 4 shows the range of elements and the absolute 3 sigma detection limits. For the K-lines
the element range goes from phosphorus to zirconium and for L-lines from palladium to
uranium. Elements from niobium to rhodium are not detectable and the elements from palladium
to antimony can only be detected with difficulties by their L-lines. This is the compromise for a
device with a single excitation source at the moment.

The absolute detection limits for a lot of elements are in the lower-pg level. This is really better
than it would have been predicted by a simple interpolation of the excitation power and the
detector area of stationary systems. The main reason is the compact design of the arrangement.

It is well known that the detection limits in real samples strongly depend on the sample type and
the contents of the matrix. More about this in connection with the application examples.

APPLICATIONS

In principle a portable TXRF-spectrometer is suitable for the same great variety of applications as
a 2 kW laboratory device. Differences in the use result from the different analytical power and
from the possibility of portability. A portable TXRF-spectrometer is especially interesting for a
measurement under outdoor conditions and for applications where a fast analysis is important for
a decision. Such applications we find for instance in art history, in forensics and in
environmental analysis.
WATER ANALYSIS

A frequently occurring problem is the analysis of water. Figure 5 presents the detection limits in water samples with different contents of matrix. The first one is the water standard NIST 1640 as an example of a sample with lower matrix contents (Figure 6). The sample was spiked with a Ga-standard in a concentration of 200 μg/L. After that a 50 μL aliquot was dried in steps of 10 μL on the sample carrier. The second sample is a waste water with a NaCl concentration in the percent range. Sometimes it is possible to improve the detection limit with a simple procedure. The third sample is the same water after a digestion procedure with HNO₃ (1:1). All samples were measured 1000 s.

The results presented in Figure 5 illustrate the wide range of detection limits depending on the matrix concentration. Nevertheless, detection limits down to the lower ppb level are possible in real samples.

AIRBORNE PARTICULATES

The analysis of aerosols is one of the most interesting applications for a portable TXRF-spectrometer. Up to now we did not have any experience in this task. For this reason we started a co-operation with the Institute for Water-Chemistry of the Technische Universität Munich. The first task was the evaluation of the portable system in comparison with a 2 kW-TXRF-spectrometer with a cut off reflector. Several types of preparation techniques like electrostatic precipitator and cascade impactor were tested.

Figure 7 presents the first results. 0.3 m³ of city air were sampled with a cascade impactor on a Celluloseacetat filter, after that a piece of the filter was spiked with 60 ng Ga and ashed with a
Figure 5: Detection limits for water samples with different contents of matrix.

Figure 6: 50 μl NIST 1640 with 200 ppb Ga as internal standard.
a cold oxygen plasma on the disk. The sample was measured with a portable and with a 2 kW stationary TXRF-spectrometer.

![Graph showing elemental analysis](image)

**Figure 7:** City air sampled with a cascade impactor on a filter and analysed with a portable and with a stationary TXRF-spectrometer.

**CONCLUSIONS**

The analytical performance of the portable TXRF-spectrometer is sufficient for a lot of applications. The limited element range caused by the single excitation source is an unfortunate limitation at the moment. That means, the next generation of this device needs a multiexcitation arrangement. To avoid contaminations a portable use of a TXRF-spectrometer needs a careful preparation of the sample. That means, a portable spectrometer needs a portable preparation technique.

**ACKNOWLEDGEMENT**

Finally we would like to thank these institutes for there supports:
- Institute for Environmental Technologies GmbH Berlin, Prof. Leonhardt
- Institute for Waterchemistry Munich, Prof. Nießner, M. Theisen,
- Institute for Inorganic and Analytical Chemistry, Rathgen-Forschungslabor, Dr. H. Bronk

**REFERENCES**