A MICRO X-RAY FLUORESCENCE (MXRF) SPECTROMETER FOR NUCLEAR RESEARCH

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ABSTRACT
In essence, the primary spectroscopic technique applied in the research of irradiated fuel is Electron Probe MicroAnalysis (EPMA) with Wavelength Dispersive Spectrometry (WDS). Spectroscopes of this type in general allow measurement of the composition of a sample using the characteristic X-rays emitted by a surface that is irradiated with an electron beam. The interaction of the sub-micrometer size electron beam with the material under investigation gives rise to a pear-shaped interaction volume from which X-rays are emitted. As a result, the spatial resolution of this technique is of the order of 1 µm in all directions for what concerns spectroscopy of nuclear fuel.

The shallow information depth obtained because of the limited interaction path of electrons with matter can be improved by using X-rays to excite the atoms in the sample (a technique called X-ray Fluorescence or XRF) and by using higher energy characteristic X-rays for the detection. A primary high energy X-ray beam penetrates much deeper in the sample (order of 100 µm) and allows the excitation of higher energy characteristic X-rays without destroying the sample. However, the primary X-ray beam cannot be focused as easily as an electron beam. The recent advances in X-ray optics now allow a focalisation of X-rays to spot sizes of the order of 10-100 µm, thus effectively rendering micro-XRF (MXRF) possible.

Recently, a microfocus X-ray source was installed in the laboratory for high and medium activity (LHMA) at the Belgian nuclear research center (SCK•CEN) in Mol. The source is adapted to an existing shielded electron microprobe (EPMA). One of the four WDS spectrometers of the EPMA has been configured in such a way that high energy characteristic X-rays, such as Xe Kα, coming from an irradiated fuel sample, can be measured.

KEYWORDS **spectroscopy, micro- X-ray fluorescence**

1. INTRODUCTION

The sole (reported) experiment using X-ray fluorescence as an analytical tool in nuclear fuel research has been carried out in 1986 at the Danish National research center Risø [1, 2]. Thin 0.1 mm slices of irradiated fuel pellets were bombarded with X-rays generated by a rotating anode X-ray tube working at 50 keV. The incident X-ray beam had a width of 4 mm wide and was sufficiently long to cover the full width of the sample.
The intensity of the generated Xe Kα (and Cs, Ba Kα) fluorescence was measured by means of a Ge solid state detector fitted with a collimator. The use of a collimator slit confined the detected area to a spot of 0.5 mm by 2 mm. In order to prevent saturation of the detector (due to the β and γ radiation of the sample) a graphite crystal was placed in-between sample and detector. The sample was positioned on a translation device, and as such a scan could be made of the measured Xe Kα signal as function of the pellet radius. A radial resolution of about 0.5 mm was obtained.
In 1990 this XRF instrument was dismantled and no XRF measurement on irradiated nuclear fuel has been reported ever since.

One of the main problems in measuring highly radioactive samples using X-ray fluorescence is the saturation of the detector. In the Risø experiment, this was solved by using thin sliced samples (reducing the total activity but destroying the sample) and by placing a broadband scattering crystal between the sample and the detector. The complete setup is built inside a lead shielded container. The conventional XRF setup in Risø used a slit and collimator to limit the irradiated and detected area on the sample surface. Such a configuration results in loss of X-ray flux through beam divergence from the source as it travels to the sample surface or from the sample towards the detector. XRF in this configuration does not generally have sufficient sensitivity for trace element analysis.

In the last decade, developments in X-ray optics and X-ray tubes have lead to the possibility for micro-XRF applications in the laboratory with a higher sensitivity and spatial resolution than conventional XRF.

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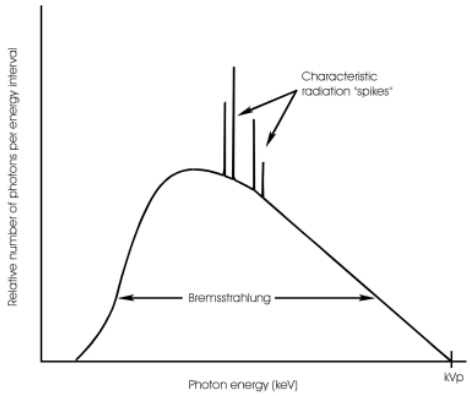
2. MICRO X-RAY FLUORESCENCE

As in XRF, MXRF uses direct X-ray excitation. The photons generated by an X-ray tube are absorbed by the sample and knock out inner shell electrons from the elements in the sample. The vacancies produced are filled by outer shell electrons. During this de-excitation X-ray photons are emitted, which are characteristic for the elements present in the sample.
In a MXRF instrument, special X-ray optics collect part of the photon beam and focus it on the sample in a small spot. The generated X-ray fluorescence is typically measured using an energy dispersive spectrometer.
The considerations one should make if one want to use MXRF in nuclear research for a similar measurement as in Risø, is that the energy of the X-ray beam is high and efficient enough to excite Xe Kα in a sample. Furthermore, the detector should have a maximum efficiency for collecting these high energy X-rays, but at the same time be resistant to the high radiation levels generated by an irradiated sample. This latter restriction rules out the use of an energy dispersive detector. An additional requirement was made: the spotsize of the incident beam has to be very small so that spatial (radial) variations can be distinguished. To obtain reasonable detection limits, the incident beam flux has to be as high as possible.

2.1. X-RAY TUBE



Generalized x-ray spectrum

In an X-ray tube, electrons from a tungsten filament are accelerated and focused in a spot on a target anode. When the kinetic energy of the impinging electron is larger than the binding energy of a particular shell in the anode material a set of characteristic X-rays in the anode is created. Another process that will occur is the creation of bremsstrahlung, which is created when the electrons are slowed down in the anode. This continuous white spectrum contains photon energies from zero up to the applied tube voltage (see fig.1,2).
In the last decade, a lot of effort has been made to increase the emitted X-ray photon flux by increasing the brilliance (W/mm^2) of the X-ray tube while keeping the anode focal spot as small as possible. A major accomplishment in this field was the development of the low power microfocus X-ray tube.
The limitations of electron impact on the target anode lies in the ability to conduct the heat away from the region of impact, hence limiting the power density on the target. The dimension of the focal spot size of the X-ray tube is thus defined by the power applied on the tube target. As the power on the tube anode is increased the focal spot size will automatically increase.
Cooling of the anode by means of water or oil has the consequence that the physical dimensions of the X-ray tube will increase which is a limiting factor for positioning the anode as close as possible to the sample.

Traditionally, X-ray analysis of heavy elements is based on L series spectral lines. This is because the more energetic K lines are more difficult to excite, since this can only occur if the energy of the photon is equal or greater than the binding energy of a K-shell electron. The energy of the K absorption edge of an element increases with the atomic number of the element. In the case of Xe, the energy of the K absorption edge is about 34.6 keV. This means that at least an incident photon energy of around 35 keV is needed to excite Xe Kα in a sample. Such high energetic X-rays can be generated by using a characteristic X-ray line of the tube anode. A tungsten anode will generate a W Kα (59.3 keV) characteristic line if the applied voltage on the tube is 90 kV (overvoltage ratio of 2/3 is required for efficient excitation). Such a high tube voltage has the consequence that the spot size on the anode increases.

Kα

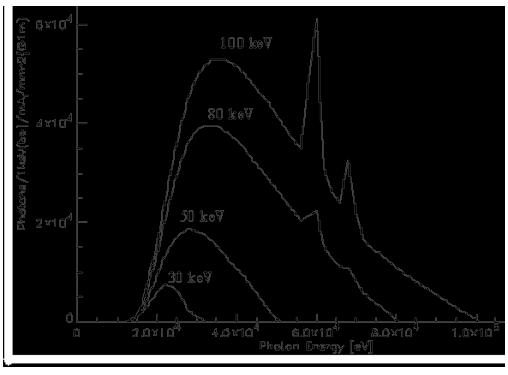


Figure 2. Influence of applied voltage on X-ray tube spectrum

Another method to gain a high energy incident X-ray beam is to make use of the white spectrum excitation. The maximum intensity of the bremsstrahlung spectrum can be found at approximately 2/3 of the applied voltage on the X-ray tube. An applied voltage of 50 kV will thus generate a maximum in the emitted spectrum at 35 keV.

As the atomic number of the anode material is increased, the intensity of the white X-ray flux also goes up. Theoretically, the intensity is directly proportional to the atomic number Z of the target material (see fig. 3), meaning that a tungsten anode is a good choice as X-ray tube target.

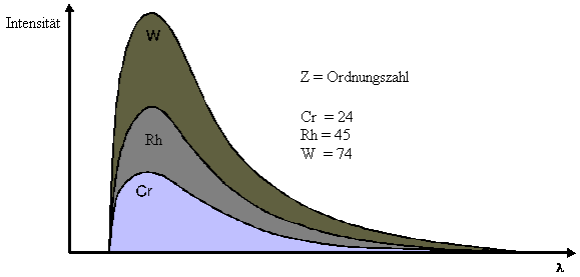


Figure 3. Intensity of bremsstrahlung increases with atomic number Z of the anode material.

2.2. X-RAY OPTICS

Micro X-ray fluorescence is based on X-ray optics which can collect photons from a source over a large solid angle and refocus them outside the tube envelope into a small spot. The major principle behind X-ray optics is based on the multiple total external reflections of X-rays from the smooth inner walls of the capillary channels (fig. 4). Reflection of the X-ray photons occurs at the boundary between media with different refractive indices. When an X-ray strikes the surface of a capillary at a grazing angle smaller than the critical angle of the material, it undergoes total external reflection. The critical angle $\sin\theta_c = \sqrt{2\delta}$ with δ being proportional to the density of the capillary material and the wavelength of the incident X-rays. Only those X-rays satisfying the total reflection condition can be effectively transported through the capillary channels.

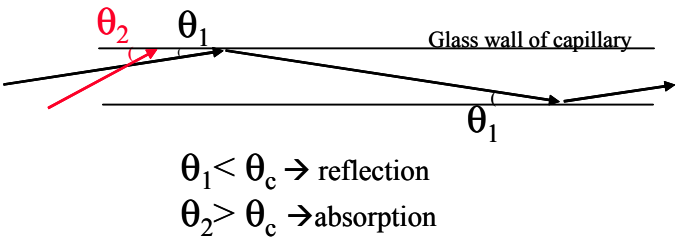


Figure 4. Total external reflection of X-rays.

The concept of guiding X-rays through a hollow capillary to avoid the $1/r^2$ loss in X-ray intensity has been known for many years. Straight monocapillaries have been used to produce X-ray beams of a few microns in diameter for MXRF applications. Tapered monocapillaries have the ability to simultaneously guide and focus X-rays for increased beam intensity. However monocapillary optics (straight or tapered) when used with conventional laboratory sources have an extremely small acceptance angle (defined by the critical angle) resulting in a rather low X-ray beam flux.

Polycapillary optics (fig .5) consists of thousands of small monocapillaries and can collect X-rays over a large solid angle to produce a small beam with high intensity.

The underlying geometric consideration for polycapillary optics is that the dimension of each capillary is much smaller than its radius of curvature to ensure that the X-rays are incident on the channel walls at angles less that the critical angle for each reflection. Most polycapillary optics are made of glass because of its high surface smoothness and formability. The recent advances in X-ray optics now allow a focalisation of X-rays in the laboratory to spot sizes of the order of 10-100 µm.

Figure 5. Polycapillary optics

2.3. X-RAY DETECTION

For the detection of the characteristic X-rays, two possible techniques are generally applied: Wavelength Dispersive Spectrometry (WDS) or Energy Dispersive Spectrometry (EDS). WDS is widely used because it has a better energy resolution (a few eV) compared to EDS which has a resolution of ~130 eV using a Si(Li) detector. Furthermore, use of diffracting crystals as energy selectors for X-rays leads to an enhanced signal to background ratio, giving WDS an increased sensitivity. On the other hand, EDS is less time consuming, as no scanning of the whole energy range has to be performed. Another disadvantage of WDS is that the acceptance angle of the detection unit is much smaller than for EDS because the Si(Li) detector can be placed closer to the sample.

However, in case of irradiated samples, the use of a Si(Li) detector is not an option as this type of detector will be in complete saturation because of the sample radioactivity, which forces the use of WDS on this material.

Only a limited selection of crystals is available for detection of X-rays in the range of 35 keV. A lithium fluoride (422) crystal is preferred over a quartz (502) crystal as it has a higher reflectivity.

Using WDS the selection of the detector is not limited by energy resolution but by detection efficiency for high energy X-rays. In the range of semiconductor detectors, the most suitable one found for collecting high energy X-rays (from a few keV to max. 1 MeV) is a CdTe detector.

3. MXRF AT SCK

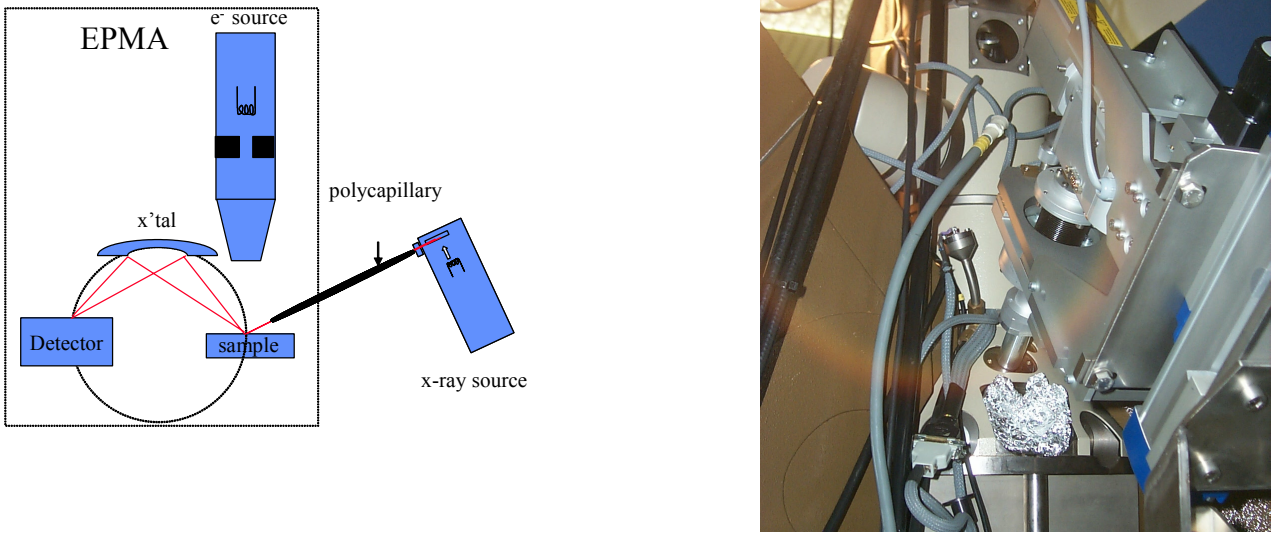


Figure 6. Schematic overview of the EPMA-MXRF instrument (left).The iMoxs module is mounted on the EDX port of the epma instrument (right)

The iMOXS module constructed by IFG consists of an air-cooled, low power X-ray tube with focusing polycapillary optics. This module was mounted on the EDX-detector port of a shielded Camebax-R EPMA (see fig. 6). A low power microfocus X-ray tube is selected because of its small size, allowing it to be mounted on the EPMA in such a way that the X-ray anode is as close as possible to the sample without having to use long optics which are difficult to fabricate. As stated before, the use of a tungsten anode is favored for the excitation of Xe Kα by means of the white spectrum. As such only a low voltage (50 kV) has to be applied on the tube resulting in a small focal spot on the anode (50 μm).
The polycapillary optics are designed and fabricated in such a way that they not only transport the X-rays from the source to the sample over a distance of approximately 31 cm but also focus the beam in a spot of approximately 104 μm for primary X-rays with energy between 25 and 30 keV (see table 1). The intensity gain in table 1, is defined as the intensity coming through a 10 μm pinhole positioned in the focal spot generated by the optics, divided by the intensity measured only using the pinhole at the same distance from the x-ray anode.

Table 1. Spot size and intensity gain as function of the energy of the primary x-rays.

E, keV	3 - 5	5 - 7,5	7,5 - 10	10 – 15	15 - 20	20 - 25	25 - 30
Spot size, μm	133	153	150	144	125	107	104
Intensity gain	1258	3290	3624	3589	3091	2205	952

One of the four WD spectrometers of the EPMA instrument is configured as a dedicated Xe channel. This means that the spectrometer consist of a curved LiF (422) crystal (Johansson type) and a CdTe detector limiting the measurable energies to a range of 24 to 36 keV.

The module was delivered with the optics already aligned to the X-ray anode (fig 7). Once mounted on the EPMA instrument the X-ray beam has to be aligned to the center of the instrument.

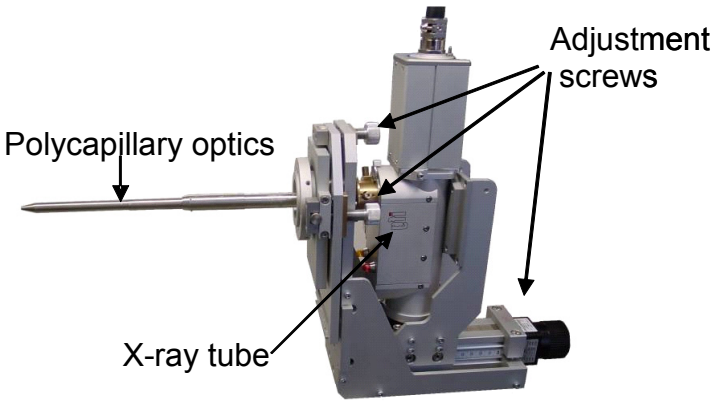


Figure 7. The iMOXS module consists of a tungsten X-ray tube and polycapillary optics to transfer and focus the X-rays on the sample

4. FIRST RESULTS

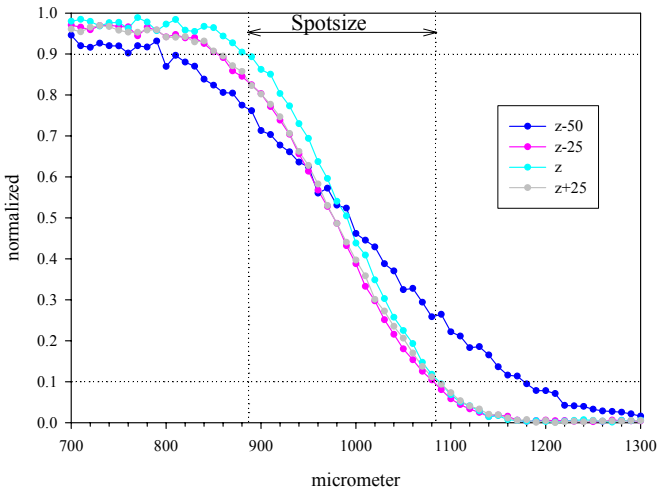


Figure 8. Measurement of the spot width generated by 6.4 keV photons emitted by the sample

The spotsize is measured using a sharp edge of stainless steel. The intensity of Fe Kα (E=6.4 keV) is measured while scanning the edge through the beam focal spot. After each measurement, the focal distance (z) is changed. From figure 8 it can be seen that the smallest spotsize achievable is around 200 μm which is close to the specifications giving for this lens (153 μm). Furthermore it can be observed that the spotsize increases very rapidly with changing of the focal distance z. A displacement of 50 μm leads to a double (approx. 400 μm) spot width.

Using the smallest spotwidth, a mapping of a sample consisting of a ring of Cu (thickness approximately 120 μm) around a circle of Ni (diameter of around 800 μm) is acquired (fig. 9).

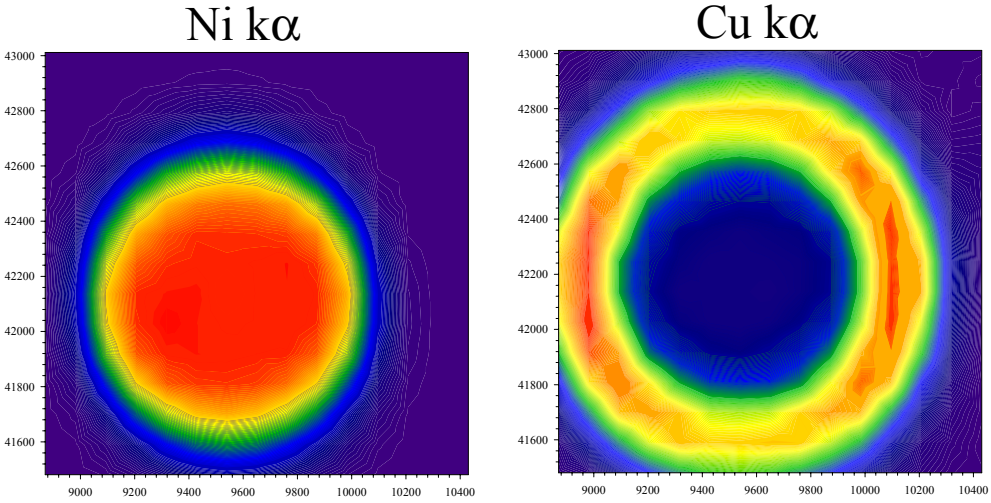


Figure 9. Mapping of a Cu-Ni target using a 200 mm spot. The X and Y axis are in μm units

The resistance of the CdTe detector to radiation from a radioactive sample was tested by loading a radioactive sample. First the background was measured in the region between 26 and 31 keV (fig. 10). It can be observed that a constant background of about 350 counts per second is introduced in the Xe spectrometer due to the presence of a radioactive specimen. This is very similar to what is measured with a proportional gas filled counter. In a next test a pure tin (Sn) standard is bombarded with an electronbeam of 45 kV and 1 μA. Subsequently the standard was also measured without the prescence of the radioactive specimen.

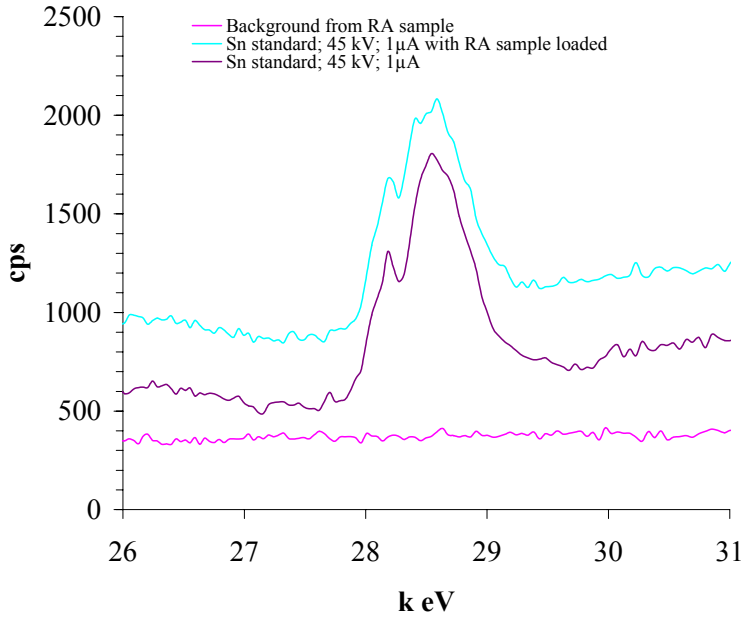


Figure 10. The influence of the presence of a radioactive specimen on the intensity in the Xe spectrometer

The construction and testing of the MXRF setup is still on-going. The first results are very encourageing and we will now start the optimisation of all parameters and geometries and finally demonstrate the possibility of Xe detection in irradiated fuel with our setup

5. REFERENCES

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