ULTRA-TRACE ANALYSIS BY MICRO X-RAY FLUORESCENCE SPECTROSCOPY

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ABSTRACT

Trace analysis performed at optimum sensitivity is of interest in many industrial sectors. X-ray fluorescence spectroscopy offers the possibility of detecting extremely small concentrations. Total reflection spectroscopy has provided the best opportunities due to advances in reduction of background radiation and sample preparation. By using a simple, specialized sample preparation technique (dried residue method), energy-dispersive X-ray spectroscopy has also achieved high sensitivity. In this paper, samples were prepared by the dried residue technique and measured by a micro X-ray fluorescence spectrometer equipped with an X-ray polycapillary lens to determine sensitivity of the method. Sensitivity in the sub-ppb range has been achieved, rivaling sensitivity achieved by total reflection spectrometers equipped with high power X-ray tubes.

INTRODUCTION

The determination of ever diminishing traces of contaminants in samples continues to attract much attention. In numerous industries beyond the traditional businesses of semiconductor manufacture and environmental monitoring, the purity of raw materials is of growing importance. This has lead to the study of various analytical techniques to reduce the lower limits of detection of impurities. X-ray spectroscopy can under specific circumstances achieve very low limits of detection. In this case, it is necessary to differentiate between sample peak and background, by focussing X-ray radiation on the sample itself. This, coupled with proper sample preparation techniques, can significantly improve results.

Total reflection X-ray spectroscopy (TXRF) provides these advantages [1,2]. A small droplet of sample solution is dispensed on a very clean, flat surface and dried. The drying process concentrates the solute sample within a small area. For samples with low total solids, the sample volume is small. Matrix interaction effects can be considered negligible and a linear relationship between concentration and peak intensity applies. Careful adjustment of the sample position in the X-ray beam provides for optimal total reflection, irradiating only the sample itself. This minimizes radiation scattering by the sample and supporting substrate, yielding improved signal to background ratio. Irradiation pathlength of the sample is also very long, leading to a preferred arrangement for sample exposure. The detector is placed directly over the sample to capture a large part of the emitted fluorescence photons. With this configuration, only a specific portion of the irradiation beam is really used for analysis, dictating severe collimation of the incident beam. The rule of longer integrating times at higher tube voltages applies. Given these factors, analysis by TXRF can yield detection limits as low as several picograms.
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For aqueous solutions, sample preparation techniques have been developed [3], which allow Micro X-Ray Fluorescence spectroscopy (MXRF) to be used in an analogous fashion to TXRF. The sample solution is placed in the hydrophilic center of a thin plastic foil. The plastic foil is hydrophobic except for the ~2 mm diameter center. As the solvent evaporates, the solute deposits in the center of the film concentrating the sample within a small area of pre-determined size and position on the foil. The sample can now be positioned within the micro X-ray beam for optimal sample irradiation yielding a high fluorescence intensity from the sample. Because the sample and sample support are extremely thin, spectral background from scattered radiation is substantially reduced.

With reflective X-ray optics, a larger proportion of the X-ray tube output can be captured and focussed in comparison to a simple aperture collimator. Reflective X-ray optics operate on a similar principle to the transport of light through a fiber optic via total internal reflection [4, 5]. This serves to transmit large radiation fluxes onto the sample improving fluorescent signal yield.

Aqueous samples were prepared on thin plastic foils and analyzed by MXRF using glass capillary optics to determine limits of detection. The option of viewing very small features makes it possible to explore dried sample inhomogeneities on the plastic foil. The results from these studies are described below.

INSTRUMENT DESCRIPTION

A prototype Eagle II XPL Micro X-ray Fluorescence Spectrometer (EDAX Inc, Mahwah, NJ) was used for this investigation. This instrument uses monolithic polycapillary bundles (a.k.a. X-ray lens) to focus X-rays on the sample [6, 7]. The X-ray lens consists of a bundle of individual capillaries with an inside diameter of between 3 to 5 microns. Each bundle in turn consists of 75,000 capillaries held together in a glass sleeve, with the following dimensions [8]:

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Dimensions [mm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Length</td>
<td>60</td>
</tr>
<tr>
<td>Entrance Diameter</td>
<td>3</td>
</tr>
<tr>
<td>Max. Diameter</td>
<td>6</td>
</tr>
<tr>
<td>Entrance Focus</td>
<td>65</td>
</tr>
<tr>
<td>Working Distance</td>
<td>12</td>
</tr>
</tbody>
</table>

Focusing of the radiation results in a ~40 μm spot measured at MoKα at the focal plane of the X-ray lens. Due to the focussing nature of the X-ray lens, the lens has a diverging beam profile out of the focal plane [8]. This allows for a somewhat larger sample area to be analyzed when the sample is positioned in the diverging beam profile. Both the fine focussing ability and diverging radiation profile of the lens were used to analyze dried residue samples.

Measurements were performed with a Rh anode X-ray tube (air-cooled, 40 kV maximum, 40 W maximum). The Eagle is equipped with an XYZ stage and CCD video microscope to position samples within the X-ray beam. Data was acquired at 40 kV with the current optimized to yield a fluorescent intensity of 10 kCPS. Power dissipation never exceeded 8 W (or 200 μA) due to the efficiency of the polycapillary lens and detector. The detector was an energy dispersive
Si(Li) detector with a sensor area of 80 mm\(^2\). This larger area provides an increase in fluorescent intensity from comparatively small samples. Energy resolution of the detector was \(\sim 200\) eV FWHM under these conditions.

Dried residue samples were prepared for this study by Process Analytics, a division of Moxtek [9]. Sample 1 was prepared by placing a 50 µl droplet of a multi-element aqueous standard on a plastic foil, AP-1 (thickness = 0.15 µm), and air-drying. This foil has a 2 mm hydrophilic center within a hydrophobic film to center the dried residue. Sample 2 was prepared in the same fashion as sample 1, except the AP-1 foil used was entirely hydrophobic to concentrate the residue into the smallest area possible.

**RESULTS**

**Investigation of dried residue distribution**

When the 50 µl droplet is dried, the hydrophilic portion of the film keeps the droplet at the center of the film. Hence, the residue is concentrated at the center of the film. Within this 2 mm hydrophilic center, the residue does not deposit homogeneously. This can be seen from the optical image (Figure 1):

![Optical CCD image of sample 1 dried residue. Red circle is about 200 µm in diameter.](image)

The distributions of individual elemental concentrations in the sample were determined by correlating signal intensity with the position of the XYZ stage relative to the incident X-ray beam. Figure 2 displays the elemental distribution of a multi-element sample for the elements Ni, Cu, Ag, and Cd. The concentrations on the edges start near 1 ppm. Measurement time per pixel was 0.5 seconds, which for a 50 x 64 pixel matrix resulted in a total analysis time of 40 minutes. Although the measured signal intensities with 0.5 second dwell time are inadequate for a good quantitative determination, they easily give a good impression of the distribution of elements within the dried residue.
In Figure 2, inhomogeneous elemental distributions are clearly visible. Elements such as Ni, Cu, and Cd are concentrated primarily in the center of the sample, while Ag is clearly more concentrated along the outer edges. The outer edge is also visible in the optical image of the sample (Figure 1). The segregation, which occurs during the drying process, is a function of several variables including cation/anion chemistry, drying rate, pH and surface energy of the sample support among others. An extensive study of the drying process and residue segregation which occurs has not been conducted up to this time [9].

In order to measure the distribution of elements in the sample more accurately, a 15 x 15 grid was superimposed over the sample. An analysis time of 150 seconds for each measurement point was used and the total analysis time was 9.5 hours. These results are presented in Figure 3.
Using this method, the entire surface of the sample can be mapped. It is obvious that to make a simple quantification of the elements in one measurement, it is necessary to measure this sample with an X-ray beam diameter comparable to the sample diameter. In the prototype system, this type of range in spot size (50 μm to 2 mm) using a polycapillary lens was not easily achieved. In addition, it is desirable to minimize the scattering from the supporting foil, by reducing the area of the sample. Therefore, a measurement performed on a smaller size residue would be advantageous.

Therefore, another dried residue sample was prepared on a film support, which was completely hydrophobic. This yielded a tighter distribution of the residue as is shown in the optical image (Figure 4).

![Optical CCD image of sample 2 dried residue](image)

**Figure 4:** Optical CCD image of sample 2 dried residue.

The following 3-D surface plots of the elemental distributions show the concentration in the sample over a smaller surface area (Figure 5). One can easily observe how all sample components have been concentrated within an area of a few hundred microns diameter. This smaller spot facilitates more efficient irradiation yielding reduced background scattering. This should result directly in higher sensitivity for determination of lower concentrations.

![3D-Elemental distributions of Sample 2](image)

**Figure 5:** 3D-Elemental distributions of Sample 2 with measurement time of 60 seconds per point on a 20 x 20 grid.
Investigation into achievable lowest Detection Limits.

Two samples with different concentrations of elements were prepared on hydrophobic film to reduce sample area. Distance between the X-ray lens and the sample was adjusted so that the diverging X-ray beam excited the entire sample. This required an additional increase of roughly 5 mm distance between the lens and the sample. Measurement conditions were 40 kV, fluorescent intensity of about 10 kCPS, and measurement time of 300 seconds.

Figure 6: Spectra of samples dried on hydrophobic plastic foil with 50 ppb (blue trace) and with 10 ppb (red trace) for the elements Mg, K, V, Fe, Cu, Se, Ag, and Tl.

Figure 6 shows the spectra collected for the two dried residues with varying concentrations of elements. Using these spectra, detection limits can be calculated (Table 1).

Table 1: Detection limits for several elements in ppb (3 σ criteria)

<table>
<thead>
<tr>
<th>Element</th>
<th>LLD (hydrophilic foil)</th>
<th>LLD (hydrophobic foil)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>Ti-M</td>
<td></td>
<td>0.15</td>
</tr>
<tr>
<td>Ag-L</td>
<td>15</td>
<td>1</td>
</tr>
<tr>
<td>Cd-L</td>
<td>7</td>
<td></td>
</tr>
<tr>
<td>Sn-L</td>
<td>10</td>
<td></td>
</tr>
<tr>
<td>K</td>
<td></td>
<td>0.1</td>
</tr>
<tr>
<td>V</td>
<td></td>
<td>0.1</td>
</tr>
<tr>
<td>Fe</td>
<td></td>
<td>0.1</td>
</tr>
<tr>
<td>Ni</td>
<td>5</td>
<td></td>
</tr>
<tr>
<td>Cu</td>
<td>7</td>
<td>0.2</td>
</tr>
<tr>
<td>Zn</td>
<td>15</td>
<td></td>
</tr>
<tr>
<td>Pb-L</td>
<td>100</td>
<td></td>
</tr>
<tr>
<td>Se</td>
<td></td>
<td>3</td>
</tr>
</tbody>
</table>
For comparative purposes, data from the dried residue on the hydrophilic/hydrophobic foil has also been included. To collect this data, the hydrophilic/hydrophobic foil sample was moved a few centimeters from the X-ray lens. As seen in Table 1, optimizing the geometry of the data collection provides significant improvement in detection limits.

CONCLUSION

These results show that specific sample preparation together with Micro-X-Ray Fluorescence Spectroscopy can yield Ultra-Trace analysis capabilities. The special sample preparation consists of the pre-concentration of the sample down to a small surface area on a flat, thin substrate. With this technique, the sample can be irradiated very efficiently. The small sample surface area and the extremely thin foil work together to produce very low backscatter. This combination results in improved detection limits reaching down into the sub-ppb domain.

This sample preparation method also yields an approximate linear correlation between MXRF intensity and concentration, analogous to TXRF measurements. This will also simplify calibration significantly and allow estimation of sensitivities as it is done in TXRF.

Further improvement in detection capability can be expected. Optimization of the experimental procedure, in particular increasing the pulse rate for samples with progressively decreasing concentrations, can be done by using higher tube current. In addition, further improvements in hardware capabilities, specifically detector resolution and pulse rate throughput, are now available [10] and can be used to reduce analysis time.

REFERENCES