

A Compact Polycapillary-Based Microbeam X-Ray Fluorescence Analysis System for Remote Monitoring of Metal Contamination

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INTRODUCTION

Long-term, remote monitoring of hazardous materials in soil, ground water, and air at the DOE sites can provide important information needed to improve the environment and the human health. Compact instruments or sensors with high sensitivity and low cost, low power consumption and low maintenance are needed to accomplish this task. We proposed to build a compact polycapillary-based microbeam X-ray fluorescence (MXRF) sensor system based upon an innovative technology – polycapillary X-ray focusing optics. The use of the optics on MXRF analysis significantly improves the detection sensitivity, and the greatly increased system efficiency makes it possible to build a compact, low-cost MXRF system for on-site applications such as remote monitoring of RCRA (Resource Conservation and Recovery Act) metals in air, water, and soil at DOE sites.

The preliminary testing performed in the Phase I of the project has successfully demonstrated the feasibility of the proposed approach. The results will be reported and discussed in this paper. Future work plan in the Phase II of the project will be presented and the applications of the technology in other industries will be discussed.

SIGNIFICANCE OF THE PROBLEM AND THE TECHNICAL APPROACH

The on-site detection and characterization of individual inorganics and RCRA metals in air, water and soil has long been an important task for DOE. Although lab-based instruments such as inductively coupled plasma mass spectrometer (ICP-MS) and X-ray fluorescence (XRF) spectrometer can provide sufficient detection sensitivity and have been used by DOE for off-site material characterizations, they are usually bulky, heavy, expensive, and require regular maintenance. Special sample preparations are also needed in many cases. All these make it very difficult to use the technologies for on-site use. In general, the low efficiency of the systems is the main obstacle for the system miniaturization.

Among different technologies, Energy dispersive XRF (EDXRF) analysis has been of great interest of DOE because of its relatively simple geometry, fast measurement speed and reasonable sensitivity. XRF analysis is also non-destructive and requires minimal sample preparation. Conventional EDXRF analysis usually examines large samples with dimension in a few millimeters. The detection sensitivity is sample dependent, ranging from a few tens of ppm (parts-per-million) to a few thousands of ppm.

One commonly used approach to increase the detection sensitivity of EDXRF analysis is to make concentrated specimens to enhance the signal-to-noise (S/N) ratio. The reduced sample size requires a small X-ray beam to match it to achieve the maximal S/N ratio. As a result, microbeam XRF analysis (MXRF) has been developed in the last decade. Another advantage of MXRF analysis is, by using a pinhole collimator in front of the X-ray detector, the detector will only collect X-ray fluorescence from a small area. Consequently the background of the XRF spectrum can be significantly reduced and the detection sensitivity can be further enhanced.

Conventional MXRF systems use pinhole apertures to achieve the small X-ray beam. The efficiency of the pinhole aperture is extremely low due to the very small collecting solid angle. The lack of x-ray intensity has been the most serious limitation to the wide application of MXRF analysis using laboratory X-ray sources. Higher X-ray intensity can be obtained by increasing the X-ray tube power, a typical approach for conventional XRF. But that means more complicated equipment, heavier shielding, and higher cost. This approach is particularly unacceptable for field deployable instrument needed by DOE.

The shortcomings of pinhole apertures can be overcome by the use of the innovative polycapillary focusing optics¹. The optics, consisting of an array of curved glass channels (capillaries) with very small diameters, collects a large solid angle of X rays from a microfocus X-ray source and guides them through the capillaries by multiple total external reflections (Figure 1). The focal spot size achieved with the optics range from a few tens to a few

hundreds of micrometers. The X-ray flux density obtained with the optic is typically more than three orders of magnitude higher than that from a pinhole aperture. The significant increase of X-ray intensity leads to a much higher detection sensitivity and

shorter measurement time. On the other hand, one can use a low-powered X-ray source (a few Watts) to achieve the detection sensitivity equivalent to that achieved with a kilowatt X-ray source. The greatly reduced power requirement will reduce the size, weight and maintenance of the X-ray source. This, combined with a compact X-ray detector and a sample handling system, will make it possible to build a compact, low-powered MXRF system for in-line or remote monitoring of compositions of different materials.

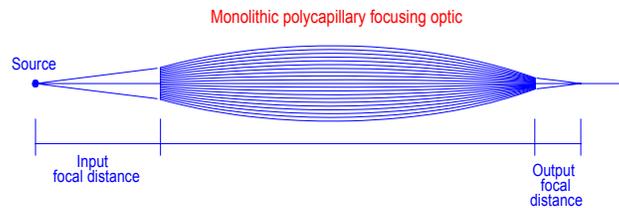


Figure 1. Schematic of a polycapillary focusing optic

EXPERIMENTS AND RESULTS

1. Prototype polycapillary focusing optic

A prototype polycapillary focusing optic was designed, manufactured and characterized at X-Ray Optical Systems, Inc. (XOS). The optic was designed using XOS proprietary ray-tracing simulation program² and made by a computer-controlled polycapillary pulling system at XOS. The profile of the optic was measured with a

microscope-based coordinate measuring system and then precisely cut based on the measured profile. The prototype optic has the following dimensions:

- Length: 60 mm
- Input diameter: 3.20 mm (hexagonal, side-to-side)
- Maximum diameter: 4.0 mm (hexagonal, side-to-side)
- Output diameter: 1.2 mm (hexagonal, side-to-side)
- Input focal distance: 50 mm
- Output focal distance: 10 mm

The optic was characterized using an Oxford XTF5011 Mo microfocus X-ray source and an Amptek energy-dispersive X-ray detector. The sketch of the experimental arrangement is shown in Figure 2. The source was mounted on XYZ stages and the movement was remotely controlled by the computer. The optic alignment with the X-ray source was obtained by maximizing the X-ray intensity on the detector while the source position was adjusted. All the motion control and data collection were achieved using a PC-based software within the LabWindows/CVI environment through an IEEE 488.2 (GPIB) interface. As the direct X-ray intensity measurement with the optic was not possible due to the detector saturation, Zr filters were used to reduce the X-ray intensity to an acceptable level. To evaluate the optic performance, the X-ray intensity obtained with a 2 mm pinhole aperture (without optic) at 100 mm to the source was also measured (base case). The X-ray flux densities (photons per unit time per unit area) were then calculated for both cases. The flux density obtained with the prototype optic was measured to be approximately 1450 times higher than that from the pinhole aperture.

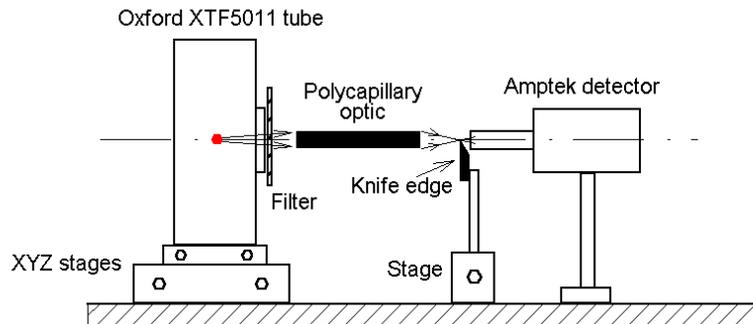


Figure 2. Diagram of the polycapillary optic characterization setup

The absolute X-ray beam intensity achieved from the source-optic combination was also measured. To obtain this value, the X-ray intensity with a 0.1 mm pinhole aperture at 1 meter to the source was measured. As the collecting solid angle of the aperture was extremely small, the detector was able to work properly without Zr filters. This result, combined with the flux gain obtained earlier, allowed us to calculate the beam intensity. The source-optic combination in our work provided a Mo $K\alpha$ intensity of 1×10^7 photon/second with the source operated at 50 kV and 1.0 mA. The flux density at the focus of the optic was 1×10^{12} photon/s/mm². Air absorption and detector efficiency were taken into account in the calculation.

The beam size was measured using the knife-edge scan method, in which a knife-edge was scanned across the X-ray beam and the intensity change as a function of knife-edge position was recorded (see Figure 2). The beam size was obtained from the derivative of the scan curve. The knife-edge used in our measurement was made of tungsten, which minimizes the edge effect due to the X-ray penetration at the energy of Mo $K\alpha$ (17.4 keV). Figure 3 shows the knife-edge scan data and its derivative taken at the focus of the polycapillary optic. The focal spot size of 30 μm , FWHM, was obtained. The output beam sizes at different output distances were also measured to determine the beam size as a function of output distance. The result is shown in Figure 4.

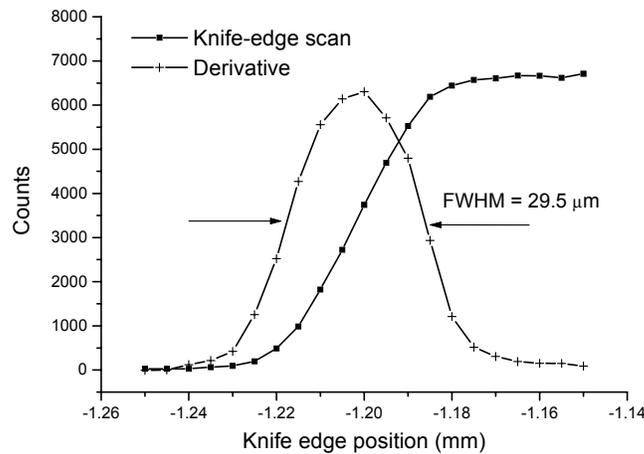


Figure 3. Knife-edge scan result at the focus of the polycapillary optic

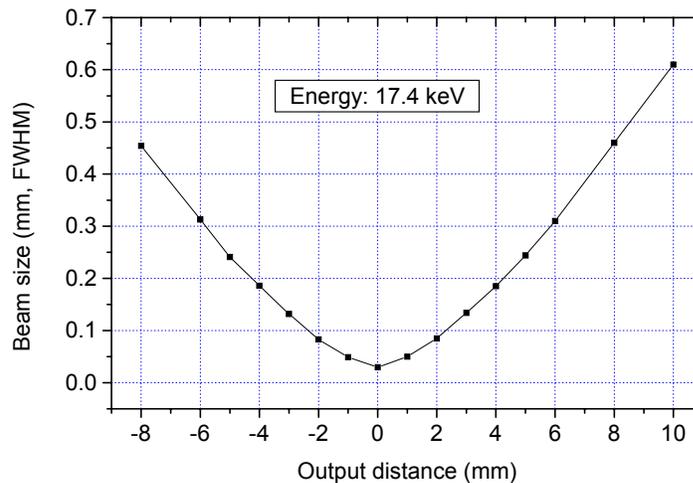


Figure 4. X-ray beam size as a function of output distance

2. System setup

The diagram of the MXRF setup used for this project is shown in Figure 5. The source-optic arrangement was similar to that in Figure 2, except that the Zr filter was removed. The sample was mounted on XYZ stages that were controlled by the control

software mentioned earlier. Two different EDS detectors, a Noran Si(Li) detector and an Amptek XR-100CR detector, were used in the measurement. The liquid nitrogen cooled Si(Li) detector had an energy resolution of 130 eV at 5.9 keV and an active area of 10 mm². Its superior performance was used to demonstrate the best achievable analysis capability of the system. The Amptek detector had an energy resolution of 210 eV at 5.9 keV and an active area of 7 mm². Despite of the inferior performance, this detector is thermoelectric cooled and has small dimensions, making it a potential candidate to be used in the proposed compact system. A pinhole collimator was attached to the detector head in both cases. As stated in the proposal, the use of pinhole collimator in front of the detector can reduce the scattering background and improve the detection sensitivity. This approach best suits MXRF analysis because the sample area analyzed is small so the collimator can efficiently collect fluorescence signals. The detector was mounted on XY stages to provide the alignment with the sample.

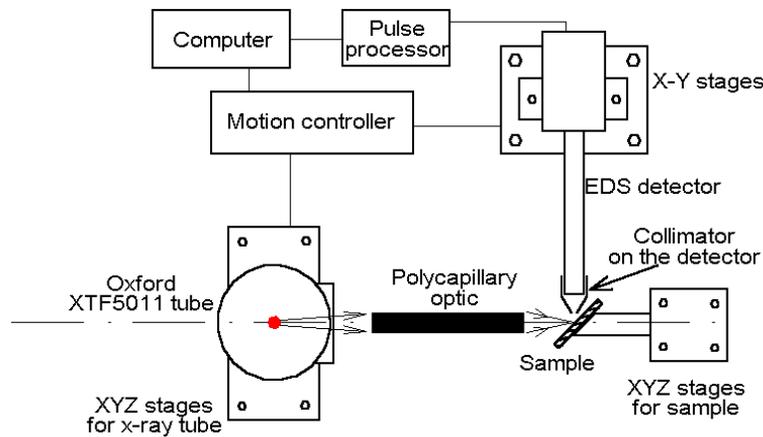


Figure 5. Diagram of the MXRF setup

The source-optic alignment procedure was similar to that described in optic characterization section, except that instead of measuring the direct beam a piece of stainless steel was placed at the output of the optic and the fluorescence signal was used to monitor the output beam intensity.

The next step was to align the sample with the focused excitation beam. The sample was first positioned at the focal plane of the polycapillary optic. It was then moved in X and Y directions while the fluorescence signal was monitored, until the right position was located. In the above alignment, the collimator on the detector was removed for easy fluorescence detection. After the sample was aligned, the collimator was mounted and the detector position was adjusted to align the collimator with the sample. Figure 5 shows the photograph of the setup with the Si(Li) detector in use.

To compare the performance of the polycapillary optic with conventional XRF analysis, a 2 mm pinhole collimator was made and could be mounted on the optic holder. The pinhole-to-source distance was 115 mm, while the total sample-source distance was the same as in the optic case.

The data acquisition and motion control were provided by the PC-based software mentioned earlier. The software also has 2-D mapping capability that can simultaneously measure the elemental distribution for up to 10 region-of-interest (RIO).

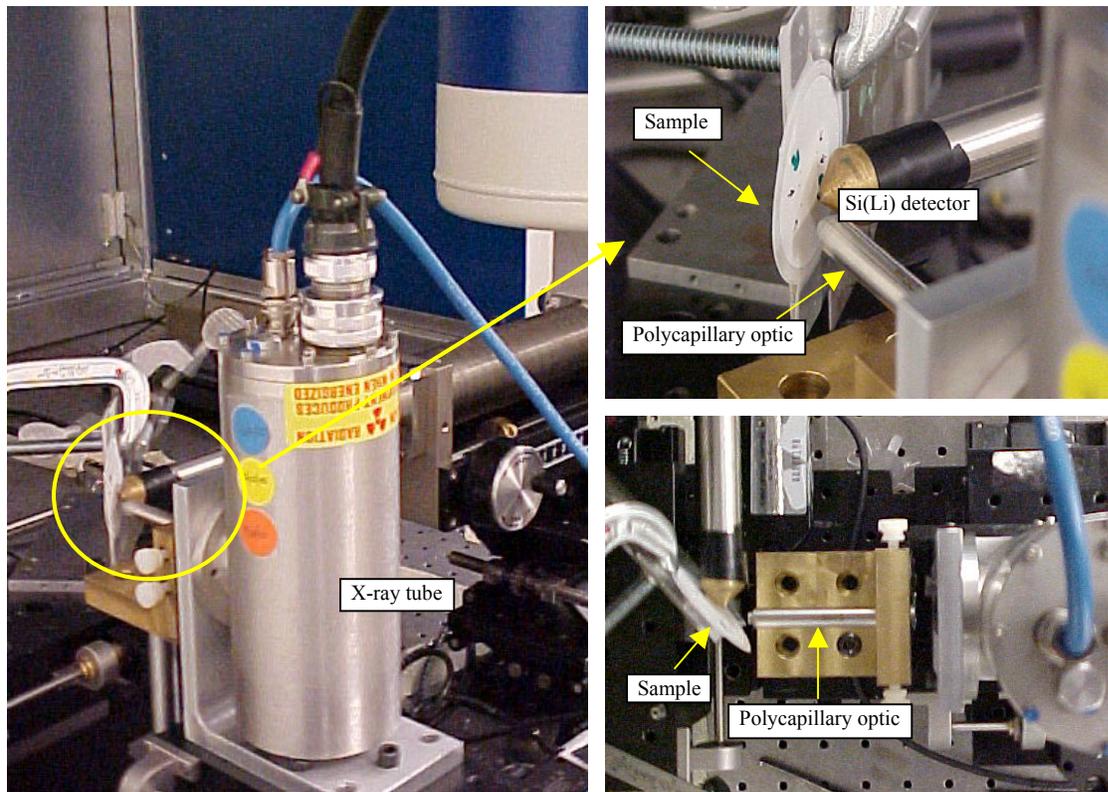


Figure 6. MXRF setup showing air particulate sample and the Si(Li) detector in use

3. Sample preparation

Three types of sample, air particulates, solution, and soils, were prepared and analyzed in our work. The air particulate sample was provided by one of our collaborator, Rupprecht and Pateshnick Co., Inc. (R&P). A proprietary sampling train was used to collect PM 2.5 ambient air samples which deposits in one hour 25 times the amount per unit area than would be collected on a standard 46.2 mm filter in a 24 hour period at one cubic meter per hour. The samples were collected on a PTFE 46.2 mm filter. Sample pairs were collected over one hour period on September 27, 2000 in local area. The material density was greatly increased with this method, making it particularly effective for MXRF analysis. Figure 7 shows a sample collected in one hour. The sample had a dimension of approximately 0.2 mm, which was determined by the nozzle diameter. As the total amount of material remains constant in the sample collection, the smaller the sample size, the higher density will be obtained. The 0.2 mm sample size matched well with the beam size of the MXRF system, and therefore the high beam flux density obtained from the polycapillary optic was efficiently utilized.

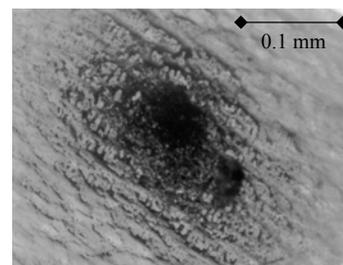


Figure 7. Microscope image of the air particulate sample

The solution sample was a NIST multi-element mix solution standard (SRM3172a) diluted 10 times in 1% v/v nitric acid. The element concentration of the diluted solution is listed in Table I. Elements such as arsenic, barium, selenium, silver and lead are of great interest to DOE and are in the RCRA hazardous metal list. Other elements interested to DOE include copper and zinc. 2 μL of the solution was then placed on a Moxtek thin film sample holder to make a dried spot sample, which was approximately 0.7 mm in diameter. The absolute amount of each element is also listed in Table 1.

Table 1. Mass fraction of elements in the diluted SRM 3172a solution

Element	Mass fraction (ppm)	Absolute weight in 2 μL solution (pg)
Arsenic	20.1	40.2
Barium	0.99	1.98
Calcium	1.04	2.08
Cobalt	11.0	22.0
Copper	10.2	20.4
Lead	10.3	20.6
Selenium	50.8	101.6
Silver	10.6	21.2
Strontium	1.05	2.10
Thallium	10.0	20.0
Zinc	10.5	21.0

The soil sample was provided by another collaborator of the project, George Havrilla from Los Alamos National Lab. The nominal concentration data of different elements in the sample, measured using ICP-MS, was provided as reference and is listed in Table 2.

Table 2. Certified mass fraction of some elements in the soil sample

Element	Mass fraction (ppm)
Aluminum	849
Barium	24.0
Iron	4822
Manganese	56.1
Strontium	7.67
Vanadium	12.1
Zinc	12.3

4. Sample analysis

4.1 Air particulate sample

The sample was analyzed using the Si(Li) detector and with the source operating at 40 kV, 0.5 mA (20 Watts). Spectra were taken with the polycapillary optic and with the 2 mm pinhole collimator. Spectrum of the blank filter was also taken for reference. The results shown in Figure 8 demonstrate the significantly superior detection sensitivity

obtained with the polycapillary optic. In contrast, only a few elements, such as S, Ca, Fe, and Pb were seen with the conventional approach (pinhole case).

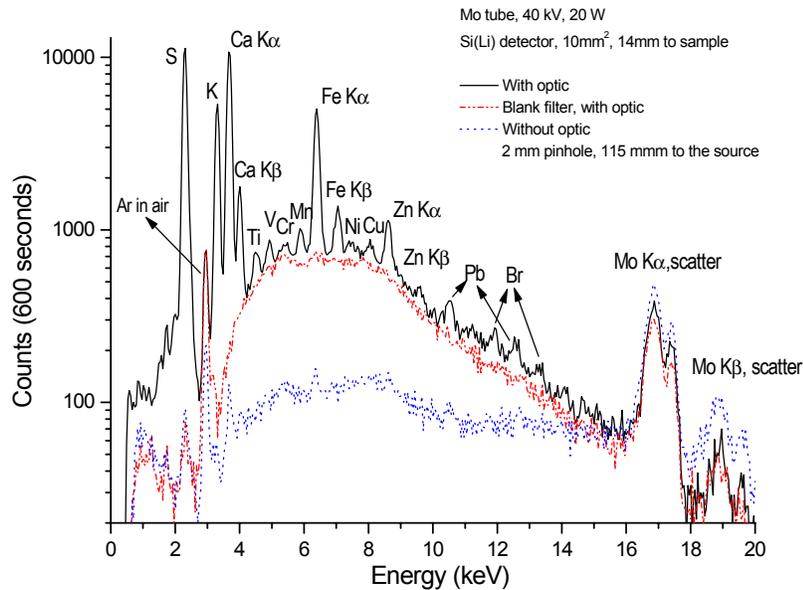


Figure 8. Spectra of the air particulate sample, taken with the polycapillary optic and the 2 mm pinhole collimator

The Amptek detector was also used to take a spectrum from the sample with the optic used. The result is shown in Figure 9. Despite the inferior performance to the Si(Li) detector, the result demonstrated that reasonable detection sensitivity could be achieved. As an Amptek detector has advantages in compactness, cost, ease of maintenance, it will play more important roles in the proposed compact MXRF system.

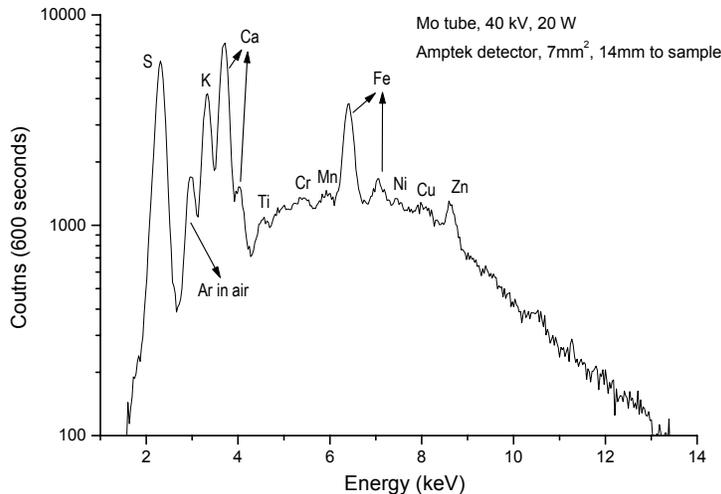


Figure 9. Spectrum of the air particulate sample taken with the Amptek detector

As the results show, the use of the polycapillary focusing optic has dramatically increased the detection sensitivity for the air particulate sample. In fact, the more than

three orders of magnitude increase of the excitation X-ray intensity over the conventional method has completely change the capability of the MXRF analysis.

4.2 Solution sample

The dried solution sample was analyzed in the similar way as the air particulate sample, except that the sample was moved out of the focus of the optic so the size of the primary beam matched the sample size, which was approximately 0.7 mm. The result obtained this way was the average over the entire sample so the possible heterogeneity effect of the dried spot sample was minimized. The results in Figure 10 shows that a signal intensity gain of 4× to 12×, depending on the energy, was obtained with the optic,

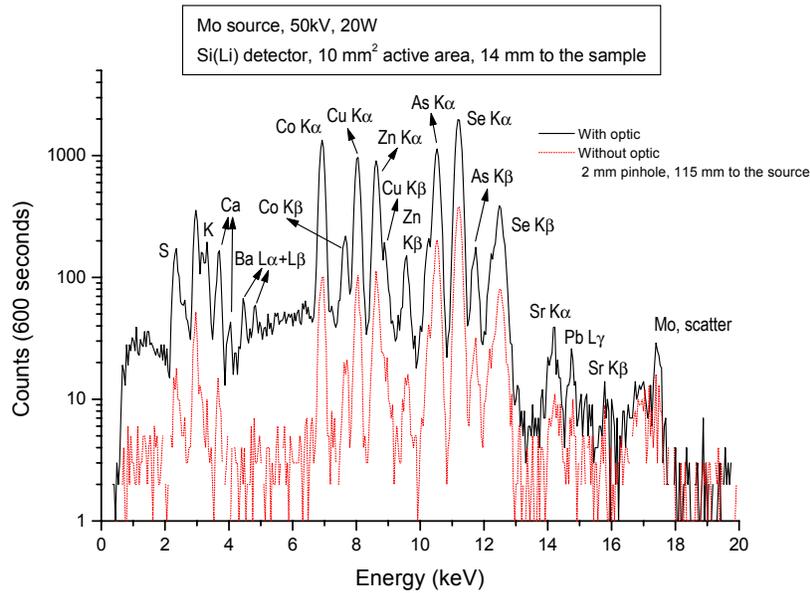


Figure 10. Spectra of the dried water sample

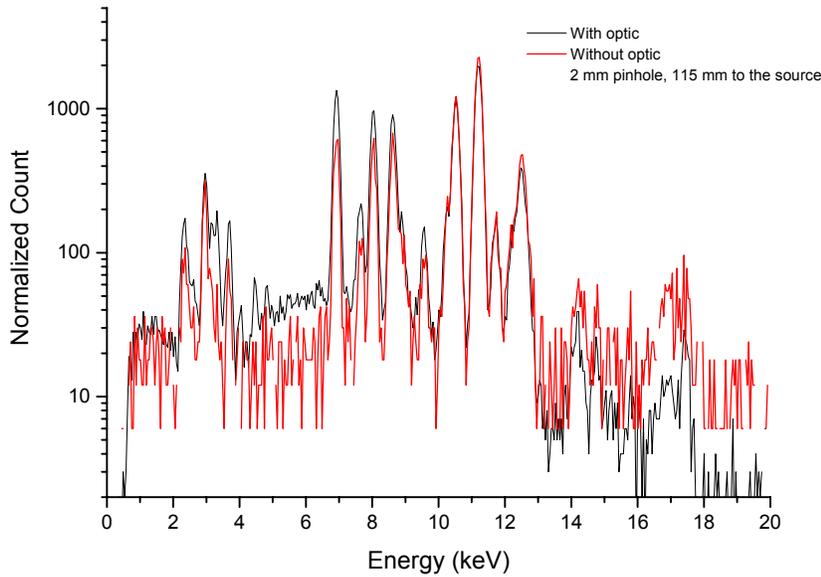


Figure 11. Spectra in Figure 10 were normalized to compare the S/N

in comparison to the pinhole case. The intensity gain is highest at low energy and decreases with energy, because the transmission efficiency of a polycapillary optic decreases with energy.

To compare the signal-to-noise ratio with and without using the optic, the spectra in Figure 10 were normalized at As $K\alpha$ (10.53 keV) and the result is shown in Figure 11. As seen, the S/N ratio is nearly identical in the two cases. Therefore the much higher signal obtained with the optic indicates that much higher detection sensitivity can be achieved. Actually the spectrum with optic clearly shows the L lines of Ba, which had a concentration of less than 1 ppm in the solution. In contrast, the Ba peaks were hardly distinguished from the background in the case without the optic.

4.3 Soil sample

The soil sample was analyzed “as is” in the preliminary test. Spectra were taken with the optic and with the 2 mm pinhole collimator. As the sample size was big (~2 mm in diameter), the sample was moved out of focus in the measurement with the optic so the beam size on the sample was approximately 1 mm. One big difference in the measurement without the optic was that the collimator in front of the detector (see Figure 5) was removed so the whole sample area could be viewed by the detector. The result in Figure 12 shows that most elements listed in Table II show up. Below 10 keV, the signal intensities with and without the optic are nearly the same, but the optic case shows much lower background and therefore much better detection sensitivity. It also shows that the lower the energy the more background reduction can be obtained in the optic case. This was attributed to the use of the collimator on detector, which blocked scattered X-rays in air. The signal intensity obtained without the optic was higher above 10 keV, which is due to the transmission decrease of optic at high energies. However, the signal-to-noise

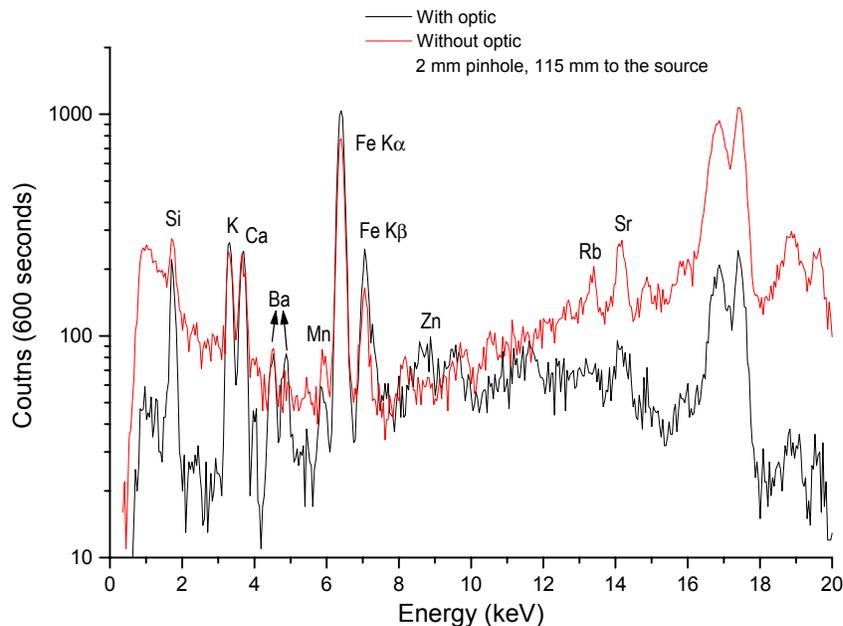


Figure 12. XRF spectra taken from the soil sample

ratios in the two cases are about the same. Because the detection sensitivity in

proportional signal and inversely proportional to the square foot of background, the detection sensitivity without the optic will be slightly better than that with the optic, for this energy range.

DISCUSSIONS

Conventional XRF analysis for air particulate is extremely difficult because the sample collected for analysis is usually very small in mass. When such small amount of air particulate is collected on a standard Teflon-membrane filter (46.2 mm in diameter), the mass density is so low that the scatter background from the membrane filter will greatly reduce the detection sensitivity. A concentrated sample can be made to increase the mass density. The sample dimension in this case will be small, and the smaller the concentrated sample the higher mass density will be obtained. The conventional XRF, however, will not benefit from the concentrated sample because the X-ray flux density (intensity in unit area) is low. In fact, the total X-ray fluorescence intensity generated from the concentrated sample would be the same as that from the non-concentrated sample. In contrast, the X-ray flux density obtained at the focus of the polycapillary optic is usually more than three orders of magnitude than that obtained with a conventional X-ray beam, i.e. through a pinhole collimator. It was both the high X-ray flux density obtained with the optic and the concentrated sample that brought the detection sensitivity of air particulate analysis to an unprecedented level. More importantly, this was achieved with a low-power X-ray source, which makes it viable for in-situ applications.

One of the unique features of the polycapillary optic is that variable X-ray beam size can be obtained by simply changing the optic-sample distance. It provides flexibility for the system to analyze samples upon different requirements. For the air particulate analysis in Phase I, the sample was precisely aligned at the focus of the optic to maximize the X-ray flux density on it. However, for the solution and soil analysis, the samples were placed off the focus so the beam was large enough to average any possible heterogeneity in samples. In fact, a fast mapping can be made for heterogeneous samples to find the “hot spots”. In this case, both local and average composition information can be obtained. The “hot spot” measurement can be important for trace elements.

FUTURE WORK

The excellent experimental results have verified the feasibility of using a polycapillary-based microbeam X-ray fluorescence (MXRF) system to improve the detection sensitivity for materials in air, water and soils. The air particulate result was of particular interest to the air monitoring industry and has generated great interests from our collaborators and business partners.

In the Phase II of the project, a prototype polycapillary-based MXRF sensor system will be designed and built. Figure 13 shows a conceptual design of the sensor head. System performance will be evaluated by examining various samples. XOS will work with collaborators to combine the MXRF sensor with a dedicated sample handling system to build a compact remote air monitoring system. The major tasks for Phase II include:

- X-ray source-optic coupling and alignment
- Compact system design and implementation
- User-friendly interface with sample-handling system

- System control
- Data analysis software development
- Data transfer system
- Continue to improve the system efficiency, including both polycapillary optics and the X-ray source – the goal is to achieve sufficient sensitivity with a 5 Watts X-ray source

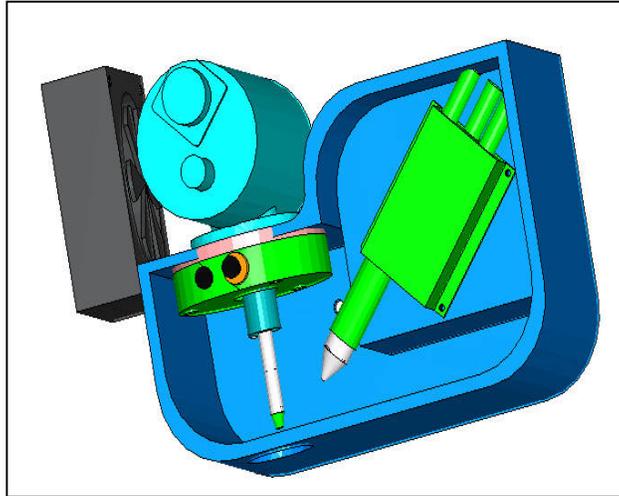


Figure 13. The conceptual illustration of polycapillary based MXRF system

The successful commercialization of the proposed MXRF sensor system will not only benefit the project-related fields, but also benefit other industries. For instance, when the sensor is coupled with a wafer-handling system, it can find a wide range of applications in semiconductor industry. The high spatial resolution makes it particularly attractive for patterned wafer examination. Besides the composition measurement, MXRF can be used for thin film thickness measurement. A compact MXRF system can be used as an in-line tool for quality control in semiconductor, microelectronics and data storage device industries. The elemental mapping capability with fast speed and high-resolution can be a very powerful research tool in geological chemistry and forensics.

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