

# **X-RAY OPTICAL SYSTEMS, INC.**

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## **Radiochemical Analysis by High Sensitivity Micro X-Ray Fluorescence Detection**

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## RESEARCH OBJECTIVES

The primary objective of the project was to develop a novel dual-optic x-ray fluorescence instrument capable of doing radiochemical analysis of high-level radioactive wastes at DOE sites such as Savannah River Site and Hanford Site. This concept incorporates new polycapillary x-ray optics technology, which can guide x rays by multiple external total reflections. A dual-optic XRF system was proposed that combines two polycapillary focusing optics, the excitation optic to provide an intense, focused excitation beam and the detection optic to collect fluorescent x rays from the excitation site and guide them into an x-ray detector. This dual-capillary design is essentially a confocal (having the same foci) design, i.e. the detected x rays are only emitted from the overlap of the two focal spots. The approach will effectively screen the radiation background from the radioactive species in the specimen and therefore significantly increases the signal-to-noise and thereby increases the sensitivity of the analysis for low-level analytes. This work will address a key need for radiochemical analysis of high-level waste using a non-destructive, multi-element, and rapid method in a radiation environment. There is significant potential that this instrumentation could be capable of on-line analysis for process waste stream characterization at DOE sites.

## MAJOR RESEARCH ACTIVITIES AND SCIENTIFIC FINDINGS

### 1. Dual-optic analyzer design

The drawing of the dual-optic analyzer “engine” is shown in Figure 1. The x-ray tube and the excitation polycapillary focusing optic is pre-aligned and coupled as a single unit and is mounted onto the base block. The detection polycapillary optic is attached to an energy-dispersive detector (Amptek XR-100) and the detector holder has a built-in alignment mechanism to allow fine adjustment of detection optic. A laser distance gauge is used for initial sample positioning.

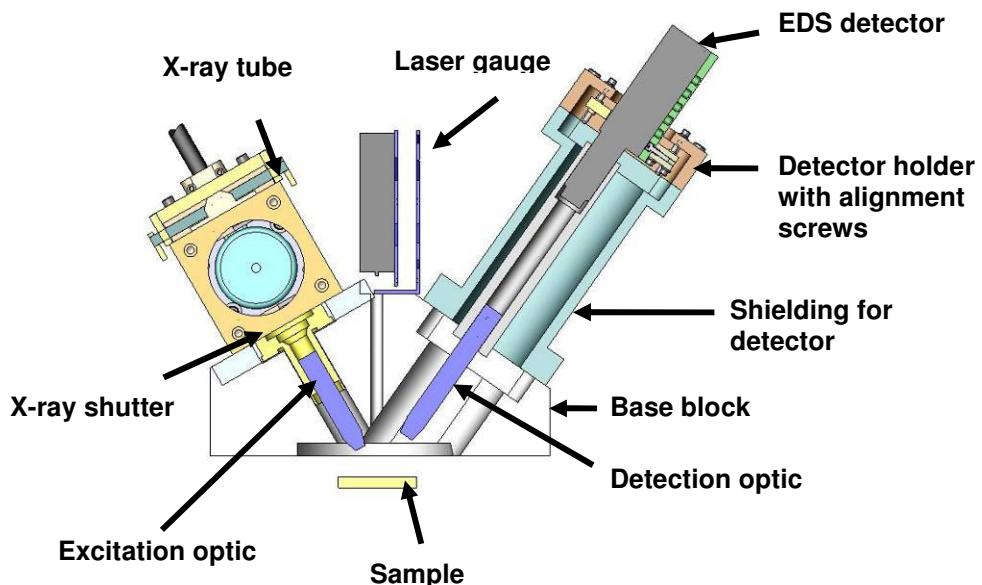


Figure 1. Drawing of the confocal XRF core design

The x-ray tube has silver anode and a spot size approximately 200  $\mu\text{m}$ . The maximum power is 50kV/25W. The Amptek EDS detector has an active area of 5  $\text{mm}^2$  and an energy resolution of 185 eV at 5.9 keV. The small active area of the detector provides the best energy resolution for this type of detector. As the fluorescent x rays are collected by the detection optic and then focused to the detector, the use of small detector, and therefore better energy resolution, will not be at the cost of sacrificing collecting solid angle, which is another unique feature of the dual-optic XRF system.

## 2. Polycapillary optics design, testing, and performance evaluation

The system performance is predominately determined by the design and the performance of the polycapillary focusing x-ray optics. After several preliminary tests in year 2002, a pair of polycapillary focusing optics with 30 mm focal distance were designed, made and tested in year 2003. The optics were integrated into the dual-optic “engine” to test the key features of the initial design: desired sensitivity and radiation rejection. The side benefit of a confocal X-ray microscope was also demonstrated.

The dual-optic analyzer “engine” was tested with the model analyte system (Sr, Pt, Pb, Pd, Mo, Cu) utilizing 1 M sodium chloride as a test matrix for the anticipated sodium hydroxide matrix from the sites. The model analyte system was a 100-ppm concentration solution of the elements listed above. All of the target elements were detected below 10-ppm detection limit with a 600-second counting time except for palladium. The Pd had a detection limit of 26 ppm due to excitation issues with the silver X-ray tube. An iron 55 source was used to determine the radiation background reduction with the dual capillary (confocal) optic design. The radiation rejection measurements showed a factor of 20 rejection ratio using an iron 55 source.

One of the more significant developments of this project is the realization that this instrument is a confocal X-ray microscope. The overlap of the two focal regions of the excitation and detection optics creates a confocal volume which can be scanned in 3-dimensions (see Figure 2). The significance of this achievement is the ability to acquire 3-D elemental maps, nondestructively. Prior to this achievement, the only way to acquire such elemental information was to use a synchrotron. Now such 3D elemental information can be obtained in a laboratory setting.

Considering the significance of the confocal XRF application and the requirement for high spatial resolution, we reviewed polycapillary optic design with the co-PI of the project, Dr. George Havrilla at Los Alamos National Lab (LANL), and decided to redesign the optics to achieve better spatial resolution. Another pair of polycapillary optics with 10 mm focal distance was designed. Based upon the simulation results, they should provide a spatial resolution of approximately 30  $\mu\text{m}$ , which is much higher than the 100  $\mu\text{m}$  resolution obtained from the 30 mm focal distance optics. The trade-off with the short focal distance design, though, is the intensity loss. To compensate for the intensity loss, a large polycapillary bundle, recently developed at X-Ray Optical Systems, was used to make the new polycapillary optics. Figure 3 shows the picture of the two polycapillary optics

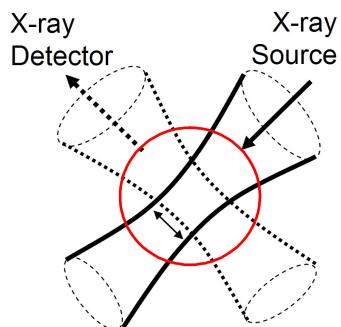
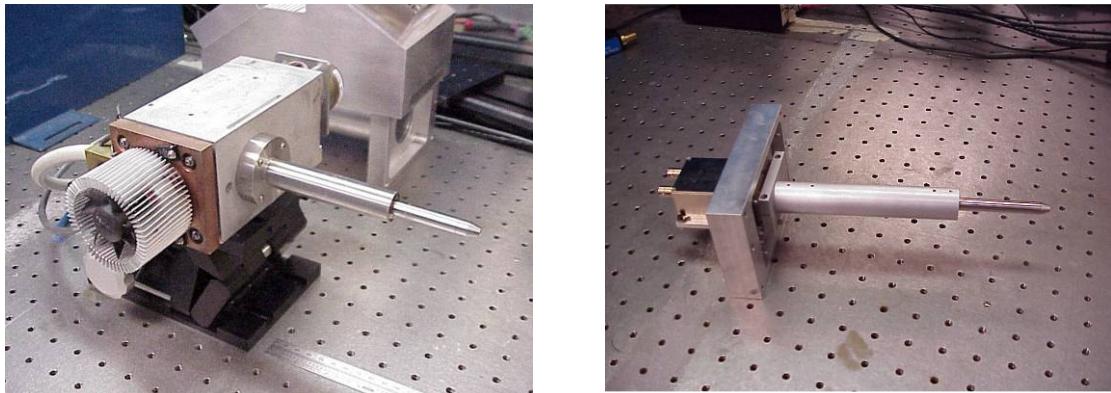


Figure 2. Confocal x-ray microscope

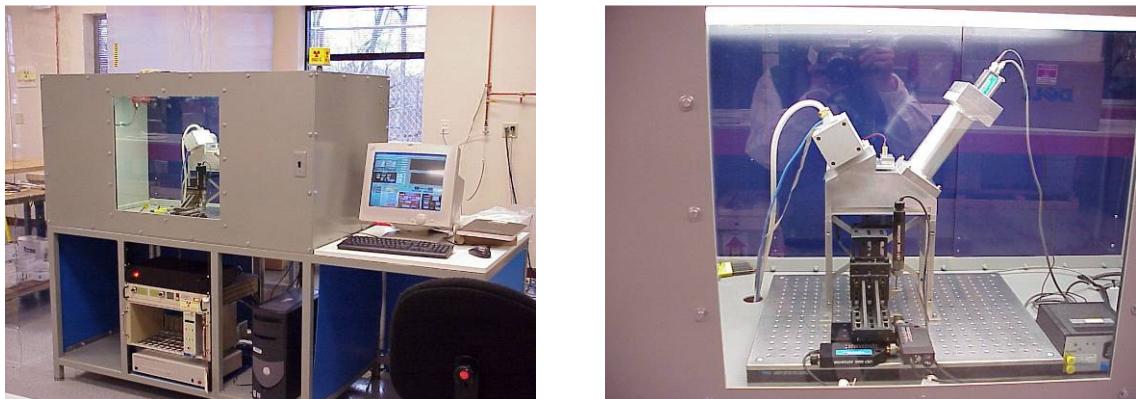
(packaged in a stainless steel enclosure) attached, respectively, to the x-ray tube and the EDS detector.



**Figure 3. Picture of the excitation optic attached to the x-ray tube (left) and the detection optic attached to the EDS detector (right)**

### 3. System integration

The dual-optic analyzer “engine” was incorporated into a chamber designed for a prototype instrument (see picture in Figure 4). The instrument is equipped with shielding, a window to view the instrument, interlocked doors, power supply and sample stage control all interfaced with a personal computer. The software control was developed by XOS. Data acquisition is accomplished via a Lab Windows interface.



**Figure 4. Picture of the complete Confocal-XRF system (left) and the picture of the prototype core (right)**

The most critical step in the system integration was the alignment between the two polycapillary optics. This was done by monitoring the fluorescent x rays from a Cu tape placed on the sample stage while adjusting the orientation and the position of the detection optic using the three fine screws on the back of the detector mounting holder (figure 5). The sample height was also adjusted in a step mode until maximum Cu signal intensity was achieved. The laser gauge was then reset to reflect the “Home” position of the sample.

The spatial resolution for depth profiling was determined by moving a thin layer of metal foil across the focal spot in vertical direction. Figure 4 shows the results for a Cu foil and a Zr foil. The depth profiling resolution is approximately 35  $\mu\text{m}$  at full width of half maximum (FWHM) for the Cu and 25  $\mu\text{m}$  FWHM for Zr. The difference comes from the fact that the spot size of the polycapillary optics is energy-dependent and the higher the energy the smaller the focal spot size.

The instrument was delivered to LANL in early May 2004, a few months past the original schedule delivery of January 2004. The delay was due to design issues and parts availability.

#### 4. Applications

The confocal capability of the dual optic XRF system was demonstrated through two significant experiments: 1) depth profile of different elements through a 13 layer paint chip; and 2) elemental mapping of iron particles in a boron nitride pellet.

The paint chip demonstration shows the layers of paint through the entire paint chip, almost 1000 micrometers thick (Figure 6). Different elements appeared at different depths showing the changes in paint particularly the use of lead years ago. Such non-invasive depth profile analysis had been done only on Synchrotron-based XRF [1] before. But we have achieved similar performance with a laboratory instrument that employs an x-ray tube with only 25 watts.

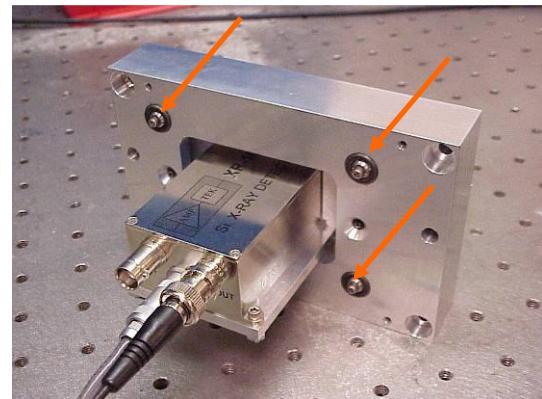


Figure 5. The three fine alignment screws for adjusting detection polycapillary optic

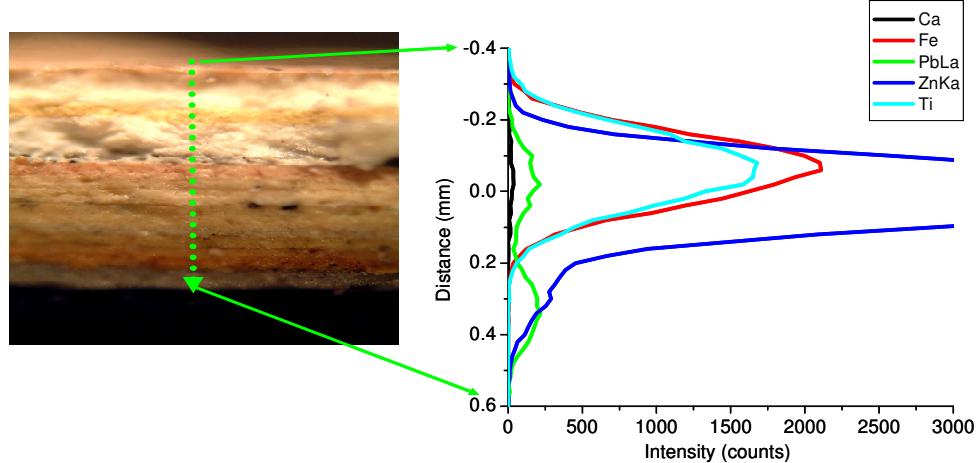
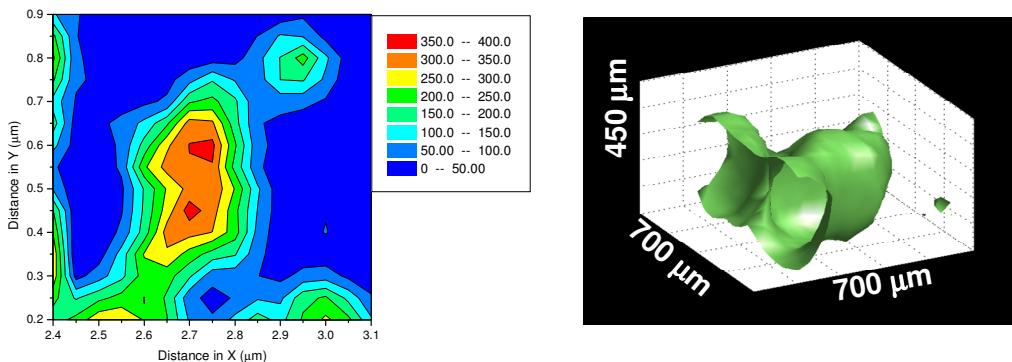


Figure 6. Elemental profiling of a paint chip obtained with confocal XRF analysis

Another experiment we had conducted was the elemental mapping of the iron particles embedded in a boron nitride pellet. Figure 7 shows both a 2D distribution of iron in the x-y plane of the scan, as well as a 3D distribution of iron to a depth of 750 micrometers.



**Figure 7. 2-D and 3-D elemental mapping of Fe particles embedded in a boron nitride pellet**

Dr. George Havrilla and his coworkers at LANL have been using the confocal MXRF system to analyze a variety of samples since the system was delivered to their lab. Some of the most recent results were recently published at American Laboratory -- April 2006. Dr. Havrilla has also been actively pursuing the opportunity to obtain a radioactive sample to test the analysis capability of the system for "hot" materials. The details will be reported in the final report they will prepare separately.

Due to the unique nature of this new capability the confocal X-ray microscope was selected as one of the R&D 100 winners for 2004.

Presentations on the confocal MXRF instrument were given at scientific conferences including the Denver X-ray conference (2005, 2004, 2003), the MRS Fall Meeting (2003), and the Federation of Analytical Chemistry and Spectroscopy Societies (FACSS) conference (2004).