Compositional Analysis with the AttoMap X-ray Fluorescence Microscope

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Background

XRF Microscopy (XFM) is a powerful atomic spectroscopy technique in which a focused x-ray beam is rastered across the surface of a sample to create a "chemical image" of the sample. It provides major intrinsic advantages over other widely used techniques. Compared to SEM-EDS, it provides orders of magnitude higher detection sensitivity (e.g. limits below sub-ppm) and higher accuracy in atomic composition measurements. Compared to LA-ICP-MS, XFM is non-destructive and can be applied to most matrix or material types (e.g. liquid), offers straightforward quantification, and be used at a wide range of spatial resolutions in a single system.

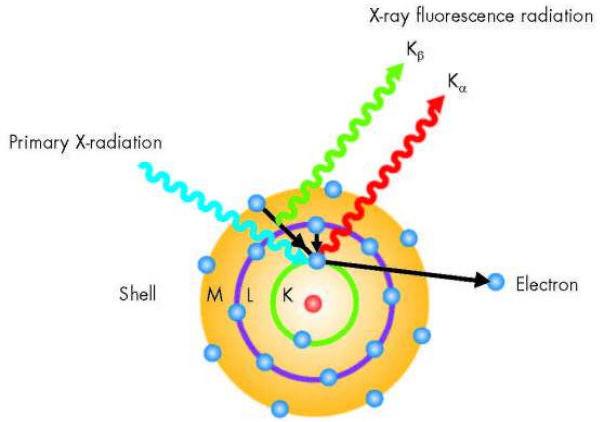


Figure 1: XRF: X-ray excitation ejects an electron. The falling of outer shell electrons into the inner shell "hole" produce x-rays with energies determined by the difference in shell energies. These emitted x-rays can be used to determine composition.

XFM furthermore provides major practical experimental advantages. X-rays also induce orders of magnitude less radiation damage than particle excitation (e.g. electrons), which is important when analyzing biological and soft materials, and microXRF can be operated at ambient pressure to enable *in situ* measurements. Its non-destructive nature also enables downstream techniques for correlative or follow-on analysis.

Challenges to Laboratory MicroXRF

Although laboratory micro x-ray fluorescence (microXRF) has been developed, such systems have been limited in resolution and sensitivity due to bottlenecks in x-ray source and x-ray optic technology.

AttoMap: First Laboratory X-ray Fluorescence Microscope with Synchrotron-like Capabilities

Enabled by major innovations, the Sigray AttoMap XFM offers outstanding performance previously only possible at synchrotrons:

- Unparalleled non-destructive thin film metrology of microns-size areas: **Sub-Angstrom** thicknesses measurements within 100s;
- Exceptional detection sensitivity: sub parts per million (**sub-ppm**) concentrations, **sub-femtogram** quantities, and <50 nm nanoparticles
- High resolution: down to **5 µm** spot analysis and/or spatial resolution in imaging
- Accurate and **precise** quantification
- High throughput: acquisition speeds of down to **5 ms/point** and simultaneous acquisition of a broad range of elements at once
- Flexibility in x-ray excitation energy choice to optimize sensitivity of most elements in the periodic table

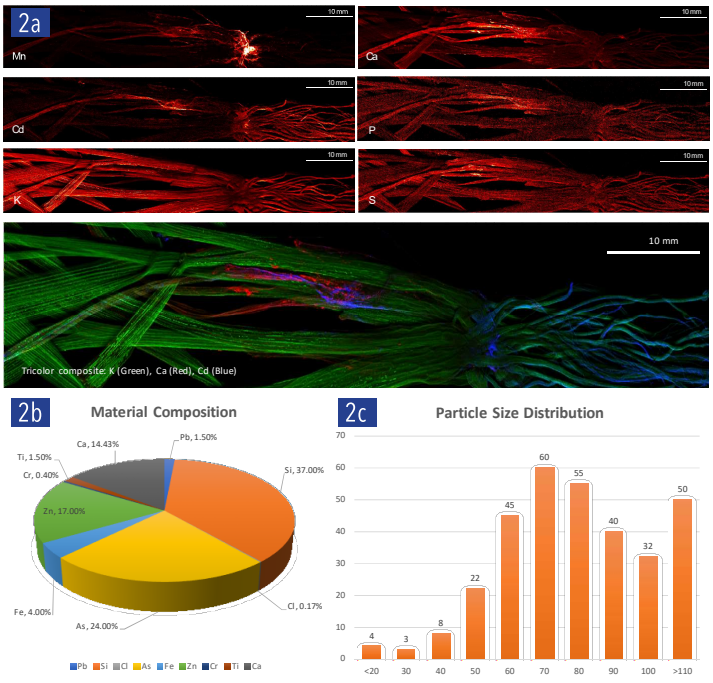


Figure 2: Examples of AttoMap's XFM capabilities: a) distribution of a wide range of elements of interest acquired simultaneously and at trace sensitivities, b) quantitative compositional analysis, and c) quantitative size distribution of elements

AttoMap X-ray Fluorescence Microscope Design

The system features several major innovations to achieve its capabilities:

1. First-of-its-kind x-ray source with a combination of ultrahigh brightness and multiple, quasi-monochromatic x-ray excitation energies enabled by a patented multi-target x-ray source design.
2. Novel x-ray optics that provides maximum efficiencies and high resolution at the focal spot
3. Optimized design integrated with optical microscope and x-ray camera for 2D x-ray microscopy

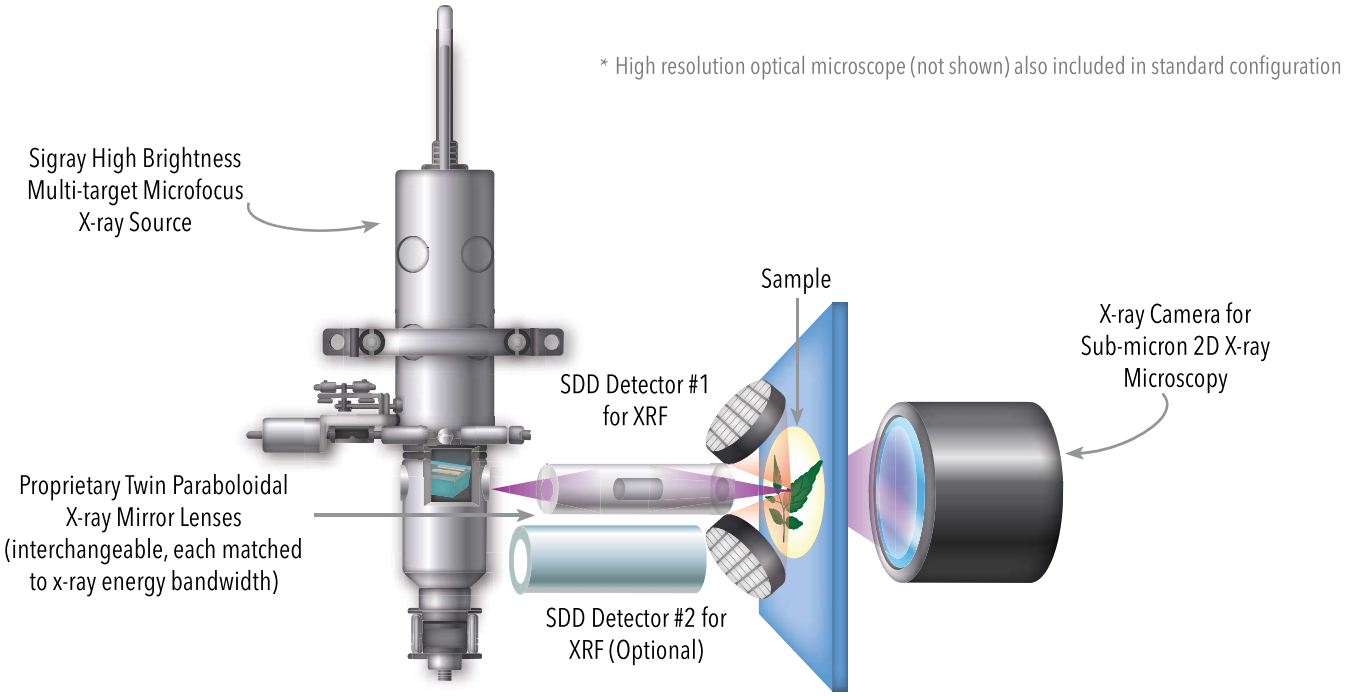


Figure 3: Schematic of AttoMap's system design, featuring multiple patented innovations

1) Advantages of Multiple Excitation Energies for XRF

X-fluorescence signal of an element strongly depends on the energies of the illuminating x-rays, because it is proportional to the ionization cross section of the element at the x-ray energy. The x-ray fluorescence signal is maximized when the excitation energy is just above the binding energy of the inner shell electrons, and no x-ray fluorescence signal is produced when the excitation energy is below the binding energy.

Sigray's AttoMap is unique in its ability to offer multiple excitation energies (up to 4 targets and their associated characteristic energies) in a single system. This enables the user to selectively increase or suppress fluorescence of specific elements.

The importance of x-ray excitation energies can be seen in Table 1, which shows that fluorescence sensitivity can vary by **orders of magnitude** depending on the x-ray illumination energy. Excitation energies represent three standard targets on the AttoMap: 5.4 keV (K-a characteristic line of Cr), 8 keV (K-a of Cu), and 2.3 (K-a of Mo) and 17.4 keV (L-a of Mo).

Fluorescence Cross-Sections for Elements by X-ray Target			
Element of Interest	Cr Target 5.4 keV	Cu Target 8 keV	Mo Target 17.4 & 2.3 keV
Potassium (K)	**655.13**	215.35	21.606
Titanium (Ti)	**8273.5**	2811.8	321.29
Vanadium (V)	0	**3710.5**	431.27
Iron (Fe)	0	**7696.2**	940.67
Selenium (Se)	0	0	**4051.9**
Zirconium (Zr)*	959.62	323.03	**7006.2**
Silver (Ag)*	**2707.8**	960.62	113.72
Platinum (Pt)	0	0	**4433.2**

Table 1: Fluorescence cross-sections in barns/atoms for a few selected elements of interest (row) vary greatly as a function of x-ray excitation energy (column) and therefore the x-ray source target selection. The three targets are all available in the AttoMap x-ray source. It is critical to have multiple x-ray targets for chemical analysis of trace-level elements.

** Indicates cross-sections given for L-a lines. All other element cross-sections given for K-a lines.*

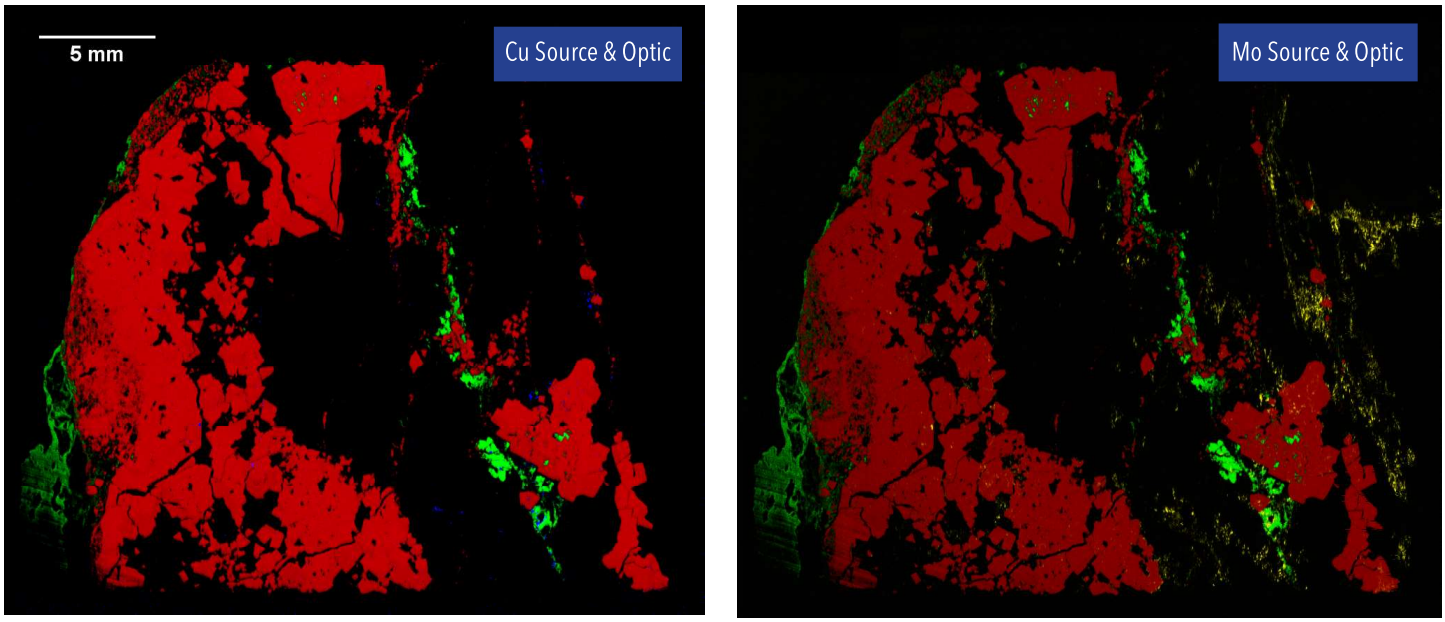


Figure 4: Importance of multiple x-ray source targets: comparison of XRF images taken at two different energies (Cu, left and Mo, right). As can be seen, the Cu source/optic combination produces better Fe (red) and K (green) sensitivity. It also enables trace detection of Ag (blue). In comparison, the Mo source/optic uniquely provides Bi (yellow) detection.

2) Sigray's Ultrahigh Brightness Source

Sigray has designed an x-ray source that offers more than 10X the brightness of the leading microfocus x-ray sources widely used in microXRF systems. This is achieved through incorporation of a diamond substrate, which provides outstanding thermal and mechanical properties. Note that to first order approximation, the brightness of an electron bombardment x-ray source is proportional to the electron power density on the anode, which is limited by the melting of the anode in conventional x-ray sources.

In Sigray's source, the x-ray targets are in close thermal contact with the diamond to allow rapid thermal dissipation of the heat generated, enabling substantially higher electron power loading and therefore brightness of the x-ray beam produced. Table 2 lists specifications of the AttoMap source.

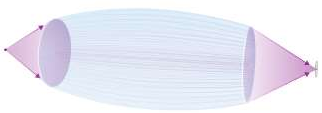
Ultrahigh Brightness Microfocus Source	
Source Type	Reflection
Maximum Voltage (kV)	50 kV
Example Target Materials & Energies	Four selectable, such as: Cu (8 keV), Cr (5.4 keV), Mo (2.3 and 17.4 keV), W (ideal for broad spectrum and 8.4 keV) More available on request

Table 2: Specifications for x-ray source

High brightness is achieved for each of the multiple x-ray targets, which can be selected through a computer drop-down menu by the user. Up to four x-ray source target materials (each target typically has one or two strong characteristic x-ray energies) for quasi-monochromatic illumination can be configured.

3) Twin Paraboloidal X-ray Mirror Optics

Almost equally important to the performance of a microanalytical system as the x-ray source is the focusing x-ray optic used. Conventional microXRF systems have relied on polycapillary x-ray optics (concentrators and not imaging optics). The AttoMap uses a powerful **achromatic imaging** optic manufactured by Sigray in a proprietary fabrication process.



5a) Polycapillary Lens
(Used by Conventional MicroXRF)

5b) Novel Sigray Optic
(Used in AttoMap)

Figure 5: X-ray optics. 5a) Left is a polycapillary x-ray lens, used by most microXRF systems. Such optics are a bundle of hollow glass tubes that guide x-rays through many internal reflections. 5b) Below is the novel Sigray twin paraboloidal x-ray optic.

The Sigray x-ray optic overcomes many of the limitations of polycapillaries, including: improved resolution, removal of chromatic aberrations for accurate quantification, increased working distance, and far better x-ray source brightness preservation.

The Sigray optic is critical to enabling the AttoMap's **rapid acquisition speeds** (down to 5 ms per point), due to the optic's superior brightness preservation and high transmission efficiency (70-80%). For comparison, polycapillary efficiencies are ~5-15%.

The AttoMap's optic also ensures accurate quantification. Polycapillary optics suffer chromatic focusing, in which the polychromatic source x-rays are focused onto a smeared spot at the sample for which diameter varies by x-ray energy. The AttoMap's optic is achromatic, so that all source x-rays are focused onto the same tightly focused spot.

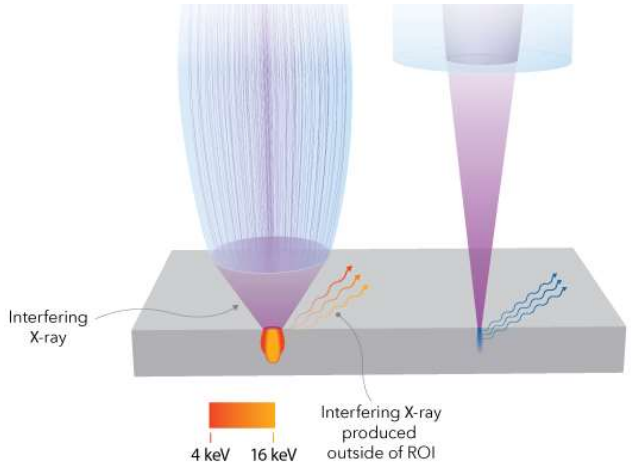


Figure 6: Polycapillary (left) produces a smeared focal spot (innermost diameter corresponds to higher energies), while Sigray optic (right) produces a single tightly focused "pencil beam"

A final advantage of the AttoMap optic is its large working distance of 30 mm (vs. 2-6 mm) that in effect renders a "pencil beam" illumination so that the focal spot size is kept constant, even for samples with topography, such as particles or dust placed on a substrate or electronic boards. In comparison, polycapillary-based microXRF systems are sensitive to surface irregularities, requiring polished samples for accurate results.

Summary

AttoMap: New Capabilities for XRF

Through its significant design innovations, the AttoMap achieves unprecedented performance in sensitivity and resolution that were previously thought only possible with synchrotron-based XRF microprobes.

This includes:

- Unparalleled detection sensitivities for **trace elements** at sub-femtogram amounts in demanding samples such as biological and plant samples
- Thickness measurements for **ultra-thin films and trace dopants** at sub-Angstrom thicknesses
- In situ and time-based measurements for material evolution studies such as battery degradation
- Rapid **particle/contaminant analysis** and reporting for near-line industrial analysis

Such examples are a sub-set of research possibilities with the AttoMap. Contact us at **info@sigray.com** to inquire about a complementary demonstration on your sample of choice.

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