

Application Note: XRF

Non-Destructive Authentication of Gemstones and Coins Using the *Orbis* micro-XRF Analyzer



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Non-Destructive Authentication of Gemstones and Coins

Introduction:

Verification of the authenticity and quality of gemstones and coins is necessary to assess the value of the object. There is a large monetary incentive to alter the appearance of a low-value, common gemstone or coin to be sold at a higher price than fair market value. Furthermore, many gemstones, including rubies, sapphires and diamond, can now be synthesized to a significant size and remarkable gemstone quality. It is essential that authentication testing is non-destructive as any destructive testing of a potentially valuable gemstone or coin will reduce the value of the article.

Alteration of gemstones and coins often adds additional chemical substances or leaves chemical traces. The gemstone synthesis process typically incorporates trace levels of catalyst materials or reactor components in the gemstone or lacks the trace elements found in a natural gemstone. Simple, non-destructive detection of additives or residuals is important for the authentication process. Energy dispersive x-ray fluorescence (EDXRF) allows elemental analysis from Na to Bk simultaneously. In the EDXRF technique, exciting x-rays are shone on the sample. This in turn causes elements within the sample to emit “fluorescent” x-rays characteristic of the source element. Fluorescent x-rays can be emitted from tens to hundreds of microns within the sample and therefore, provide important information about a sample that has been masked at the surface. EDXRF is a non-contact, non-destructive measurement like a medical x-ray system or an airport luggage scanner. Sample objects can be analyzed as is without coating or use of other destructive sample preparation treatments.

In this application note, we will examine several gemstones, including diamond, black pearl and sapphire, and a German coin minted in the 1920’s.

Instrumentation:

For this series of problems, we will demonstrate the use of the Orbis micro-XRF spectrometer. The Orbis is equipped with a low-power (50 W, 50 kV) micro-focus Rh x-ray tube. A Mo anode X-ray tube is also available as an option. The Orbis is equipped with x-ray optics to generate smaller x-ray beam sizes for various applications. The standard Orbis version can be fitted with 100 μm or 300 μm mono-capillaries and/or 1 mm / 2 mm collimators for larger spot sizes. The sample is viewed with a 10x color CCD camera for coarse sample positioning and 100x color CCD camera for fine positioning under the x-ray beam. The Orbis PC version of the instrument is fitted with a high-intensity poly-capillary (PC) lens that focuses the beam down to 30 μm . The Orbis fitted with collimator or poly-capillary is equipped with a computer-controlled 6 filter primary beam conditioner. Primary beam filters are used in some of the examples presented to improve detection limits or reduce diffractive noise. A motorized, computer-controlled XYZ stage is used in both versions. The large sample chamber can be operated in air or vacuum. Vacuum is required to detect low-energy elements, for example Na, Mg and Al. The system is supplied with an electrically cooled Silicon Drift Detector (SDD) for detection of elements from Na to Bk or, as an option, with a large area Si(Li) detector, cooled by liquid nitrogen.

Case 1: Diamond

Diamonds have long been valued for their beauty. The value of a diamond is based on the carat (i.e. weight), color, clarity and cut. Individual characteristics such as yellow tint, cracks and inclusions can dramatically influence the value of the diamond. Diamond is essentially a pure carbon lattice perhaps with a few trace impurities. For example, the color is affected by various extremely low-level impurities. Therefore, in an XRF measurement, we should only expect to see scattered x-rays and the characteristic signature of the x-ray tube, which is dictated by the anode material.

A practice, which has become more common, is to fill cracks in gemstones to mask their appearance to the naked eye. This is done by choosing a filler material which has an index of refraction approximating that of the gemstone. For diamond, one filler material is glass doped with heavy metals such as lead (Pb). The heavy metal dopants increase the index of refraction of the glass.

In this case, the configuration of the Orbis was as follows:

Orbis configuration: 10x / 100x CCD cameras
Mo x-ray tube
2 mm collimator with a Mo x-ray filter

The goal was to examine a large area of the gemstone at one time. Therefore, the system was fitted with the largest collimator, i.e. 2 mm diameter.

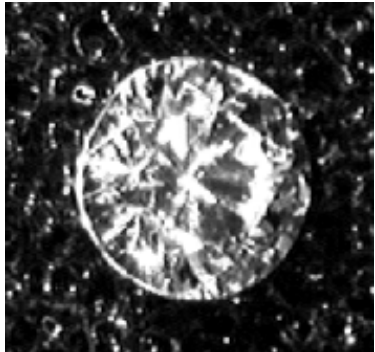


Figure 1: Orbis image of a diamond at 10x magnification.

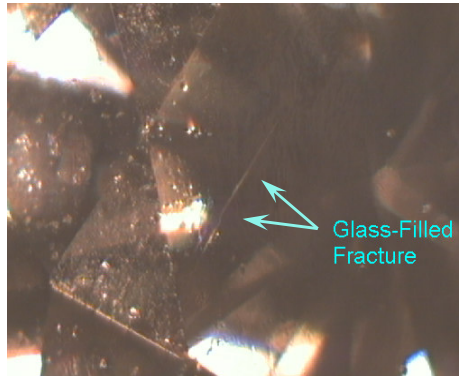


Figure 2: Orbis image of an area around a crown facet of the diamond at 100x magnification.

In Figure 1, we can see the diamond from the view of the 10x camera of the Orbis. This allows for quick, coarse sample positioning. The sample is finely positioned under the x-ray beam using the 100x color camera. A view from the 100x camera is shown in Figure 2. In Figure 2, you can see an optical anomaly. It is not necessary in this case to have this spot precisely positioned, since the 2 mm collimator produces an x-ray beam which covers almost the entire field of view of the 100x camera.

In Figure 3, we show a section of the resultant XRF spectrum. Two characteristic x-ray line series are observed. One corresponds to Pb and the other to Bi. These elements do not occur

naturally in this diamond and are associated with a glass filling, which was used to fill a crack in the diamond.

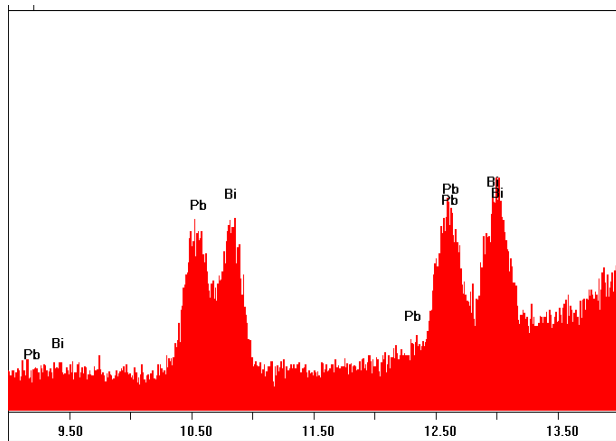


Figure 3: XRF spectrum of a diamond suspected to contain a glass-filled crack.

Case 2: Black Pearl

Long prized for their lustrous splendor, pearls are organic gemstones produced by oysters. Within the family of pearls, black pearls are especially prized and valued. Figure 4 shows an example of black and white pearls. Pearls are composed of layers of calcium carbonate surrounding some tiny seed particle that has irritated the oyster. The coatings of calcium carbonate are the oyster's way of protecting itself from the irritant. Traces of Sr can be found in the pearl since Sr is a natural lattice substitute for Ca and Sr is found in low-level concentrations in seawater. Therefore, in an XRF spectrum, we should expect to see Ca and Sr peaks.



Figure 4: White pearl necklace with a black pearl pendant.

It is relatively easy to plate Ag onto smooth objects, such as a pearl. This has led to the practice of taking a white pearl and plating it with Ag to give it the appearance of a higher value black pearl. Here, we look for a characteristic Ag x-ray signature in the XRF spectrum.

In this case, the configuration of the Orbis was as follows:

Orbis configuration: 10x / 100x CCD cameras
Mo x-ray tube
2 mm collimator with a Mo x-ray filter

Again, the goal was to analyze a large area of the gemstone quickly. Therefore, the system was fitted with the largest collimator, 2mm.

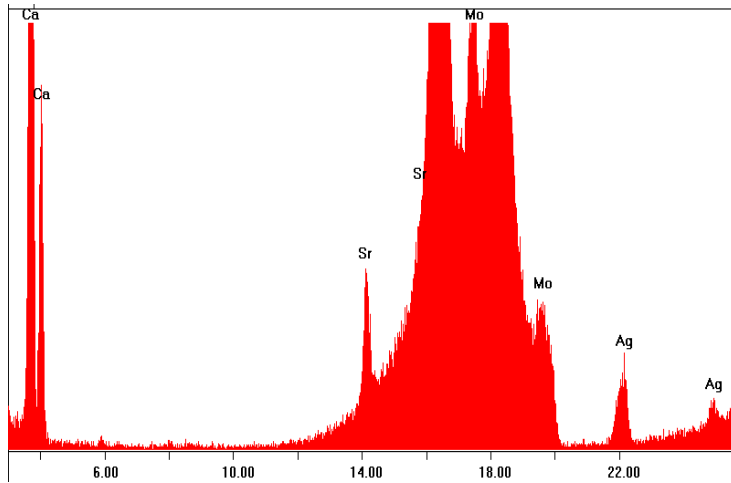


Figure 5: XRF spectrum of a suspected faux black pearl.

In Figure 5, nearly the full XRF spectrum from a suspect black pearl is displayed. Of course, x-ray lines from Ca and Sr occur. The broad peaks from 16 keV to 20 keV result from the scattering of the filtered Mo tube. At 22 keV and higher, the Ag x-ray series is observed confirming that the “black” pearl is really a more common white pearl plated with Ag.

Case 3: Natural versus Synthetic Sapphire

Sapphire is an aluminum oxide mineral also known as corundum. Sapphire is well-known with blue coloring; however, sapphires can range in color from blue, green, yellow and purple with the coloring arising from the presence of individual or combinations of trace impurities including Fe^{3+} , Ti^{4+} , Mg^{2+} and Cr^{3+} .



Figure 6: Blue Sapphires

Sapphire can be readily synthesized to a substantial size with a quality equal to natural gemstones. In this case, 2 sapphires, one synthetic and one natural, were measured using an Orbis equipped with a Rh tube, 1 mm collimator and computer-controlled primary beam filter accessory. A spectral comparison is shown in Figure 7 with the natural blue sapphire shown in solid red and the synthetic blue sapphire shown in blue outline.

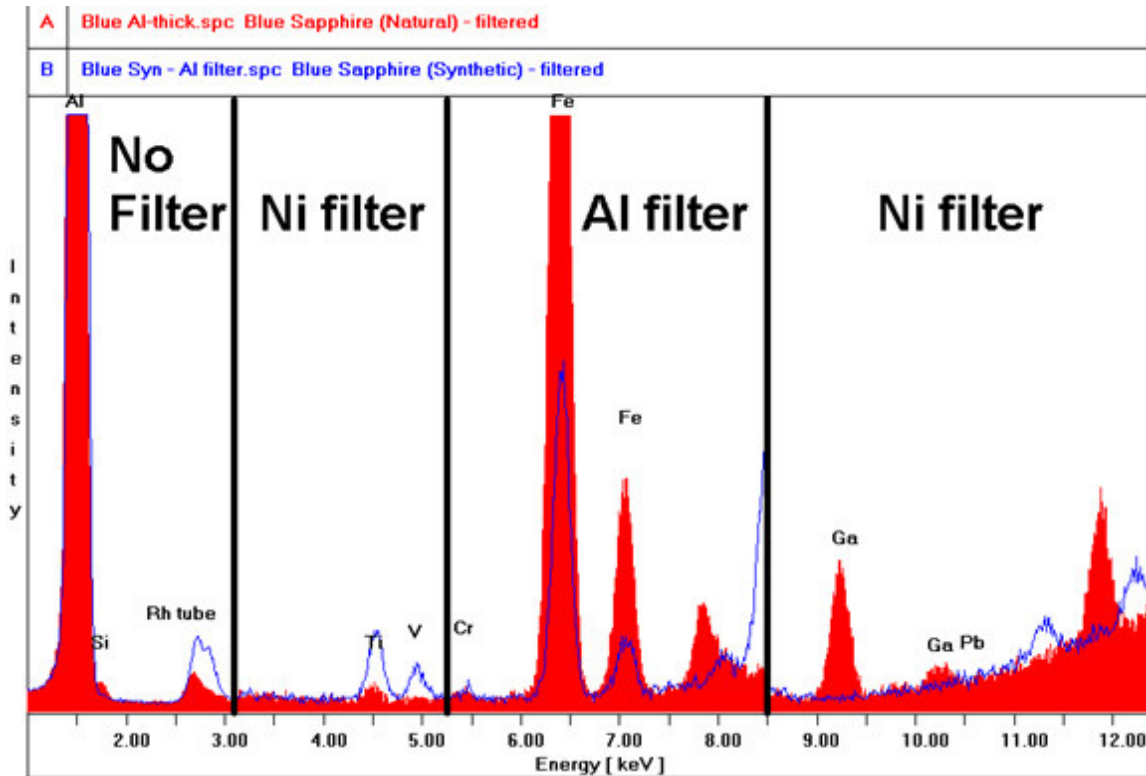


Figure 7: An XRF spectral comparison of natural sapphire (red) to synthetic sapphire (blue). The spectra were measured under 3 different filter conditions for improved detection limits: No filter < 3.1 keV; Al filter from 5.3 to 8.5 keV; and Ni filter from 3.1 to 5.3 keV and > 8.5 keV.

Various primary beam filter conditions were used to improve detection limits for relevant elements across the spectral range. Filters minimize unwanted background noise and diffractive peaks while increasing peak to background ratios.¹ No filter is used at the low end of the spectrum to acquire elements like Al and Si since the Be window on the X-ray tube already acts as a primary filter in this spectral region.

The Al(K) peak corroborates the identity of the base matrix as an alumina as opposed to a silica glass or crystal, which would display a major Si(K) peak in the spectrum instead of Al(K). The natural sapphire shows a large Fe(K) peak which generates the blue color and a Ga(K) peak which is a typical impurity in natural blue sapphires. The synthetic sapphire shows a much smaller level of Fe and other trace impurities of Ti, V and Cr. Ga is absent in the synthetic sapphire spectrum which is a strong indicator of the synthetic nature of the gemstone.

In Table 1, quantitative results are presented on the natural and synthetic sapphires. Quantification was done via fundamental parameter modeling methods without the use of standards. Trace element quantification is useful to assist in distinguishing natural from synthetic gemstones as well as determining the geological source of the natural gemstone.² Pb was included in the spectral analysis as an indicator of the use of glass fillers to repair cracks in the stones. No Pb signal was observed in these samples indicating that no glass filler was applied to either sapphire.

¹ For example, see: Sandborg, A. and Shen, R. "The Use of Filters in EDXRF," *EDAX Editor*, **14**, 8-12.

² Muhlmeister, S., et al. (1998), "Separating Natural and Synthetic Rubies on the Basis of Trace-Element Chemistry," *Gems & Gemology*, **34**, 80-101.

Oxide	Natural [PPM]	Synthetic [PPM]	Filter	Comments
MgO	< LOD	< LOD	None	
Al ₂ O ₃	Balance	Balance	None	
SiO ₂	2967	~ 100	None	
TiO ₂	245	890	Ni	
V ₂ O ₃	< LOD	155	Ni	
Cr ₂ O ₃	69	53	Al	
Fe ₂ O ₃	4022	906	Al	
Ga ₂ O ₃	245	< LOD	Ni	
PbO	< LOD	< LOD	Ni	No glass filling

Table 1: Quantification results on the natural and synthetic sapphire spectra shown in Figure 7 using “standardless” fundamental parameter quantification methods.

Case 4: German 2-Reichsmark Coin

In 1927, a limited number of 2-Reichsmark coins were minted and, therefore, the value of high-quality 2-Reichsmark coins from this year is high. This coin is counterfeited by altering the year of the coin, typically from another 1920’s coin of a lesser value. Figure 8 displays an image of a counterfeit 1927 Reichsmark coin to be analyzed using the Orbis.



Figure 8: Orbis 10x image of a counterfeit 2-Reichsmark coin (1927).

The counterfeit has been treated with sulfuric acid to highlight where the coin has been altered; however, acid treatment is a destructive test and could damage or degrade the quality of an authentic coin. The Orbis micro-XRF spectrometer is ideally suited for non-destructive analysis of coins. In this analysis, the Orbis PC was employed with a 30 µm poly-capillary.

Orbis PC Configuration: 10x / 70x CCD (with 3x digital zoom) color cameras
 Rh anode tube
 X-ray poly-capillary Lens (30 µm FWHM spot size)

Initially, the qualitative composition of the numeral “2” and the numeral “7” in the year “1927” were evaluated by micro-XRF. If the numerals were of different composition, one could conclude that the “7” was forged on the coin. As can be observed in Figure 9, there is little difference in the qualitative elemental analysis of the two numerals in the year. Note in Figure 9, that the sulfur line at 2.3 keV in the analysis of the “7” comes from the sulfuric acid treatment.

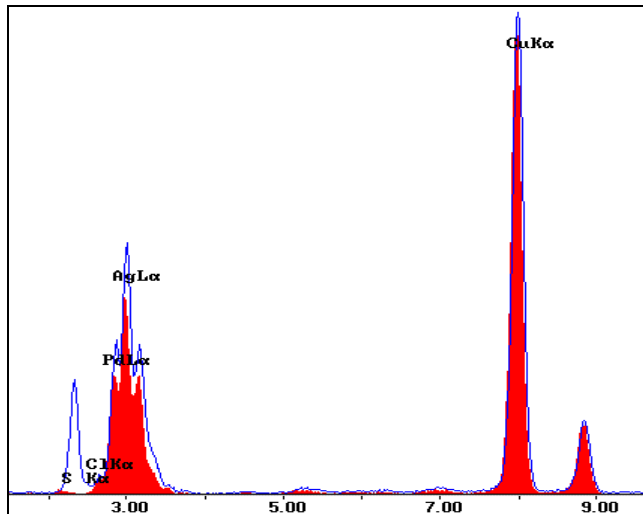


Figure 9: XRF analysis of the “2” (red) and “7” (blue) in the year “1927” on the coin.

The Orbis also has the capability to map differences in elemental composition. An area encompassing the year on the coin was selected for elemental mapping analysis with the following conditions:

Pixels	64 x 50
Dwell Time	0.3 s / pixel
Total Time	approx. 20 minutes

Figure 10 displays the elemental maps for Ag (L line) and Cu (K line). Ag is more prevalent in the background of the coin while Cu is more prevalent in the raised numerals and ornamentation (i.e. the Eagle’s tail and feet). The Cu map clearly shows an underlying numeral “6” overlaid by the numeral “7”. Thus, this 1927 Reichsmark coin was forged from a 1926 coin of far lower value.

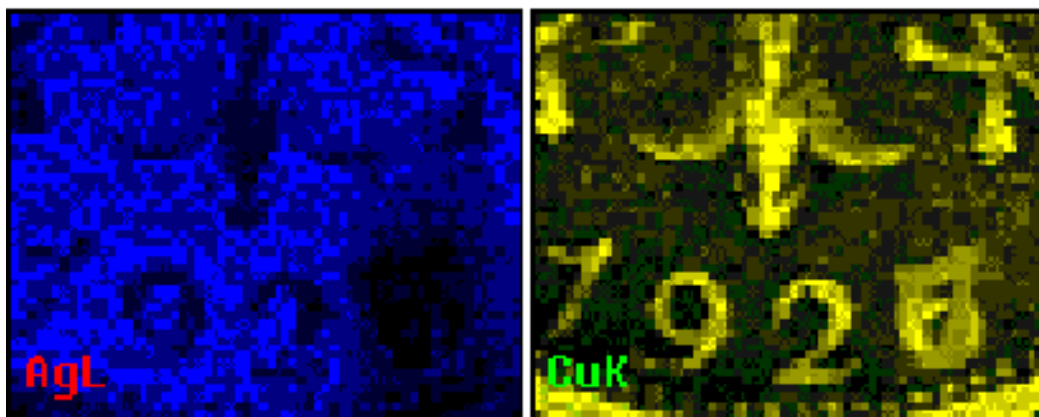


Figure 10: Elemental mapping distribution of Ag (L line; blue) and Cu (K line, yellow)

Summary:

The Orbis Micro-XRF system has been successfully used to authenticate various potentially high-value objects. Authentication was done non-destructively, since the Orbis analysis is based on low-power x-rays and does not require any potentially destructive pre-treatment of the sample. Authentication was readily achieved by determining the inorganic elements which makeup the sample. The presence of elements, which are inconsistent with the sample's chemical composition, history and/or source, can indicate whether that object has been truthfully represented. In a rapid single analysis, Pb and Bi were found in the altered diamond; the synthetic blue sapphire lacks Ga; and Ag was found on the faux "black" pearl. The trace element composition of gemstones as determined by micro-XRF can provide a consistent basis for comparison between gemstones and assist in determining the geological source of a natural gem. In the case of the German coin, a single analysis can be quickly repeated to look for the distribution of an element (i.e. elemental imaging). In this example, Cu was found (in the shape of a numeral 6) in places on the coin where it should not have been.

The Orbis is available in 2 configurations: standard - 100 μm or 300 μm mono-capillary; and PC - high intensity poly-capillary lens yielding a beam spot down to 30 μm . Both Orbis configurations are supplied with a computer-controlled 6-filter primary beam conditioner and are available with 1 mm and 2 mm collimators as an option.