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By Don Kloos

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XRAY V

USING X-RAY FLUORESCENCE FOR ASSAYING JEWELRY AND KARAT MATERIALS WORKS— AS LONG AS YOU'RE NOT EXPECTING A MAGIC BOX

ISION

BY DON KLOOS

Once upon a time, if you wanted to know the gold content of jewelry or karat materials, your only option was to perform a destructive fire assay. Today, however, companies and institutions all over the world turn to X-ray fluorescence—or XRF—for the electronic assay of jewelry and karat materials.

XRF is a relative newcomer to the field of jewelry assay. For practical purposes, the era began in 1987 when I introduced the Seiko XRF instrument to the industry. Since its commercial inauguration, the technique has grown in popularity and in use. The need to accurately assay jewelry and karat materials in a non-destructive way made interest in XRF technology inevitable, but it is still surrounded by controversy and speculation.

From my years of experience, I have concluded that attitude is everything when it comes to making XRF work in the jewelry industry: One has to want to make XRF work in the first place. Common sense, good judgment, experience, and good technique—as well as an understanding of XRF and its limitations—are required to benefit most fully from the technology.

XRF is an instrumental chemical analysis, and performing such an analysis is still not quite as routine as, say, Xeroxing copies or stapling papers. Expectations of a magic black box are far more than the XRF method can live up to. But for jewelry and karat alloy analysis, in conjunction with fire assay and other techniques, XRF has a lot to offer—if you understand what it can and cannot do.

HOW XRF WORKS

For a basic understanding of XRF, consider this analogy: When light strikes a fluorescent poster, your eye picks up the different colors of light fluorescing from the paint. Your eye sends an electro-chemical signal to your brain, which interprets the signal into a color and image composition.

Likewise, the XRF machine sends X-ray light onto the jewelry sample, which subsequently emits new X-ray light back, the colors and intensities of which depend on the composition of the jewelry.

A detector (eye) 'sees' the emitted X-rays and acts like a prism to separate them into the different colors, or wavelengths, and convert them into distinct electronic signals. The signals are sent through the electronics to the computer (brain), where they are processed into elemental composition as a percentage of gold, silver, copper, etc. The main difference is that XRF is using 'colors' that are invisible to us, but not to the instrument.

While the basic principles behind XRF are simple, there are a couple of important considerations to keep in mind. The XRF analysis is surface-oriented and is effectively just 0.001 inch deep. Small volumes of material much less than $^1/_{1000}$ of a cubic centimeter and masses of only 30 millionths to a few tenths of a gram are analyzed. These numbers vary somewhat, depending on the equipment used and the alloy, but they are generally quite small.

THE QUESTION OF ACCURACY

When discussing the accuracy of XRF, it is important to distinguish accuracy from precision. Precision relates to the repeatability of the instrument measurements, while accuracy refers to the measurement's closeness to the "true value," often considered to be the overall fire assay value. (To learn more about the accuracy of fire assay, visit *AJM Online* at *www.ajm-magazine.com*.)

In this case, the equipment's precision has a profound effect on the perception of XRF accuracy.

PRECISION

Understanding the precision of XRF measurement requires some understanding of general statistical principals. Again, consider the analogy of how XRF works.

If you took just a very quick glance at the fluorescent poster in dim light, you might be uncertain of all the colors, hues, and shapes present. If you glanced at it multiple times, or took a longer, closer look under brighter light, you would be much more certain (or, statistically speaking, "confident") of what you saw. This is assuming your vision is good and you're not color blind (i.e., you have good equipment).

Likewise, in statistical terms, XRF assays exhibit normal uncertainties in the data. This uncertainty, or "measurement precision," is one of the most commonly misunderstood aspects of XRF jewelry analysis, and it is often erroneously attributed to bad accuracy.

In statistics, precision is rated, or indexed, in units of the "standard deviation" (SD), which is calculated from the data using a basic formula. A smaller SD means better precision.

Since we want the most confidence in our XRF assays, we seek to minimize SD. Practically, this usually means performing longer individual measurements, compounding replicate measurements, or using more powerful and effective equipment to improve the precision. SD is commonly expressed as a percentage, or a plus/minus, of the average result for a given level of confidence. Here's what a typical set of XRF data with statistical interpretation might look like:

• One hundred XRF measurements at 100 seconds each are taken on the same spot of a ring shank. They average 58.33 weight % gold with an SD of 0.1 weight %

TABLE 1. XRF MEASUREMENT PRECISION

Number of Measurements	100	100
Measurement Time, seconds	100	25
Average of 100 meas., wt% gold	58.33	58.33
Standard Deviation, SD, wt% gold	0.1	0.2
68% Confidence Interval, 1 SD, wt% gold	58.23 to 58.43	58.13 to 58.53
99.7% Confidence Interval, 3 SD, wt% gold	58.03 to 58.63	57.63 to 58.93

gold. This can be expressed as 58.33 ± 0.1 weight % gold at a 68% (1 SD) confidence level. In other words, 68 of those 100 measurements fell between 58.23 to 58.43 weight % gold. The range would be greater at a higher confidence level (see Table 1).

• This example is identical to the previous example, except only 25 seconds are used for each measurement. The average is still 58.33 weight % gold, but the SD is now twice as high at 0.2 weight %, or 58.33 ± 0.2 weight % gold at 68% (1 SD) confidence level. In other words, 68 of these 100 measurements fell between 58.13 and 58.53 weight % gold, and the range would be even greater at a higher confidence level (see Table 1). Shorter measurement times produced poorer precision and a higher SD, but the average was the same: 58.33 weight % gold.

In the examples above, if you take just one short measurement at 25 seconds, the SD is 0.2 weight % gold, and the result falls somewhere between 57.63 to 58.93 weight % gold at the highest level of confidence. In this case, you might incorrectly interpret that XRF is inaccurate. However, the problem lies in the procedure; the large statistical fluctuation is due to the short measurement time.

You can gauge the quality of the results (and the XRF instrument) partly on precision. But you must also consider accuracy as a separate factor.

ACCURACY

If precision means how narrow the range of measurements is, accuracy means how closely that range centers on the "true" value. There has been much study and debate about the accuracy of XRF, meaning the parity between fire assay and XRF readings. It is imporant to note that fire assay is not absolute and is also subject to error and statistical fluctuations. Based on my study and experiences, I have compiled accuracy guidelines to be used as a rule of thumb for jewelry and XRF (see Table 2). Keep in mind that these guidelines are somewhat application-specific.

WHAT'S IN IT FOR YOU?

Essentially, the benefit of using XRF comes down to money—in terms of material, time, process control, efficiency, risk, competition, and reputation. Each segment of the jewelry industry, including casting/manufacturing, wholesale/retail, and refining, can make good use of the technology in different ways.

ELECTRONIC ASSAY FOR CASTING

This is the ideal situation for XRF. It is essentially an instant "electronic fire assay," since the accuracy and precision between the two are most comparable in this case. The items to be tested are usually limited to a finite number of known karat alloys, and sample preparation can be effectively controlled. Both of these factors enhance the efficacy of XRF.

In casting, I see the primary benefit of XRF to be karat-control, permitting reduction of overkarat margins and protection against underkarat alloy. By using XRF prior to casting, the karat fineness is accurately validated before the melt is cast or the jewelry undergoes further processing steps. This approach has been used for over 10 years by many large and small manufacturers, and it has saved them kilos of gold and millions of dollars.

There are also additional benefits to XRF analysis: You can obtain results in minutes; the use of acids, lead, silver, cupels, and lab overhead are reduced or eliminated; and information about the whole alloy composition is obtained, such as the amount of silver, copper, zinc, and nickel. (Trace elements, such as silicon or boron, are usually not detectable.)

Typical procedures using XRF in casting might look like this:

• **Pindip Test** In the furnace room, tongs are used to dip a glass vacuum tube, which is called a pindip tube, into the crucible to withdraw a few grams of the melt. The pindip tube and sample are quickly thrown into water to quench the metal in a homogenous state. The resulting metal pin sample is rolled flat, cleaned, and placed into the XRF instrument chamber for analysis. I've seen the whole procedure take just a few minutes, and the results are usually within 0.1 weight % of fire assay.

• **Shot Test** Grains produced by a casting machine, or by pouring molten metal from the crucible into water, are flattened, cleaned, placed into the XRF instrument chamber, and analyzed. In some cases, no preparation of the grains is necessary. Results are comparable to the pindip test.

• **Miscellaneous Testing** XRF is also used in manufacturing environments to check metal production grindings, sink washings, rinse waters, and scrap melts for precious metal content. This helps keep tabs on the gold for accounting purposes.

TABLE 2. TYPICAL AVERAGE XRF ACCURACY

Category	Accuracy, wt% Gold	Comments
Casting	0.05	Pindips, shot, grains
Finished Goods	0.05 to 0.25	Cast: homogenous, no plating or solder
Finished Goods	1 to 2	Plated, soldered, stamped
Refining	0.1 to 0.5	Solids: pindips, scraps, drillings

KARAT SCREENING OF FINISHED GOODS

Finished goods present a different set of conditions and challenges for XRF, since you do not have control over the sample preparation as in the casting environment. Finished jewelry requires a different application of the technique with different goals in mind.

The main purpose is to protect the consumer. In doing so, you preserve the company's reputation and investment in merchandise, as well as comply with trade and stamping laws and reduce your liability.

Real quality assurance is active—it's not a passive reliance on vendor certifications or promises. By law, the seller is ultimately responsible for his or her goods and therefore is responsible to ensure their quality. Because XRF, unlike fire assay, is non-contact, non-destructive, and relatively quick, finished goods analysis would seem to be an ideal application for the technology. However, XRF has limitations.

For finished goods, accuracy can be affected for a variety of reasons. The sample geometry can affect the results on some instruments, which may be designed to measure large areas on flat samples. In addition, the parent alloy in finished jewelry may or may not be homogenous, the sample alloy is often unknown, and calibration standards may not be handy.

For example, cast yellow gold charms and ring shanks are fairly homogenous and ideal for XRF, but composite jewelry, such as Black Hills jewelry, is not. It may comprise different alloys and solders, or plated, bombed, and pickled materials—all in one piece. Many chains, ropes, and stamped goods fall into this category as well. In short, the accuracy of XRF testing of finished goods can be 'spot on' or off by up to a karat, depending on the type of jewelry.

Which brings us to a real quandary. Jewelry demands vigorous, non-destructive testing, but the XRF technique might not absolutely guarantee that the legal requirements are met in some instances. With no other non-destructive, accurate alternative, what is the viable solution? Don't assay at all? Test just a few pieces and take a chance? Fire assay all of your jewelry?

The answer is what I term "karat screening"—the judicious use of XRF in quantitative and semi-quantitative modes to find suspect underkarat goods.

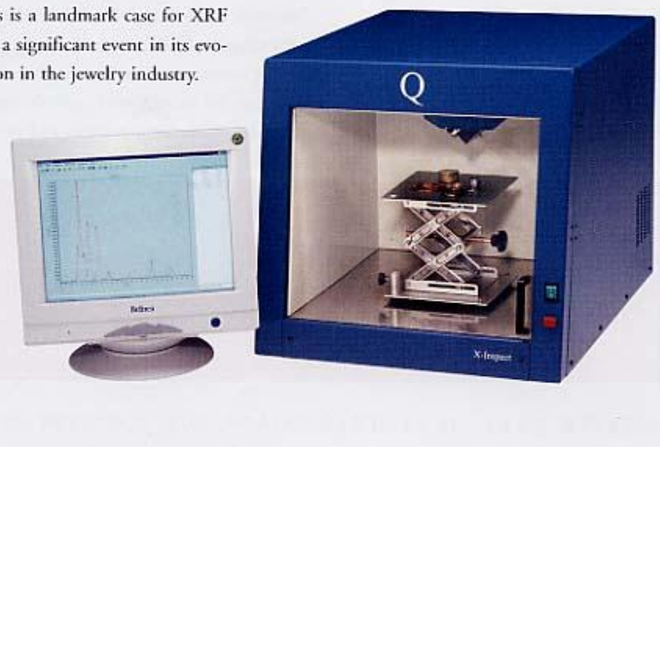
Over the last 14 years it has come to be more accepted by retailers, wholesalers, distributors, manufactures, assay offices, and industry oversight organizations. By applying common sense, experience, and understanding, jewelry can be effectively screened using XRF as a first wave defense to indicate suspect underkarating.

XRF is fully capable of providing "clear and convincing evidence," says Cecilia Gardner of the Jewelers Vigilance Committee (JVC), and fire assay can be called upon for further substantiation when necessary. In a recent precedent-setting case for XRF, the JVC employed XRF testing to screen jewelry from within the state of New York. This resulted in the prosecution of Manhattan jewelry distributors and retailers by New York Attorney General Eliot Spitzer, full public disclosure of the defendants' identifications, and fines levied to two importer/distributors and 18 retailers totaling over $100,000. This is a landmark case for XRF and a significant event in its evolution in the jewelry industry.

Here are some practical examples of how karat screening for finished goods might look:

• **Simplest** The sample is a solid cast ring or charm of yellow alloy. The examiner's experience identifies that it is homogenous and that there is a suitable calibration in the instrument that accommodates the sample alloy. The reliability of the measurement in this circumstance is quite high—especially if several measurements are taken or an entire area is scanned. In this case, any negative deviation from plumb is highly suspect.

• **Most Difficult** A chain or rope sample, more complicated because of its heavy coating of gold plating and solder, characteristically reads a fraction of a karat higher than might be expected. The XRF elemental analysis also shows the presence of solder alloy in addition to the expected parent karat alloy. If the expected higher readings are not obtained, further investigation may be necessary. At this point, the solder or plating can be polished away in a small area and it can be re-tested again to increase measurement reliability. There is now evidence that no significant negative deviation from plumb is indicated. The sample is passed with much higher assurance than before it was tested.



QUICK SETTLEMENT AND PRE-ANALYSIS

For refiners and karat scrap brokers, XRF serves a valuable function by providing a reasonable estimate of metallic scrap value in a very short time. It is mainly used for pre-screening to enable a quick partial settlement payment of refining lots, and for pre-analysis purposes to help prepare for efficient refining of the materials.

The expectations for accuracy in these circumstances are usually relaxed some, since there is a reasonable margin for error built into the transaction, and the final determination is based on fire assay for large lots. In my experience, an accuracy of 95 to 98 percent has been palatable under these circumstances. Also, the reliable detection and quantification of valuable metals besides gold is a nice bonus.

For very small lots (up to several ounces), XRF is routinely accurate enough to complete a transaction at the point of presentation. XRF has also been used effectively to analyze sweeps and liquids for precious and strategic non-precious metals. The only caveat here is that the

TABLE 3. XRF EQUIPMENT RELATIVE COMPARISON

CATEGORY	WDXRF	LAB-EDXRF	MINI-EDXRF	MICRO-EDXRF
Price, $ US	100K to 500K	65K to 100K	35K to 40K	15K to 40K
Maintenance	highest	high	moderate	lowest
Ease of Use	most complex	complex to moderate	moderate to complex	easy to complex
Accuracy	highest	high	high	high
Precision	highest	poor, moderate	poor, moderate	high
Minimum Detection Limit	best	good	moderate	poor
Detector Type	crystal with gas proportional	solid state Si(Li) or SDD	solid state Si pin diode	gas proportional
Elemental Resolution	highest	moderate	poor	worst
Measurement Time	shortest	long	long	short
Measurement Diameter, mm	5 to 31	2 to 25	2 to 10	0.3 to 0.5
Sample Types	flat smooth solids, liquids, pressed powders	flat or curved solids, liquids, or powders	flat or curved solids, liquids, or powders	flat or curved solids, small samples

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refiner must be sure that the XRF instrument is able to account for all the metals in the sample. To do this, it must be able to separate all the elements, as well as to see lower concentrations and lighter elements. This requires knowledge of the equipment's specific limitations.

XRF PRODUCTS

Prior to the introduction of the Seiko XRF in the late 1980s, there were few, if any, commercial offerings of XRF equipment directed at the jewelry industry. Since then, I have seen many new product offerings at various levels of performance and different price points, ranging from $10,000 to $500,000. Equipment can best be evaluated with a price-versus-performance frame of mind, keeping the main analytical goal in focus. Higher price generally means higher performance, maintenance, and complexity, and the converse is true.

There are basically two types of XRF categories, EDXRF (Energy Dispersive XRF) and WDXRF (Wavelength Dispersive XRF), with minor subcategories. There are very few instruments designed specifically for jewelry analysis. No single WDXRF or EDXRF product currently possesses all the strengths and benefits the technology has to offer for analyzing jewelry and karat materials. All machines have strengths and weaknesses.

WDXRF, with its ultimate performance, traditionally defines the limits of the XRF technique. Carrying the highest price tag, WDXRF is designed for large, flat samples, not curved jewelry.

On the more affordable end, the Micro-EDXRF has been widely used over the past decade for jewelry analysis. This model is attractive because of its small measurement area, relatively low price, and good precision, but it has poorer element resolution and detection limits.

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In the last few years, a trend has produced no less than six new Mini-EDXRF instruments that use a new, smaller detector called the Silicon Pin-Diode. The use of these lower-cost detectors allows equipment manufacturers to offer these machines for more affordable prices, but with a sacrifice in relative performance. (For general guideline purposes, relative XRF product characteristics are cataloged in Table 3.)

But no matter which model you use, it's important to remember that XRF is not the magic black box of jewelry analysis. It is rather an instrumental analysis technique replete with unique advantages, limitations, and rules.

The acceptance and use of the technique has grown immensely since I first became involved in the jewelry industry, and major breakthroughs in product and price improvements are on the horizon. It is my hope that increased use of XRF will continue to advance the goal of greater quality, process control, and compliance in the jewelry trade.

Don Kloos is a chemist and marketing specialist with 25 years of experience with XRF technology, 15 of them with jewelry applications. He can be reached by e-mail at donkloos@earthlink.net *or by phone at 1-714-897-9779.*

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For more suggested reading on XRF, visit *AJM Online* at *www.ajm-magazine.com.*