

Analysis of Gold Karat Alloys Using Proportional Counter Based Micro-EDXRF

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Introduction.

The analysis of gold karat alloys is a central function in manufacturing and distributing jewelry as well as brokering and refining related gold karat scrap. In particular, gold karat alloys containing large quantities of Au, Ag, and Pd, as well as base metals Cu, Ni, and Zn need to be accurately monitored and controlled. XRF is commonly used for elemental analysis of precious metals for such screening and production control purposes. Advances in spectral processing and quantitative fundamental parameter algorithms have expanded the usefulness of the proportional counter-based Micro-EDXRF spectrometer. This work presents a description of: 1) basic XRF theory, 2) a low cost proportional counter-based Micro-EDXRF spectrometer, 3) analytical technique, and 4) analysis data of gold karat alloys. Data is presented comparing fire assay versus Micro-EDXRF.

1) XRF Theory and Principles

Stokes Law defines fluorescence as a process in which an atom or molecule absorbs a photon of one energy and subsequently emits another photon of lower energy. The specific fluorescence process on which XRF analysis is based is called the Photoelectric Effect. An orbital electron, usually of the K, L, or M shell is ejected from the atom after initial absorption of an incident photon of sufficient energy, leaving a 'vacancy' behind. The vacancy is filled by another orbital electron from within the atom which 'jumps' down from a higher energy orbital. The difference in energy between the two involved orbitals is emitted as an X-Ray photon of electromagnetic radiation that is characteristic to that particular atom. See figure 1, below.

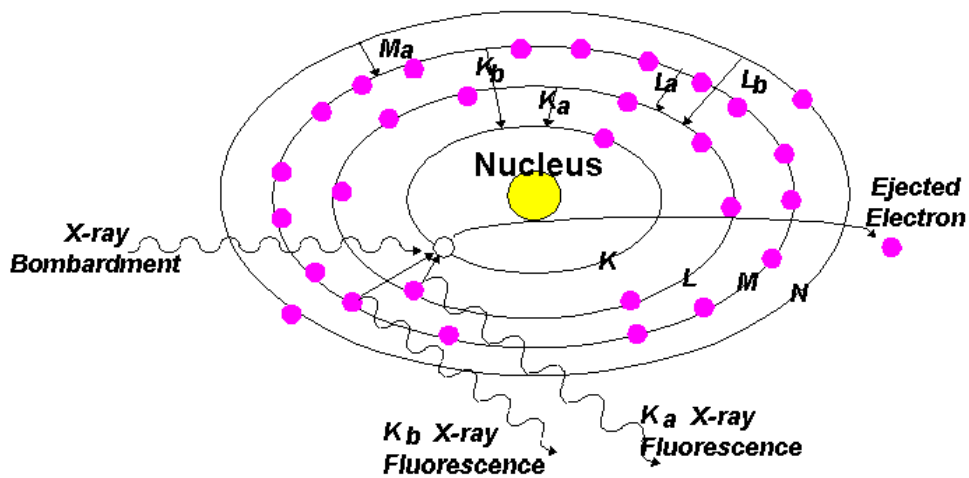
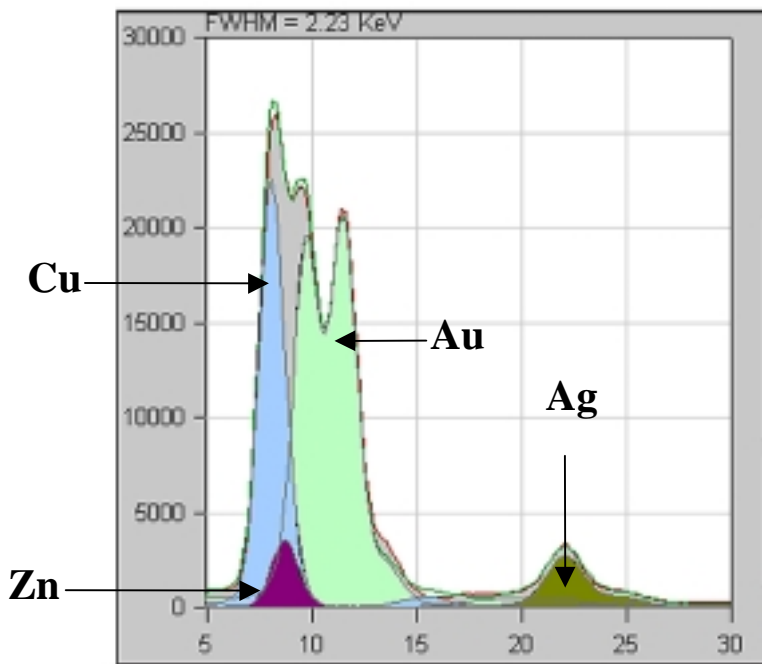


Figure 1. X-ray Fluorescence: the photoelectric effect

Thus each element will fluoresce its own unique characteristic secondary X-Rays, or usually, a family of X-Ray lines when exposed to sufficiently energetic X-Ray radiation. The intensity of the characteristic secondary X-Rays produced in the sample are related to the analyte concentration, the sample matrix, and excitation and detection conditions. An example of a 14K yellow gold karat alloy X-Ray spectrum is shown in Figure 2, below. Note in this X-Ray Fluorescence spectrum, the number of photons, or intensity, is plotted on the Y-axis and the energy, in KeV units, of the photon is plotted on the X-axis. This plot results in each element being represented by a peak, or group of peaks, which may or may not be totally resolved from one another. (1)

Figure 2: 14KY Spectrum



Worth mentioning here, is the Gaussian statistical law that governs the precision, or repeatability, of XRF measurements. Precision should not be confused with accuracy, as they are two different parameters of the quality of the analysis. Accuracy pertains to the closeness to ‘true value’ and precision to repeatability.

The statistical index that quantifies repeatability is the ‘standard deviation’. When ‘N’ number of X-Rays are counted, or collected, during a measurement, then the uncertainty, or standard deviation, of the measured quantity ‘N’ is simply the square root of ‘N’. For example, if 100 Au X-Rays are collected during a measurement, then the standard deviation is 10 Au X-Rays. Thus, this measurement would have a 10% relative standard deviation. To improve the precision it would be necessary to collect more counts, which is usually done by increasing the measurement time, or further optimizing the other measurement conditions. See Table 1, below.

Note that ultimately, it is not just the total number of counts, N, that matters, but also the peak-to-background ratio of the analyte X-Ray intensities since the precision of the background intensities are propagated into the overall precision as well. For further treatment of statistics and X-Ray counting, the reader may refer to Bertin (2) and Jenkins et al (6).

Table 1: Gaussian X-Ray Counting Statistics

$$SD \sim \sqrt{N} \quad (N = \text{Analyte Counts})$$

<u>N</u>	<u>SD</u>	<u>%SD</u>
100	10	10
10,000	100	1
1,000,000	1000	0.1

2) The Micro-EDXRF Spectrometer

The basic ‘kernel’ of the Micro-EDXRF spectrometer is shown in Figure 3. A pin-hole fixture (“collimator”) typically 0.3mm in diameter, is used to collimate X-Rays from a 50KV microfocus X-Ray tube source onto the sample, which is placed below on a high precision motorized programmable 12”x 12”x 6” XYZ stage.

The stage serves to ‘raster’ the sample back and forth under the X-Ray beam to enhance uniform sampling, change measurement locations, or move a new sample into measurement position. Samples are observed on CCTV with an overlaid crosshair reticle that facilitates accurate and repeatable positioning of the primary X-Ray beam on the sample measurement site within 10um.

The fluoresced X-Rays are captured with a 2” diameter cylindrical Xe-filled sealed gas proportional counter, also mounted above the sample. The X-Rays captured by the detector generate electric pulses in the gas that are amplified and sent to the computer to be processed by a multi-channel pulse height analyzer.

The resulting X-Ray spectrum (Figure 2) is treated with spectral processing algorithms and then interpreted quantitatively by an advanced comprehensive fundamental parameter algorithm. Results are displayed directly on the PC’s CRT, printed, or archived for statistical treatment.

In addition to quantitative bulk elemental analysis, the Micro-EDXRF spectrometer, or ‘small spot XRF’, has the unique added dimension of analyzing the distribution of elements within a material. That is, it can ‘map’ the elemental uniformity of the sample by analyzing multiple areas with a small spot, or by scan-averaging large areas. Material uniformity is also important in understanding a manufacturing process in addition to just knowing the overall bulk material composition. For example, an entire casting tree can be analyzed at various points to ensure uniformity of Au distribution from top to bottom in addition to overall bulk Au content. Figure 4 shows a Micro-EDXRF spectrometer.

Figure 3: Micro EDXRF Optics

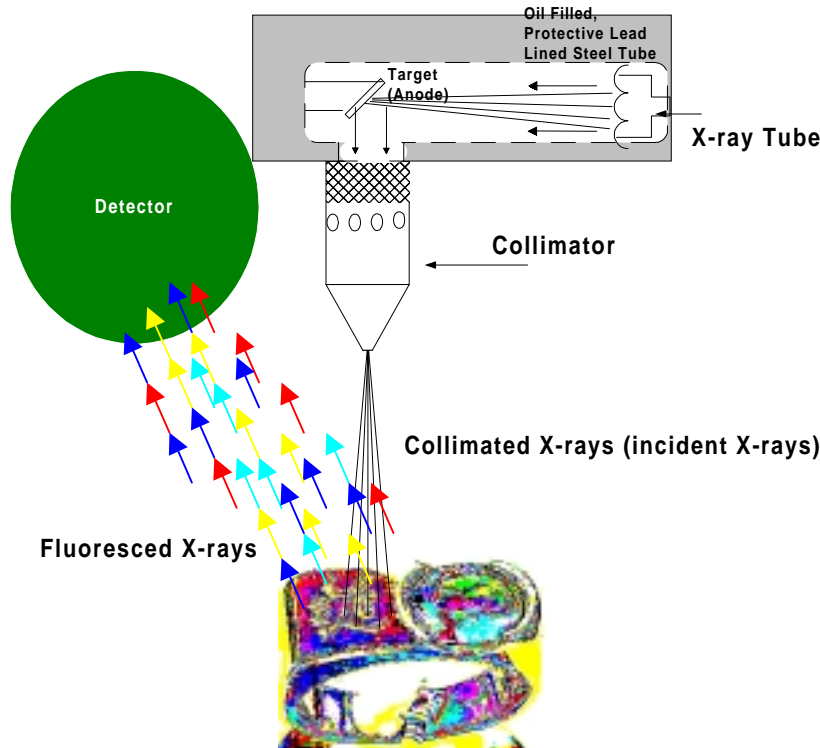


Figure 4: Micro-EDXRF Spectrometer (courtesy CMI International)



3) Analytical Technique

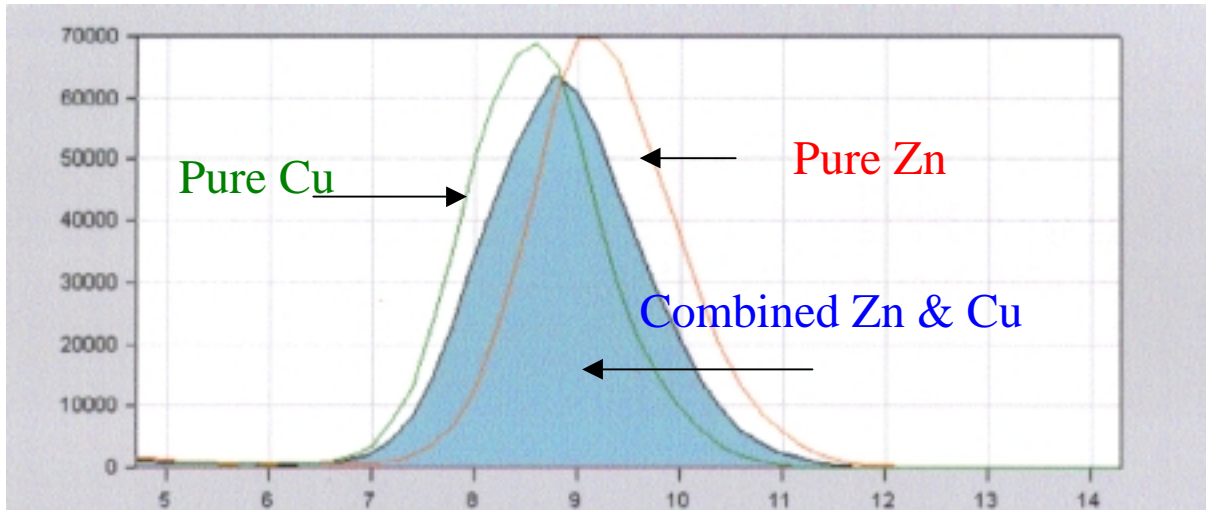
Spectral Processing With A Proportional Counter EDXRF:

Figure 2 shows the X-Ray spectrum of a yellow 14 Karat gold alloy containing Au, Ag, Zn, and Cu. Notice that the proportional counter spectrum is actually almost one continuous complex curve function wherein the constituent elemental peaks are sometimes not resolved one from another. It is necessary, then to further process the gross spectrum and deconvolute the overlapping signals from each element present. The resulting resolved element spectral peaks are also overlaid onto the gross spectrum in Figure 2. It is these separate net calculated peak intensities that are passed over to the fundamental parameter algorithm for quantification of elemental concentration. Any error in extraction of true peak intensities will cause subsequent error in the calculated elemental concentrations.

As mentioned above, the major challenge and limitation of the proportional counter is that the resulting spectrum typically involves the overlap of individual analyte peaks that must be resolved for accurate quantitative analysis. A simple example is shown in Figure 5 of how the deconvolution of overlapping Cu and Zn spectra, two elements typically found in gold karat materials, using a linear fit approach is achieved.

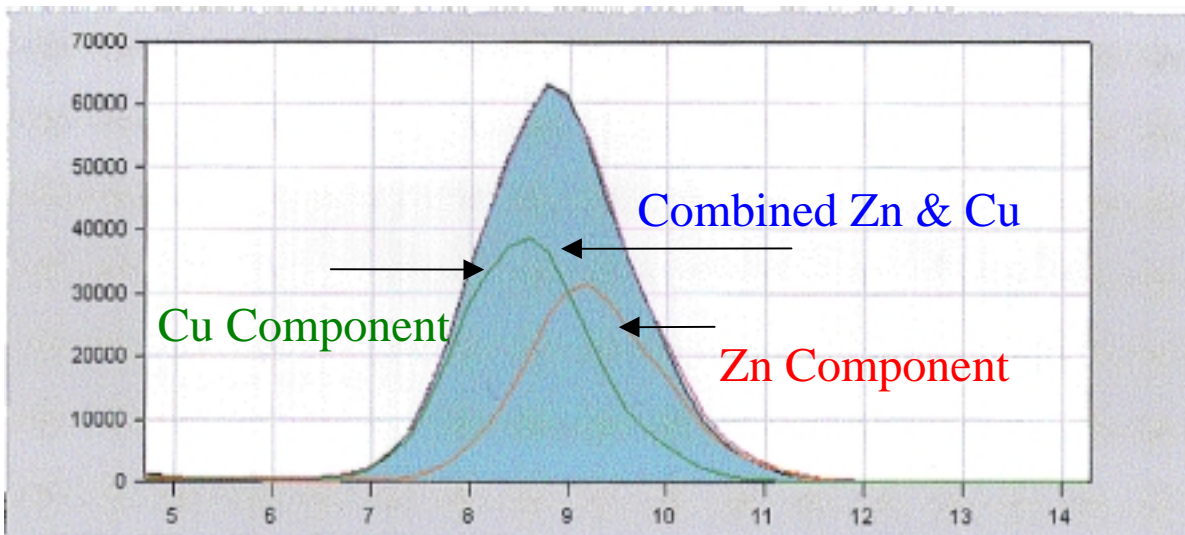
Figure 5: Zn-Cu Separation

Zn and Cu Spectra



In this technique, the individual spectrum of each pure element is measured and represented by a separate curve that can be described by a corresponding equation. The Zn-Cu sample's combined overlapped multi-element spectrum is also 'fit' to an equation after subtraction of background, and is the linear combination of the weighted individual pure element spectra, in this example Cu and Zn. See Figure 6

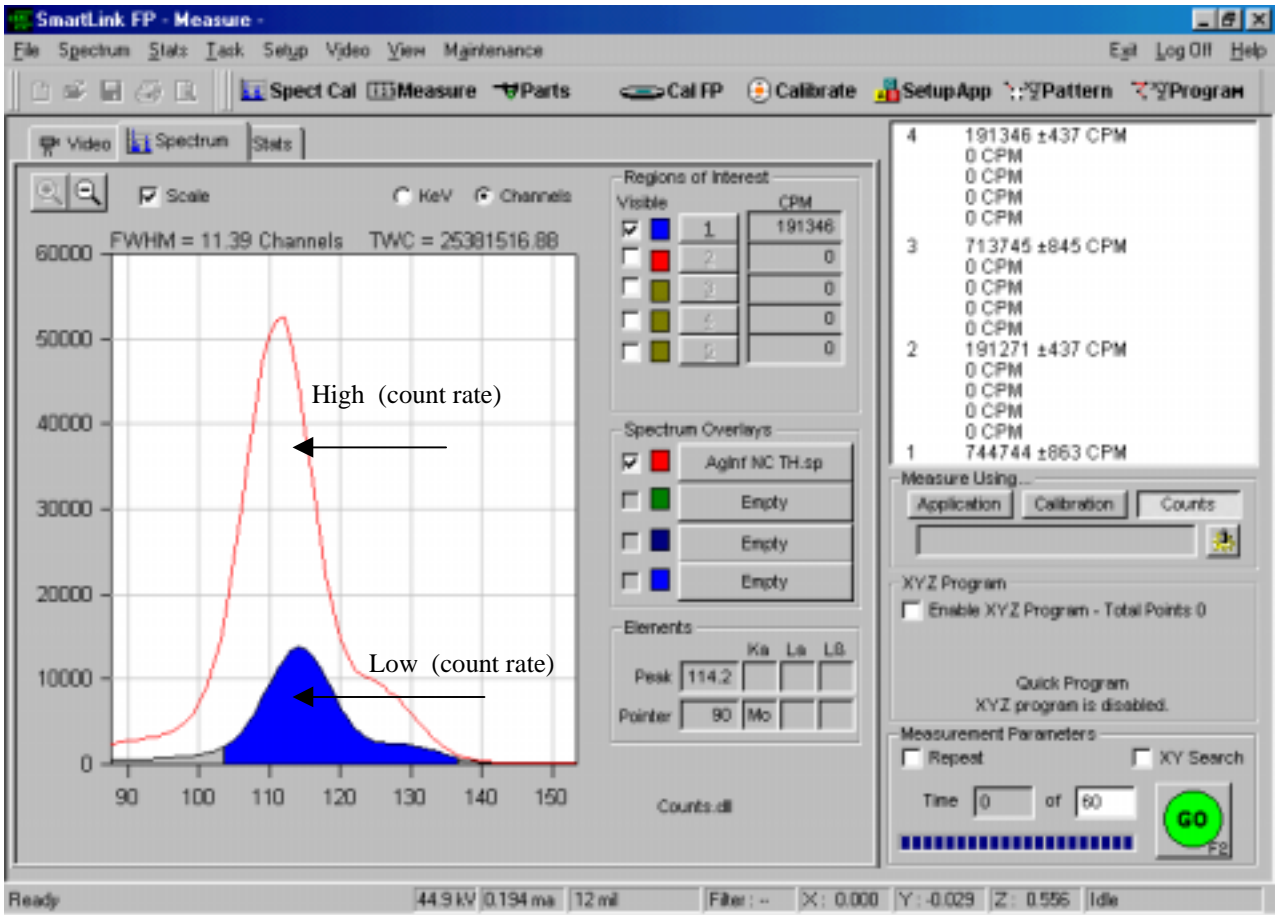
Figure 6: Zn-Cu Spectrum: Linear Fit



Thus, the complex gross spectrum can be effectively deconvoluted by solving for an appropriate linear fit of the combined individual analyte spectra of Zn and Cu. One must select, in advance, which elements to attempt to fit to the sample spectra when using this linear fit method. Additionally, background models can be applied to the spectrum to remove background counts from the analyte intensity.

The linear fit model is effective only when the proportional counter's normal drift characteristics can be effectively accounted for. A major drift characteristic of this type of detector is count-rate-induced peak shift (3). That is, the location and shape of the peaks can change as the number, or rate, of the X-Rays processed increases or decreases, as is shown in Figure 7. To account for this, a complex peak shift algorithm is applied to all the spectra of the calibration standards and samples so that each spectrum is correctly processed to obtain true net intensity.

Figure 7: Peak shift of pure silver spectrum at high and low intensities



This processing overcomes the proportional counter's typical resolution limitations and allows for analysis of more complex sample analyte combinations. The linear fit, peak shift, and background removal models expand and define the analytical capacity of the proportional counter well beyond what its intrinsic characteristics would normally allow. In this application alone, overlapping elements Au-Cu-Ni-Zn, Ru-Rh-Pd-Ag, and even Pt-Au or Pt-Ir can be successfully separated and used.

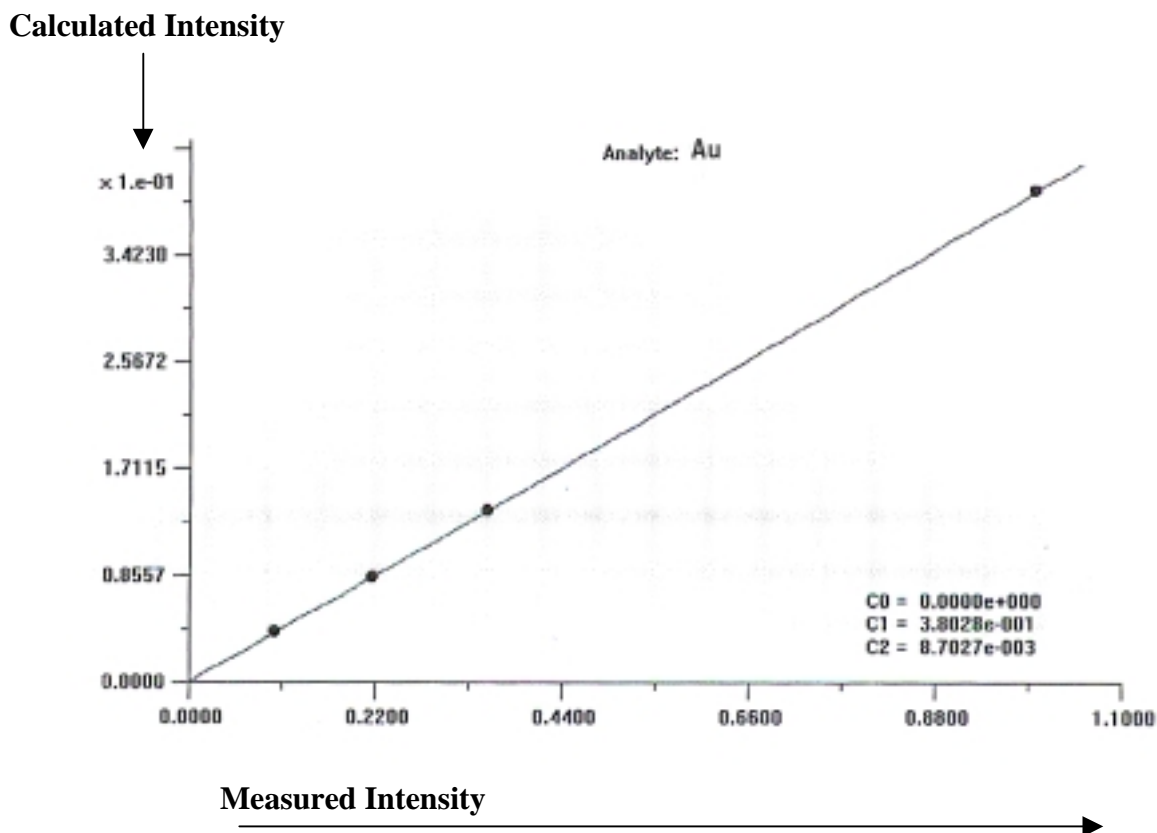
Quantitative Analysis Using Fundamental Parameters:

Fundamental Parameters, known as FP, is an atomic physics algorithm which theoretically describes the interaction between the X-Ray spectrometer and the sample analytes. It is the engine that basically interprets the processed X-Ray spectra into elemental composition and takes into consideration the physical parameters of the spectrometer, generation of primary X-Rays from the X-Ray tube, secondary fluorescent X-Ray production in the sample, inter-element matrix effects, and in some cases, detection of X-Rays. It has become more advanced and more popular in XRF instruments over the last 10-15 years and is now fairly commonplace, especially in high-end XRF spectrometers. (4) (7)

The incorporation of a complete and comprehensive FP program into a 'low-end' proportional counter-based Micro-EDXRF spectrometer is unique. This considerably simplifies operation and enhances the analytical range of the instrument to address more complicated sample matrixes with the use of fewer calibration reference materials. In fact, it is not necessary to use specific 'type-standards' at all for instrument calibration when using FP for screening applications, however, it is recommended for the high accuracy needed in the quantitative analysis of precious metals. Hence the analysis of complex matrixes of gold karat alloys, or other precious metals, theoretically involving up to 25 elements at once, can be achieved with relative speed and ease. It should be noted that, spectral processing techniques notwithstanding, the proportional counter is practically limited to less than 25 elements at one time. Gold karat alloys and scraps matrixes usually involve between 2-10 elements simultaneously which is favorable for this technique. Figure 8 shows an example of an FP calibration.

Earlier classical empirical calibration curve models required large suites of standards to fully and accurately analyze the sample. The number of standards required can be generally expressed as: $(N+2)^2$, where N is the number of elements to be analyzed and accounted for in the sample. Thus Analysis of Au, Ag, Cu, Zn, Ni would require 49 standards to completely develop a calibration that fully characterizes this sample matrix. Usually, this approach would be accurate for routine testing of a finite set of known materials and when copious amounts of reference standards are available (5).

Figure 8: Example of Au FP Calibration Curve



The “Golden Rules”:

A prerequisite for achieving high measurement accuracy and precision of gold karat alloys with the Micro-EDXRF is careful adherence to basic analytical protocol of instrumental analysis for sampling, calibration, and measurement. It should be stressed that these are not merely guidelines, but are requirements that are necessary to follow in order to fully realize the potential analytical value of the instrument and technique. As such, it seems appropriate here to title these precepts “**The Golden Rules**”, though they also apply to quantitative instrumental analysis in general.

Golden Rule I: The Sample Must Be Homogenous

Homogeneity is a relative term that relates the concentration of the elements to their spatial distribution in the sample matrix and needs to be defined. For example, are we

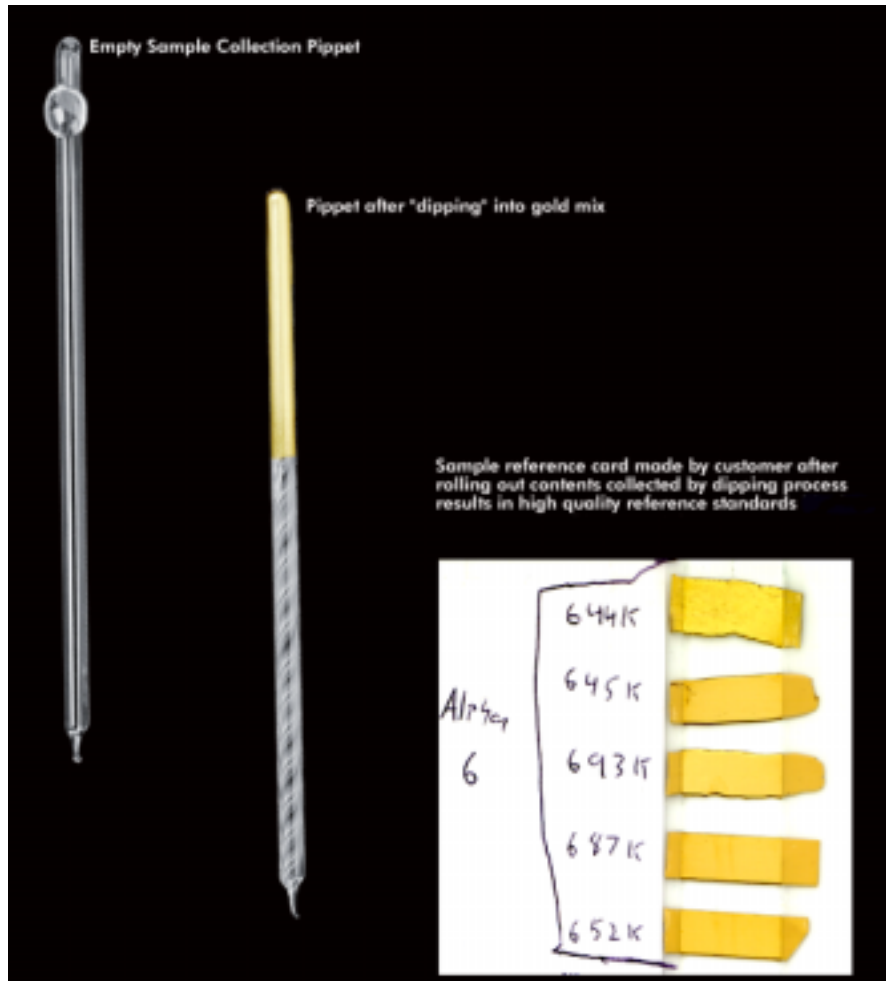
spatially looking at uniformity from batch-to-batch, sample-to-sample, micron-to-micron, atom-to-atom, and are we trying to chemically resolve whole karats, weight percent, parts per thousand, parts per million? This depends on the goal of the measurement, but for quantitative bulk analysis, it is often most important that the small volume of material sampled by the instrument represents the overall bulk composition of the entire sample. For most jewelry applications, the 'scale of homogeneity' for this Micro-EDXRF approach might typically be characterized as a chemical resolution of one or more parts per thousand and a spatial resolution of approximately a millimeter.

The XRF technique effectively measures within 10 to 50 microns of the sample surface, depending on the gold karat alloy composition and the element being considered. At any one time, the instrument is only 'seeing' a volume that is defined by this depth and the irradiated area under the primary X-Ray beam. In this case, the irradiation area is usually 0.3mm in diameter, which corresponds to an average analysis volume of $2 \times 10^{-6} \text{ cm}^3$. For a typical gold 14K alloy this would be approximately only 30ug (micrograms) of material representing the whole sample at one given time! This is analogous to an entire trainload of coal that must ultimately be represented by just a few grams of sample for analysis of Sulfur and other components. It should be noted that the same sampling principle applies to the fire assay method as well. As such, it is extremely important that the irradiated area is representative of the entire sample to obtain the average bulk analysis.

To accomplish this, molten samples are drawn with glass vacuum tubes, or pindip tubes, and quick-quenched immediately within a few seconds in water. If the original melt was stirred and mixed well itself, this technique can 'capture' the alloy in a random enough state before macro-segregation can take hold. The resulting pin sample is rolled flat and the surface cleaned with medium sandpaper in random or circular direction and washed with water or alcohol. It is not necessary to polish the surface of the sample to an optically smooth surface, but it is essential to remove any contamination or layers where depletion or enrichment may have occurred during solidification and cooling in the glass tube and water. This strip when placed in the sample stage is then raster scanned to cover a large area to obtain thorough averaging to account for sample heterogeneity and ensure that accuracy is optimized. Shot or grain can be similarly used to obtain good results. Plate that has been rolled and annealed multiple times has also been used. See Figure 9 for an example of pindip tubes and samples.

The importance of raster scanning is apparent when one considers that a 0.3mm beam would collect data only from about 30ug of material ($\sim 424\text{ug/mm}^2$) in one point, 6800ug (6.8mg) of material in a 4mm x 4mm area scan, and 127,000ug (0.13g) from a 10mm x 30mm scan of a pindip strip. Thus an increase in mass sampling on the order of hundreds to thousands of times is achieved by uniformly raster scanning larger areas of the material. Note with this approach, the benefits of a classical large spot XRF are achieved while still retaining the convenience and attributes of the small spot Micro-XRF. Small curved and irregularly shaped, or multi-alloy parts can still be effectively assayed as well as examining homogeneity and bulk values of large samples.

Figure 9: Example of Pindip Tubes and Samples



It should be emphasized that most karat alloys and scrap material are *not* inherently homogenous at the Micro-XRF scale. Even white gold (Ni-containing) pindip strips prepared as outlined above have been observed to vary by almost 1 weight% Au from spot to spot within a given strip. Sheet, tubing, wire, extrusions, and electroformings are typically heterogeneous, especially on the surface skin where an apparent enrichment and depletion can occur depending upon the alloy and process used. This effect frequently comes into play with ingots and especially finished jewelry that is further segregated by plating, bombing, pickling and soldering. Solid cast jewelry generally tends to exhibit more uniform characteristics.

It should be noted that the analytical protocol of the XRF technique *completely forbids* the simultaneous analysis of different karat alloy systems juxtaposed within a piece of

jewelry. For example, a multi-colored piece of jewelry with white gold next to yellow gold, irradiated simultaneously under a large X-Ray beam is not allowed and results in false readings. It would be analogous to analyzing a piece of steel and a piece of brass at the same time in the measurement chamber. Solder or plating on jewelry can also be viewed in this way. Tables 2 and 3 show clearly the effects of Au plating and surface enrichment on XRF results.

Table 2 shows the increase in the XRF karat fineness reading when 24k is plated over the gold karat alloy. For both samples, the apparent Au fineness increases significantly with only 5.1 total micro-inches (μI) of over-plate - about $\frac{3}{4}$ karat increase for the 14KY sample and $\frac{1}{4}$ karat for 18KY. Note the relative increase in Au is more severe with the lower karat alloys.

Table 2: Homogeneity: Effects of 24K Au Overplating

<u>Plating, μI</u>	<u>14KY</u>	<u>18KY</u>
0.0	58.10	75.08
1.9	59.19	75.47
3.2	59.94	75.76
5.1	60.90	76.21

The sample in Table 3 is a 14KY plate that was rolled from a bar. The surface of the plate reads too Au-rich with the XRF until sufficient surface material has been sanded off. This seems to suggest surface enrichment, or possibly stratification in the original bar that survived the rolling process. Jewelry stamped from such a plate would also then assay high with XRF.

Table 3: Homogeneity Effects of Alloy ‘Stratification’: 14KY Rolled Plate

<u>Surface Condition</u>	<u>XRF, Wt% Au</u>	<u>Change, Wt Au</u>
Original, As Is	59.12	--
Lightly Sanded	59.06	- 0.06
Grind Off ~ 2 Mil	58.43	- 0.69

By far, the biggest misconception of the XRF technique for gold karat analysis is based in the misunderstanding of sample homogeneity and how it affects the measurement accuracy, especially for finished jewelry. It is often a matter of sampling methodology rather than XRF technique.

Golden Rule II: Sample and Calibration Standards Must be Matrix-Matched

As mentioned, it is necessary to calibrate the instrument using reference materials, or type standards, that reflect similar elemental compositions as the unknowns to be measured. The accuracy of the measurement is ultimately tied to the accuracy of the reference materials used to calibrate the instrument and the gold karat reference standards used in this study were fire assayed and chemically characterized by ICP, AA, or gravimetric means. It is an important advantage to base the instrumental analysis upon one's own internal accepted reference technique, rather than rely on third party standards or instrument manufacturer-based pre-calibrations. So, a jewelry manufacturer may produce its own fire-assayed standards to calibrate with in order to maintain a high correlation between fire assay and XRF data.

In order to achieve maximum accuracy, a “one-standard FP” approach works best when adequate standards are available. Every element in the unknown must be represented in this calibration standard and at similar concentrations. Ideally, the unknown and the standard are identical materials, as is typically the case in production casting where the same recipes are routinely produced. In this case, one standard is used for each alloy recipe. Thus, a ‘recipe-readback’ comparator situation is established which tends to neutralize any systematic, or non-linear errors, eliminate error propagation from multiple standards, and provide the most accurate results possible with the XRF technique, typically well within 0.1wt% for Au. As a rule of thumb for this approach, the elemental concentration for each element in the standard should be within one or two weight % of the sample's, or 25% relative –whichever is smaller- to be most effective. The software is able to automatically search and select one standard from a bank of standards that best matches the sample's matrix, use it to calibrate the FP algorithm, and calculate concentration from the processed sample spectrum.

Alternatively, when measuring unknowns, or when ample calibration standards are not as readily available, an FP ‘curve’ may be generated using a small suite of type standards that span the expected elements and concentration ranges. Fortunately, the $(N+2)^2$ rule for standards and calibration does not apply here and typically a full range calibration can be established for the element set of Au, Ag, Cu, Zn, and Ni with as few as two standards, 4 to 8 standards being typical.

If no type standards are available, or a pre-screening is all that is necessary, analysis can be performed with FP without the use of calibration standards on almost any type of jewelry alloy. The accuracy of this approach depends on the sample matrix, but typically is between 5-15% relative.

Golden Rule III: Acquire Enough Analyte X-Rays for Adequate Precision

The concept that one XRF measurement result is not absolute is commonly misunderstood for XRF and analytical techniques in general. The X-Ray Gaussian counting statistics and measurement precision introduced in the Theory section must be

adequately understood and practically applied in order to obtain the best possible results. What this means practically, is that enough time or reps must be spent measuring the sample and acquiring X-Ray count data to achieve the desired level of precision. The precision is rated in terms of 'standard deviation' (SD), the measured and calculated index of the repeatability of a group of N replicate measurements on the same location of the same sample.

As a practical example, we consider a 14K gold alloy sample with a gold fineness of 58.40 wt%. The typical experimentally observed SD for this Micro-EDXRF is 0.08 wt% Au for a 90-second measurement. In Gaussian statistics, one SD corresponds to a 65% confidence level, two SD's corresponds to 95% confidence, and three SD's corresponds to 99+% confidence. So, at 65% confidence the measurement would be plus/minus 0.08 wt%, at 95% confidence the measurement would be plus/minus 0.16 wt% (2 x 0.08), and 99% confidence would be plus/minus 0.24 wt% (3 x 0.08), or:

65% confidence: 1 SD (0.08 wt% for our example)
95% confidence: 2 SD (0.16 wt% for our example)
99% confidence: 3 SD (0.24 wt% for our example)

(Note: units are wt% Au)

So if this 14KY sample were measured 100 times in the same spot at 90 seconds per measurement with a mean value of 58.40 wt% Au and a SD of 0.08wt% obtained, then the result would be interpreted:

65% confidence: 58.40 ± 0.08
95% confidence: 58.40 ± 0.16
99% confidence: 58.40 ± 0.24

Yet another way to express this is, 65 of the measurements would be within 0.08 of 58.40, 95 measurements would be within 0.16 of 58.40, and 99 measurements would be within 0.24 of 58.40, or:

65 of 100 measurements: 58.32 - 58.48
95 of 100 measurements: 58.24 - 58.56
99 of 100 measurements: 58.16 - 58.64

Increasing the measurement time improves precision, according to the square root law. If the measurement time were tripled from 90 to 270 seconds (or the 90 second measurements were averaged together in groups of 3) then the SD would improve to 0.05 and the precision data would now look like 58.40 ± 0.05 :

65 of 100 measurements: 58.35 – 58.45
95 of 100 measurements: 58.30 – 58.50
99 of 100 measurements: 58.25 – 58.55

By increasing the measurement time from 90 to 270 seconds, the 99% confidence (three SD) *range* of measurements goes from 0.48wt% Au in 90seconds down to 0.30wt% Au in 270 seconds — a significant improvement:

Range of measurements 3 SD, 90 seconds measurement time: 0.48wt%

Range of measurements 3 SD, 270 seconds measurement time: 0.30wt%

An important note here is not to confuse the range of measurements (maximum minus minimum reading) with the error. From this example, a range of 0.48wt% does not mean a result will be 0.48wt% above or below 58.40, but indicates the spread in the data for the measurement time of 90 seconds. At 99% confidence these measurements will be 0.24wt% above or below 58.40wt%, and not more than 0.15wt% above or below for 270 seconds.

Likewise, if the same 14KY sample were sent out to 100 fire assay labs, or 100 times to the same fire assay lab, an average result with its own SD and range of measurements would also be obtained, as it would be for any analytical technique applied, assuming Gaussian distribution. It is appropriate to note here, that though fire assay is used to anchor the XRF measurements by virtue of the calibration standards data, fire assay itself is not absolute and statistical measurement variability as well as systematic error also are intrinsic to this technique.

To summarize, the SD is tied to the number of X-Rays the instrument collects during a measurement and the more X-Rays that are collected, the better the precision. Practically, this usually means the longer the measurement, the better the precision gets. Alternatively, multiple shorter measurements can be averaged, or grouped, together to obtain a statistically equivalent precision of one longer measurement. There is a point of diminished returns for measurement time and this all is governed by well known statistical law, so the XRF user has some control over precision and % confidence of the data. The measure of the power and quality of the XRF instrument can be directly related to its measurement precision in a given amount of time.

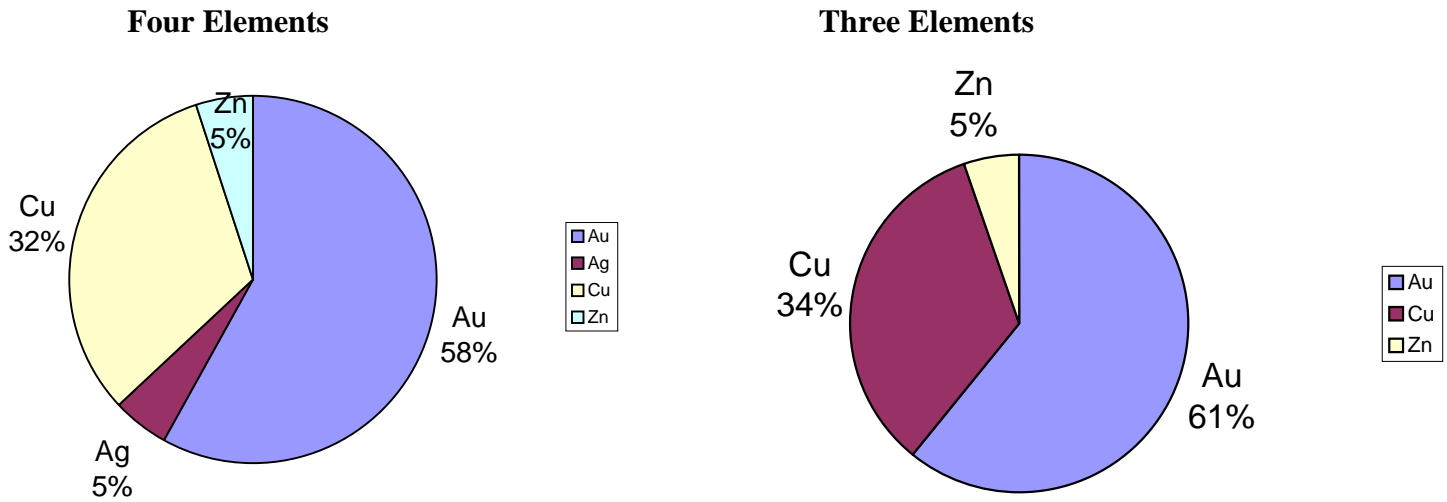
Golden Rule IV: The Analyte Concentrations Must Fall Within MDL / UDL

At first glance, it seems obvious that an element must be above the Minimum Detection Limit (MDL) or below the Upper Detection Limit (UDL) of the instrument to be properly quantified. However, this has ramifications on whether or not the Au is properly quantified for a variety of reasons.

When using FP, all of the elements analyzed in a measurement will be normalized to a sum of 100%. An element, or group of elements, present in the sample at concentrations below the MDL, will not contribute to the total analyzed mass nor will their matrix effects be included to correctly quantify element composition. The remaining mass balance, which is less than 100%, will be normalized to 100% resulting in error.

For example, consider a sample containing 58% Au, 5% Ag, 5% Zn, and 32% Cu that is analyzed with the XRF, but suppose the Ag is not included in the measurement for various reasons. This means the resulting Au, Zn, and Cu values will make up the difference through normalization, each increasing by 5% relative. Thus, the Au would now read about 61% instead of 58%. An error has occurred from normalizing due to an element being ‘left out’ of the mix. See Figure 10, below.

Figure 10: Normalization



Likewise, if 5% of the mass of the sample above were distributed amongst numerous elements that were too light or too low in concentration to measure, then a similar error would occur. This is why it is important to measure and account for all the elements and mass in the sample – precious and non-precious- and not just the Au alone.

The proportional counter Micro-EDXRF in this study analyzes elements from Ti – Bi on the periodic chart at concentrations generally above approximately 0.5 -1.5wt% and below approximately 99wt%. These values depend upon the degree of spectral overlap from neighboring elements that may be in the sample matrix. Practically, the magnitude of error from trace elements and light elements does not have an appreciable effect on the Au analysis of most karat alloys. Additionally, sub MDL concentrations of adjacent overlapping elements may sometimes become included into neighbors which somewhat offsets error. For example, low concentrations of Ni and Zn at say 0.2wt% each may be measured as 0.0wt%, but they may ‘show up’ as neighboring Cu to some extent.

The measurement of ‘three-nines’ or ‘four-nines’ (99.9, 99.99wt%) Au is not possible with the proportional counter *or any other XRF*, in theory. Consider that 99.9wt% Au leaves only 0.1wt%, or 1000 ppm of mass distributed amongst the approximately 100

non-radioactive elements in the periodic chart. This implies that verification of all 100 elements down to 10ppm each is required to ensure 99.9% purity, and only 1ppm for each element to ensure 99.99% purity. This is far beyond XRF capability and any apparent data or claims to the contrary are scientifically unfounded.

A basic equation of MDL is given by Currie's formula for 95% confidence of detection:

$$3.29 \sqrt{B} / (T * S)$$

Note the MDL is defined by the background counts B, instrument sensitivity S (analyte X-Ray counts per wt%), and measurement time T.

4) Analysis Data for Gold Karat Alloys:

Data for Jewelry Casting Environments:

Generally, jewelry casting is the most ideal use of XRF for gold karat alloy analysis, since it involves known alloys and well-characterized standards under carefully controlled conditions. When the Golden Rules are applied correctly in a manufacturing environment where casting is done, then the Micro-EDXRF becomes virtually an electronic fire assay machine. The recipe readback comparison mode yields the highest correlation between fire assay and XRF. It is possible to take a pindip from the melt and have an accurate and reliable assay within minutes, prior to casting or the next production step. This is a good compliment to fire assay and provides additional process control that can be used to closely manage overkarat and underkarat margins in Au alloys. Additional useful alloy composition data is also provided along with the Au analysis.

Table 4, below, shows XRF vs. Fire Assay for production casting samples. Site one data (courtesy of Michael Anthony Jewelers, NY) is from a variety of 14K yellow, white, and pink alloys that were scanned for 90 seconds each with a 12mil, 0.3mm, collimator size. Note that all measurements were within 0.1 wt% Au of the corresponding fire assays and the average difference (including polarity) between the two for this set of data was less than 0.01 wt% Au.

At site two (courtesy of A&A Jewelers, Canada), similar results were obtained, though each data point is the average of five 220 second measurements with a 12mil collimator size.

At site three (courtesy of Excell Manufacturing, RI) three 14KY casting grains (shot), as received, were scanned for 90 seconds three times each with a 12mil collimator size. XRF and Fire Assay parity in this case were slightly closer than for the pindips.

Table 4: Accuracy for Casting

	<u>Site 1</u>	<u>Site 2</u>	<u>Site 3</u>
Avg. Difference, Wt.% (XRF - FA)	0.005	0.005	-0.007
Max Difference, Wt.% (XRF - FA)	0.09	0.08	-0.02
Sample Type:	Pindip	Pindip	Shot
Alloy Types:	14Y, 14W, 14P	10Y, 14Y, 18Y	14Y

In addition to measuring pindips and shot, ‘dog tags’ attached to trees have been used as process monitor samples. Additionally, an entire tree, after cleaning, can be placed into the instrument chamber and various sites analyzed to detect concentration gradients. Thus, the Au uniformity of the product is readily verified so that overkarat and underkarat product will not be further processed and shipped from the same tree.

Data for Finished Jewelry:

As previously mentioned, finished jewelry is often heterogeneous in nature. The use of soldering alloys during assembly, plating, bombing, pickling, heat treatment, or just the intrinsic nature of the parent alloy, can make finished goods less than ideal samples for the surface-oriented XRF technique.

Generally, cast goods such as rings and charms loan themselves best to XRF analysis and Table 5, below, contains data from such samples. Most data was taken at 90 seconds measurement time using a 12mil, or 0.3mm, measurement beam. The average difference between fire assay and Micro-XRF for both cases is within 0.2wt%. The maximum observed difference is -0.67wt% Au for one reading, which probably reflects some heterogeneity in the sample matrix.

The parity to fire assay is close enough for karat screening of finished goods. Micro-XRF is currently being used effectively for receiving inspection of jewelry to efficiently and non-destructively identify suspect underkarat product. This is done for compliance to federal stamping law, and protection of reputation, customer, and investment.

The biggest quandary for the retail and wholesale jeweler is that in order to actually know the karat fineness and ensure compliance and quality, the sample must be destroyed partially, or fully, by fire assay. To retain complete original integrity of the article, and thus its full value, fire assay must be avoided – thus increasing risk. These two opposing realities are best resolved by screening finished goods at statistically high sampling rates

using Micro-XRF. Fire assay of an insignificant portion of samples from one lot, or lots of jewelry, does not provide enough quality assurance to be of value. Similarly, micro-fire assay of small amounts of scrapings from an article is not necessarily representative of that sample (refer to homogeneity discussion, above.). Thus, ‘*Burn and Know*’ vs. ‘*Sell and Risk*’ is best resolved by vigorous Micro-XRF screening to find suspect articles with fire assay used as a backup for final adjudication of any product in question.

Table 5: Accuracy for Finished Goods

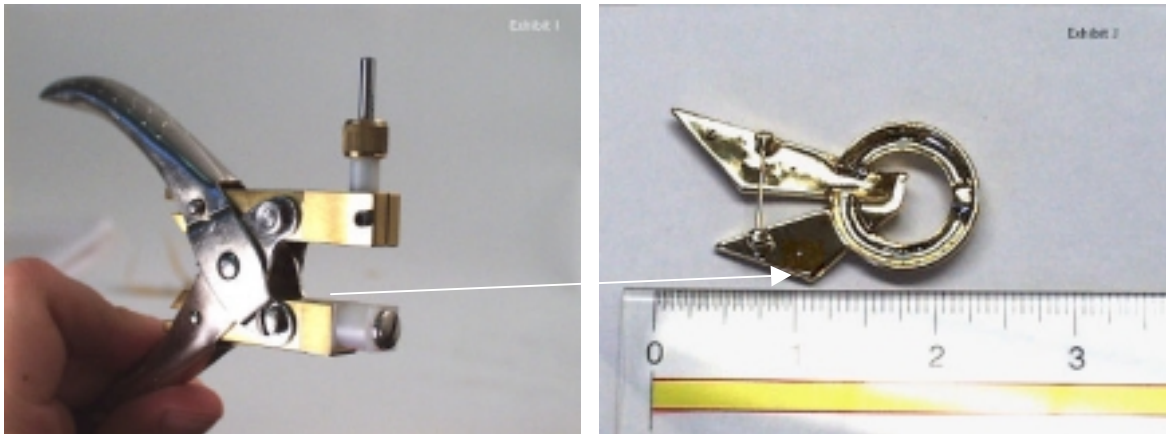
	<u>Case 1</u>	<u>Case 2</u>
Avg. Difference, Wt.% (XRF - FA)	- 0.02	- 0.16
Max Difference, Wt.% (XRF - FA)	0.39	- 0.67
Sample Type:	Cast (Ring, Charm, Bracelet)	Cast (Rings)

The Micro-XRF is not susceptible to most sample geometry effects such as curvature, tilt, and uneven or rough sample surfaces due in part to the small measurement area used, and in part to the normalization of the quantitative results by the FP engine.

Additionally, composite jewelry assembled with components of different color alloys (yellow, white pink, green, red, etc.) and other dissimilar alloy systems (sterling silver, platinum, gold) are more readily accessible by using the small measurement beam that the Micro-XRF technique employs. In this case, each component may be discretely analyzed non-destructively and the overall average taken of the sample. As mentioned, it is not permitted by the XRF technique to try and ‘wash’ the entire composite jewelry sample at one time and average the different alloy types together. This causes significant error.

In order to circumvent the affects of a heterogeneous jewelry surface, a micro-polishing tool was successfully designed and tested that removes approximately one or two thousandths of an inch from the sample surface in a very small area that conveniently accommodates the primary X-Ray beam. This effectively removes Rh plating from white gold, Au plating, solder, and the Au-enriched/depleted ‘crust’ often found on sample surfaces. The results of using the device showed improved results for measuring finished goods and the polish site is fairly unnoticeable – being barely visible to the naked eye. This approach prohibits the use of scanning, however, the improvement in accuracy in some cases outweighs the improvement from obtained through scanning. The device and a polish site on a sample are shown below in Figure 11.

Figure 11: Micro-polish tool and micro-polished sample



Data for Gold Karat Jewelry Scrap:

Karat alloy scrap is the most diverse ‘unknown’ material type covered in this study. It basically is a mixture of the various jewelry manufacturing alloys (10K, 14K, 18K, yellow, white, green, red, etc.) with their constituent elements Au, Ag, Cu, Zn, Ni, and now more frequently Pd and Pt, too. The more severe diversity of the scrap sample matrix makes the issue of properly matched calibration reference standards more critical to the accuracy of the analysis.

Like the products it comes from, jewelry scrap is also usually heterogeneous unless it has been re-melted and sampled correctly for XRF by pindip or shot methods. In addition, there may be a greater number of trace elements in the sample. In the end, the accuracy for this application is determined by how closely the ‘Golden Rules’ could be adhered to, and the challenge is to prepare or homogenize the sample, identify all the elements correctly, and apply the appropriate quantitative approach as described above in ‘Golden Rule’ II.

The data in Table 6, below, shows three typical categories of gold karat scrap materials with corresponding Micro-XRF and Fire Assay data. The first group, “Plate, Wire, Solids” is essentially pieces of jewelry or stock material that have been cut up and the data is similar to that for finished goods, above. The bar drillings show correlation to fire assay that averages about one half wt% Au, and the pindip sample reflects data that has been generated under more ideal adherence to the ‘Golden Rules’. That is, this pindip was properly prepared and homogenous, its matrix fit well within the framework of the calibration standards used, and enough measurement time was employed, which all taken together, yielded close correlation to fire assay.

Table 6: Accuracy for Gold Karat Refining Scraps

	<u>Avg. Difference</u>	<u>Max. Difference</u>
Plate, Wire, Solids (Ground Surfaces)	- 0.05	- 0.26
Bar Drillings	0.59	1.71
Pin Dip *	0.03	0.03

*** Used Multi-Standard FP: Units in wt% Au**

The results in table 6, above, indicate that the product characteristics and performance loan themselves to the gold alloy scrap application in several ways:

- 1) Pre-Screening: Rapid qualitative and semi-quantitative analysis of unknown materials for effective and efficient process preparation.
- 2) Pre-Settlement / Quick Settlement: Rapid quantitative analysis of Au, Pt, Pd, Ag to provide a secure basis for advancing payments prior to fire assay.
- 3) Small Lot Final Settlement: Rapid quantitative analysis accurate enough for final settlement of ounce(s) size lots.

Conclusion/Summary

The range of accuracy possible with this Micro-XRF technology, the relatively low product cost / maintenance, the ease of operation, the speed of analysis, and overall flexibility match up well to the analysis requirements and needs of jewelry production casting, karat screening of finished jewelry, and gold karat metal recovery operations. This has been made possible by advances in the comprehensive quantitative analysis FP engine, spectral processing techniques, hardware refinements, and methods development that have been infused into this basic Micro-EDXRF spectrometer.

Bibliography

- (1) Bertin, E.P., "Principles and Practice of X-Ray Spectrometric Analysis", second edition, Chs. 1, 3, 6; Plenum Press, New York
- (2) Bertin, E.P., "Principles and Practice of X-Ray Spectrometric Analysis", second edition, Ch. 11, Plenum Press, New York
- (3) He, T., CMI International, "Spectrum Processing Techniques for a Proportional Counter Based XRF System", Denver X-Ray Conference Technical Symposium, 1999
- (4) Bertin, E.P., "Principles and Practice of X-Ray Spectrometric Analysis", second edition, Ch. 15.6, pp690-696, Plenum Press, New York
- (5) Bertin, E.P., "Principles and Practice of X-Ray Spectrometric Analysis", second edition, Ch. 15.5, pp685-688, Plenum Press, New York
- (6) Jenkins, R.; Gould, R.W.; Gedcke, D.; "Quantitative X-Ray Spectrometry", Marcel Dekker, Inc., 1981 NY, NY, Ch5: pp293-328.

(7) Jenkins, R.; Gould, R.W.; Gedcke, D.; “Quantitative X-Ray Spectrometry”, Marcel Dekker, Inc., 1981 NY, NY, CH10: pp445-496.

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