THE NOVEL USE OF XRF SPECTROMETRY IN THE REFINING OF GOLD

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ABSTRACT

X-ray Fluorescence Spectrometry (XRF) is used at various stages of gold refining. Initially, incoming impure gold is analysed for deleterious elements such as As, Cd, Hg, Se, and Te. Based on the levels of these impurities the material can be returned to the client or accepted for refining. XRF is also used to determine the metal concentrations after the impure gold has been melted and sampled. This information is used to assist the final Fire Assay determination of gold and silver. An energy dispersive XRF is used to determine the end point of chlorination refining step.

World Gold 2011
Proceedings of the
50th Annual Conference of Metallurgists of CIM
Montreal, QC, Canada
Edited by G. Deschênes, R. Dimitrakopoulos, J. Bouchard

INTRODUCTION

X-ray Fluorescence (XRF) spectrometry has been applied to many aspects of the gold refining operations. The main advantage of using XRF was the ability to analyse solid samples with minimal sample preparation. This method has provided fast results with adequate accuracy and precision. XRF works on the principle that a broadband excitation source (X-ray tube or radioactive isotope) induces atomic fluorescence from the elements within the sample. The resulting fluorescent X-rays can be qualitatively identified for each element present in the sample and the measured counts are proportional to the concentration of the elements in the sample. There are two types of XRF spectrometers: energy dispersive and wavelength dispersive. The energy dispersive XRF collects the fluorescence from elements simultaneously with a given set of measurement conditions. Wavelength dispersive systems collect this data sequentially with specific conditions for each element. In general, the wavelength dispersive systems have better resolution and higher count rates than energy dispersive systems. A complete explanation of XRF spectrometry can be found in Willis and Duncan [1] and Vrebos [2].

In the Royal Canadian Mint's refining operations XRF spectrometry has been applied in three areas. The first (order of operation) was to check impure gold entering the refinery for deleterious elements such as As, Cd, Hg, Se, and Te. These elements can be harmful to human health in high levels. Although there is excellent protection for refiners, it is preferable not to accept gold with excessive amounts of these elements, especially mercury. A bench top XRF spectrometer has been installed at the point of entry to screen incoming gold for these deleterious elements. The second application was using a wavelength dispersive XRF in the Assay department to estimate the concentrations of gold and silver to assist the fire assay process to determine the exact concentrations of gold and silver for settlement with the client. Fire assay is a gravimetric analysis method that has been an industry standard in determining precious metals [3, 4]. XRF has been reported to be useful in assaying gold in jewellery alloys [5]. In the case of jewellery XRF can be very accurate due to the limited range of known jewellery alloys that one typically analyses. For impure gold coming in from different mine sites, the range of precious and non-precious metals can vary significantly. The third application was to use a very simple energy dispersive XRF on the refinery floor to determine the endpoint of the Miller's chlorination process [6] used to refine gold to a point where it can be sent to electrolysis which is the final refining step.

EXPERIMENTAL

Spectrometers

Three different X-ray Fluorescence (XRF) spectrometers were used for the three different applications described in this paper. For the determination of deleterious elements in gold deposits being received, portable XRF configured in a non-portable bench top station (Delta model, Innovx Systems, Bedford, MA, USA) was used. This was an energy dispersive XRF with a 4 W tantalum X-ray tube and a silicon drift detector. The XRF was controlled through a laptop computer and is locked in a work station with an enclosed sample chamber. The vendor's RoHSS/WEEE analysis program was adapted by the vendor to determine As, Cd, Hg, Se, and Te in gold using pressed powder standards prepared at the Royal Canadian Mint. RoHS means: Restriction of Hazardous Substances and WEEE means: Waste Electrical and Electronic Equipment. An analysis time of 240 seconds was used in order to determine the deleterious elements at sufficiently low concentrations.

A wavelength dispersive Axios XRF (PANalytical, Almelo, NL) was used in the Assay Department. The XRF was equipped with a 4000W rhodium X-ray tube and three detectors: scintillation, flow counter using P10 gas, and a sealed Xe detector. It was custom ordered to include 5 dispersive crystals, 3 different collimators, masks, and sample cups for 6, 12, 27, 41 mm diameter apertures. An autosampler was included to handle the large number of samples that occur at peak times and minimize operator time at the spectrometer. Elements are measured sequentially and the total analysis time is approximately 4 minutes per sample. The spectrometer settings for this application are summarized in Table 1.

Table 1 - Summary of the wavelength dispersive XRF parameters used for determining Au, Ag, and other elements to complement fire assay analysis

Element	Line	Crystal	Detector	Tube Filter	Angle 2Θ**
Au	Lα	PX10	Scintillation	None	36.9148
Ag	Kα	PX10	Scintillation	100μm Brass	15.9656
Cd	Kα	LiF220	Flow	100μm Brass	21.6370
Cu	Kβ	LiF220	Scintillation	None	58.5196
Fe	Kβ	PX10	Flow + Xe	None	51.7036
Ni	Kα	PX10	Flow + Xe	None	48.6200
Pb	Lα	PX10	Scintillation	None	33.8804
Pd	Kα	LiF220	Scintillation	100μm Brass	23.7328
Pt	Lα	PX10	Scintillation	None	38.0032
Zn	Kα	LiF220	Scintillation	None	60.5318
As*	Lα	PX1	Scintillation	None	22.8082
Rh*	Lα	PX10	Scintillation	None	17.5184

*As and Rh counts used for line overlap corrections only and were not reported

** Background correction points selected (not included in table)

The energy dispersive XRF used to determine the endpoint of chlorinating gold deposits was a Spectro 200 XRF with an Americium 241 radio isotope (^{241}Am) excitation source (Spectro, Marble Falls, TX, USA). The unit comes with a simple built in controller and a sealed counter detector. Ag and Pd were determined with a source filter and Cu was determined without a source filter. An analysis time of 300 seconds was set in order to determine Ag and Cu with sufficient precision. The reader should note that Pd was measured only because it overlaps with Ag and a correction must be done.

Standards

Calibration standards were made from molten and cast gold samples there were either typical of materials normally analysed or contained abnormally high concentrations of elements that are occasionally found to extend the calibration range of each method described. The castings were quickly cooled to minimize grain size and to ensure the homogeneous distribution of elements throughout the material.

Shavings were taken from the sides of the cast standards that will be presented to the XRF spectrometers. The shavings were then analysed by either Fire Assay (for Au and Ag) and/or inductively coupled plasma – atomic emission spectrometry (ICP-AES) for all other elements. For ICP-AES determinations, approximately 0.5 g of shavings were dissolved in 10 ml of aqua regia (1 part HNO3 + 3 parts HCl) and heated in a 50 ml plastic vial to 105^{o}C for 1 hr. This process was repeated with 5 ml of aqua regia to ensure complete dissolution of the elements of interest. Standards that contained high levels of As, Cd, Hg, Se, and Te were dissolved at room temperature to minimize volatilization losses during dissolution. The final solutions were brought to 50.00 ml volume with deionized water. If necessary the solutions were further diluted to ensure element concentrations stay within the calibrated concentration range of the ICP-AES method. Results from Fire Assay and ICP-AES were combined. The element concentrations were summed and checked to ensure that the sum of elements is 100% (± 0.5%). A certificate was issued and the values entered into the software of the XRF spectrometer for calibration purposes.

Sample Preparation

Deleterious Elements Within Incoming Gold Deposits

For incoming gold that is cast into bars, a drill is used to take material from the bar for analysis by XRF. Paper is placed underneath the bar and is used to collect the shaving removed using a 3/16 inch diameter drill bit. The first shavings from a depth of 1 mm are collected but set aside because the material from the outside edges of most bars contains anomalously high concentrations of deleterious elements. The shavings from 1 to 4 mm are collected for analysis and are more representative of the material. A clean 6 μm mylar film is stretched across a 15 mm diameter sample cup by a locking cap. The shavings are poured into the cup and gently tamped to loosely pack the shavings. The mylar film side is presented to the XRF aperture for analysis. Afterwards all the shavings 0.5 – 1 g are placed in labelled small paper envelope and taped to the deposit to ensure the customer gets the credit for all the material.

Au, Ag, and Other Elements in Gold Deposits for Fire Assay

After being received and weighed, incoming gold deposits were individually melted by induction heating. Once the deposit was completely melted, pin tube samples and a dip sample were taken. The dip sample was taken by dipping a hollow cylindrical steel mould (1 cm id x 0.5 cm depth) attached to a 50 cm steel rod. Lamp black in kerosene was used to coat the mould to release the solidified gold sample. This sample along with the pin tube samples were send to the Assay laboratory for analysis. The dip was flattened with a hydraulic press and polished by wet sanding with two different aluminum oxide papers (150 and 400 mesh). The polished samples were examined to ensure they were flat and would completely cover the 12 mm aperture at the bottom of a stainless steel sample cup used to introduce solid samples into the XRF spectrometer. The samples were then affixed to the cup with clear adhesive tape to prevent movement, placed in an empty position in the autosampler and programmed for analysis.

Ag and Cu in Chlorinated Gold

There is minimal sample preparation for this method. The molten impure gold is sampled by dipping sampling mould. The mould is a small cylindrical steel mould (30 mm diameter x 20 mm deep) welded to a 50 cm steel rod. This is treated with lamp black in kerosene to prevent the solidified sample from sticking. As soon as the gold solidifies it is taped out onto a steel table and placed in a water bath to quickly cool. The flat bottom side of the sample is examined for craters or material adhering to the bottom surface. If either of these conditions are observed the sample is re-cycled back into the melt and another dip sample is taken. When cool and dry, the sample is presented to XRF (Spectro 200) for analysis.

RESULTS AND DISCUSSION

Deleterious Elements in Incoming Gold Deposits

A portable or hand held XRF was purchased with intention to non-destructively analyse incoming lower grade gold bars or gold deposits that come into the Mint for refining. Unfortunately, the outside surface of these bars contained much higher concentrations of deleterious elements than the bulk material. Gold is a good absorber of X-rays so the analysis depth is very short (50 – 100 μm) in impure gold bars. So it was not possible to get good representative measurements with out extensive cleaning of the outer surface (such as using an abrasive disk on a high speed drill). This cleaning process then requires personnel to use a vented hood and personal protective devices to minimize exposure to fine particles containing high concentrations of deleterious elements. The analysis of drilling samples taken from the bulk offered a much more convenient and safer method. These drilling samples were easily collected and presented to the spectrometer for analysis.

Using portable XRF spectrometers in Canada requires certification from Natural Resources Canada which was found to be a costly and time consuming process. By placing the portable XRF in a workstation with safety interlocks, the XRF now becomes a bench top XRF and operators do not require certification because it is no longer an open source of X-rays. The drill samples can be conveniently placed in plastic cup fitting with a 6μm mylar films stretched across the aperture. The mylar film acts to contain the drilling samples and is essentially transparent to X-rays at the energies of interest. It was also found that long analysis times of 240 seconds were required to have useful lower reporting limits with this type of XRF. In a bench top configuration the times are easily attained whereas operators found that holding the portable XRF in position with the trigger depressed (as per Canadian regulations) is challenging for a time of 4 minutes.

With the measurement time of 240 seconds, limits of detection (LOD) and reporting limits at 20% RSD were observed to be well below the maximum allowable limits of deleterious elements that are permitted by the Mint in material accepted for refining (Table 2). The limit of detection was determined from the standard deviation of ten replicate determinations of a high purity Au standard (99.99%). The resulting standard deviation for each element was multiplied by a factor of 3 for the calculation of the LOD. The method was intended to be a screening tool to quickly assess the risk of accepting material into the Mint for refining therefore setting a reporting limit at an RSD of 20% (standard deviation from high purity Au multiplied by 5) for these deleterious elements was concluded to be acceptable. The reporting limits were found to be at or below the maximum allowable limits for As, Cd, Hg, and Se. In case of Te, the reporting limit is slightly higher than the limit of 300 ppm. For determined values between 300 and 500 ppm, the drill samples can be dissolved and Te determined by either flame atomic absorption spectrometry or inductively coupled plasma atomic emission spectrometry. To date, this situation has not occurred.

Table 2 – Summary of maximum element concentrations and method determination limits for each deleterious element

	As ppm	Cd ppm	Hg ppm	Se ppm	Te ppm
RCM Maximum Limit	100	1000	2000	5000	300
Limit of Detection (k=3)	60	350	420	430	300
Reporting Limit @ 20% RSD	100	580	700	720	500

The accuracy and precision of the method were assessed by determining the deleterious elements in two standards that were not used in the calibration process. Table 3 shows the results of these experiments. Replicate measurements (n=5) of both quality control standards, PA1 and AuDA1, indicate quite good measurement precision. The RSD values of deleterious elements in PA1 were between 4 – 10%, with concentration values for Cd, Hg, and Se near the RCM maximum limit concentrations. AuDA1 has generally higher concentration values for Cd, Se, and Te than PA1 and as a consequence the precision was quite low (0.4 – 2% RSD in solid form and 1 – 3% RSD drillings).

The method accuracy, expressed as %Error, as compared to concentration values obtained from ICP-AES measurements were not optimal. However, given that the method was designed for screening purposes, it was decided the method was fit for purpose. This was based on the analysis of standard PA5 which has concentrations of Cd, Hg, and Se near the maximum acceptable limits (see Table 2). The bias or %Error was thought to be acceptable: -8% (Cd), -13% (Hg), and 8% (Se). The determination of arsenic is challenging because there is an overlap with the AsKα line and Pb Lα line. Both are the most sensitive lines for each element. The AsKα line also close to several Au L lines which are extremely large. The low resolution of the spectrometer (159 – 161 eV) coupled by the low signal intensity of the As lines at these low concentrations may couple to cause this bias. The large bias observed for Se in standard AuDA1 may also be due to a more severe overlap between the SeKα line and Au Lg3 line. It also should be mentioned, that at the time of writing, there were very few standards that contained high trace concentrations of these elements in a gold matrix. It is expected that as more standards are made, characterized, and applied to this method, better accuracy should be attained.

Table 3 – Deleterious element concentrations determined for two quality control standards from five replicate measurements

	As	Cd	Hg	Se	Te
QC Standard PA5					
Average	10200	2720	2410	4570	2150
Standard Deviation	1010	270	100	380	170
RSD	10%	10%	4%	8%	8%
ICP-AES value	12020	2941	2789	4229	2521
%Error	-15%	-8%	-13%	8%	-15%
QC Standard AuDA1 (solid)					
Average, ppm	9983	10360	< LOD	10690	10950
Standard Deviation, ppm	66	729		318	409
RSD	1%	7%		3%	4%
ICP-AES value, ppm	9790	10670		9820	11500
%Error	2%	-3%		9%	-5%
QC Standard AuDA1 (drillings)					
Average, ppm	10120	12200	< LOD	8092	10860
Standard Deviation, ppm	45	374		207	207
RSD	0.4%	3%		3%	2%
ICP-AES value, ppm	9790	10670		9820	11500
%Error	3%	14%		-18%	-6%

It was observed (from Table 3) that there was little difference between the element concentrations in AuDA1 determined from a solid piece and from drilling samples taken from the same piece for As and Te. Larger differences were observed for Cd and Se however these values were within ± 20% of the ICP-AES concentrations and were considered to be acceptable for the purposes of a screening method.

Assaying Gold and Silver by XRF

Although fire assay has been the definitive method for determining gold and silver in materials, XRF has proven to be useful in providing additional information and estimates of gold and silver to compliment the fire assay process. There are two steps in traditional fire assay of bullion gold. The first step (or Button Fire step) is to take a set of 500 mg samples (exact masses determined), wrap them individually in 5 g of Pb foil, and place them in heated cupels in a furnace. The Pb melts and acts as solvent to dissolve the base metal and leaving the gold and silver in the cupel. The remaining sample is weighed to obtain the fraction of Au and Ag in the sample. In past years, the colour of the remaining gold and silver sample or bead was compared to known standards made from gold and silver. The estimated concentration of gold and silver was used to calculate the amount of extra silver added to fresh samples for the Assay Fire step (second step). Fresh 500 mg samples of the bullion sample were weighed and separately combined with an amount of silver that was approximately twice the amount of gold in the sample less the amount of silver that is estimated to be in the sample and wrapped in Pb foil. Each piece was again placed in a cupel in the furnace and a large silvery bead is collected. The silver from the bead was dissolved in nitric acid which left a solid piece of gold. This could be easily weighed and the composition of gold was determined. The silver was determined by difference from the fraction gold and silver determined in the first step.

The XRF is now used to estimate the composition of gold and silver in the bullion sample right at the start so this eliminates the need for a colour estimate of samples from the Button Fire. This permits both fire assay steps to start simultaneously which considerably shortens the total analysis time. In addition, other elements such as Cu, Fe, Ni, Pb, Pd, Pt, and Zn were determined which at high levels can interfere with the fire assay method. By knowing information on the other elements, the analysts can make the necessary adjustments to the fire assay method to counter the effects of these elements. Abnormally high levels of these elements were also communicated to the refinery to assist in the further refining of the material.

The precision and accuracy for gold and silver in various gold deposits as determined by the XRF method are summarized in Table 4. The corresponding gold and silver concentrations, as determined by fire assay, are used for comparison. The nominal precision for XRF from at least 3 replicate determinations is approximately ± 0.04% for both Au and Ag. The differences between Au and Ag determined by the XRF method are very similar to the values determined by fire assay. One main reason for the difference is that due to gold's high absorbance of X-rays the amount of material being analysed is very small (50 - 100 mg) compared to 500 mg quantities used by fire assay. The XRF method is more than adequate to provide a very close estimate of Au and Ag for the purposes of calculating the amount of extra silver to add to samples for the Assay Fire.

Table 4 – The comparison between Au and Ag determined by XRF (single replicate) and Fire Assay (4 replicates Au and 3 replicates Ag; ± 1 standard deviation)

Deposit Identifier	Au by XRF %	Au by Fire Assay %	Ag by XRF %	Ag by Fire Assay %
113383	64.89	65.15 ± 0.01	7.72	7.85 ± 0.06
113593	75.85	75.67 ± 0.02	13.53	13.37 ± 0.06
116057	56.16	56.49 ± 0.06	8.01	7.93 ± 0.11
116148	90.88	90.37 ± 0.02	4.63	4.55 ± 0.10

Table 5 shows the precision and accuracy of Au, Ag, Cd, Cu, Fe, Ni, Pb, Pd, Pt, and Zn determined in the quality control standard INQ12QC2 over a period of 20 days (40 replicate determinations). The data shows that the elements are determined with excellent precision (low RSD) and accuracy (low % Error) compared to concentrations values determined by fire assay (Au and Ag) and solution ICP-AES (Cd, Cu, Ni, Pb, Pd, Pt, and Zn). For the analyst conducting the fire assay of gold deposits it is very important to know if high concentrations of these elements (> 1%) are present in the sample. Different strategies within the fire assay method can used when high concentrations of these element are known before the analysis has started.

Table 5 – Summary of replicate data from the measurement of a quality control standard containing Au, Ag, Cd, Cu, Fe, Ni, Pb, Pd, Pt, and Zn over a 20 day period (40 replicates) and comparison to values obtained by fire assay (Au and Ag) and by ICP-AES (other elements)

	Au %	Ag %	Cd %	Cu %	Fe %	Ni %	Pb %	Pd %	Pt %	Zn %
Average	62.02	8.36	1.31	18.91	0.54	2.27	2.23	0.155	0.317	3.73
Std Dev	0.05	0.04	0.03	0.08	0.02	0.02	0.03	0.005	0.005	0.01
RSD	0.1%	0.5%	2%	0.4%	3%	1%	1%	3%	2%	0.4%
Certificate	62.38	8.47	1.42	18.23	0.50	2.23	2.35	0.162	0.335	3.75
Difference	-0.36	-0.11	-0.11	0.68	0.04	0.03	-0.12	-0.007	-0.017	-0.02
%Error	-0.6%	-1%	-8%	4%	7%	2%	-5%	-4%	-5%	-0.7%

Since the XRF method has been implemented, the number of repeat analysis due to composition problems has been reduced and the analysis time has been reduced by nearly 40% for fire assay analysis. The XRF method allows the two streams of fire assay to be started independently of each other which has been a major time reduction step.

XRF as Endpoint Determination for Chlorination

A very simple XRF spectrometer was installed on the refinery floor to monitor the amount of Ag and Cu left in a melt of several gold deposits during the Miller chlorination process. The endpoint of the chlorination process was reached when the sum of Ag and Cu reached to a pre-determined value. When the endpoint was reached, the chlorination process was stopped and the Au was poured into specially shaped anode bars that will be put into the electrolysis process. A limit of Ag and Cu was necessary to minimize the impurities going into the electrolysis process. Reducing the amount of Ag and Cu entering the electrolysis solutions ensures high gold purity on the cathode and reduces the need for frequent electrolysis solution replenishment.

The XRF method was designed to measure Ag, Cu, and Pd. Refiners must sum the Ag and Cu concentrations to determine if the endpoint was reached. Palladium was measured because Pd Kα line overlaps with the Ag Kα line used to measure Ag. Palladium typically is very low but it was measured to ensure accurate Ag values. The simple built in data processor of the XRF cannot selectively sum elements as is the case in more sophisticated spectrometers.

Table 6 shows the results for Ag and Cu from the quality control standard used daily from 140 replicate measurements. The accuracy of the Ag and Cu measurements was very good (≤ 5% Error). The precision as expressed by the standard deviation and RSD was good for Ag (8% RSD) and was poorer for Cu (24% RSD). This was expected because Cu was poorly excited by the ^{241}Am source. The excitation potential for Cu is 8.98 keV and the gamma rays emitted from ^{241}Am are at 26.4 and 59.57 keV. Whereas, Ag is very well excited because it has an excitation potential of 25.517 keV which is slightly lower in energy and very close to the gamma ray emission from ^{241}Am.

Table 6 – Determination of Ag and Cu in TP361 QC for Spectro 200 Chlorination Method (140 replicate measurements)

	Ag %	Cu %
Average	0.217	0.248
Standard Deviation	0.022	0.059
RSD	8 %	24 %
Certified Value	0.225 ± 0.020	0.262 ± 0.035
Difference	-0.008	-0.014
% Error	4	5

Normal samples presented to the XRF spectrometer on the refinery floor were not as smooth and polished as the quality control sample because sample preparation equipment takes up too much space and capital for the few measurements done each day. As a consequence, one would expect poorer precision and accuracy for normal chlorination samples than for the quality control sample

CONCLUSION

It has been shown in this paper that XRF spectrometry has been used throughout the gold refining process to provide useful element concentration results. This information was useful for health and safety of the refiners (deleterious elements) and for identifying material that could cause problems for the refining process. XRF spectrometry has also be useful enhancing fire assay, and for determining the endpoint of the Miller's chlorination process.

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