Development and Application of a Tantalum Based Internal Standard Method for High Accuracy Copper Analysis

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Introduction

In XRF techniques the observed fluorescent X-ray counts are not directly proportional to concentration but must be corrected for absorption-enhancement effects caused by the influence of all other elements in the samples. Matrix correction is typically carried out by analyzing all major elements likely to be encountered, using extensive standard suites for all elements and by generating alpha correction factors using fundamental, empirical or regression methods or a combination of these approaches.

We present a new inexpensive technique using a tantalum (Ta) internally doped flux type 12:22 (35.3% lithium tetraborate/64.7% lithium metaborate) developed by X-Ray Flux Pty Ltd and proven by TWOTHETA Pty Ltd. This new method has the potential to revolutionize currently used XRF methods for the analysis and quality control of copper. A calibration was created using reliable copper standards including copper tails, feeds and concentrates. The wide range of copper standards (0 to 40% copper) used for the calibration were Australian CRMs (Oreas 90 to 99) with Cu concentrations up to 26%, the now scarce BGS 100 CRM (35.9% Cu) and an OTML concentrate (both courtesy of Ok Tedi Mining Ltd), and 2 additional CRMs – CCU-1c (25.62% Cu) and VS 2891-84 (a Russian CRM with 40.4% Cu).

Whilst the method is an XRF technique, it is independent of conventional ά-correction XRF procedures and relies solely on the ratio of the Cu K-alpha to Ta L-alpha peaks with significant advantages over conventional XRF analysis for copper on fused glass discs. This includes insensitivity to problems associated with glass disc curvature due to molds becoming convex over time and variation in XRF cup quality. Both these factors lead to serious progressive decreases in precision.

Tantalum Oxide Internal Standard technique

For the analysis of copper it was decided to pre fuse conventional 12:22 flux (35.3% lithium tetraborate/64.7% lithium metaborate) with tantalum as an internal standard in the form of tantalum oxide, as the K- alpha peak of copper does not suffer from any interfering absorption edges and Ta will not be present in the unknown samples in other than insignificant sub-ppm levels. Because of this the ratio method of Cu K-alpha to Ta L-alpha lines is applicable. Further, tantalum oxide is commercially available in high purity and fuses well with 12:22 lithium tetraborate and other ratios of lithium tetraborate/lithium metaborate flux.

The concentration of copper is directly proportional to the ratio of the 2 peak intensities. Constants can be determined using a suite of standards and the ratio of copper and tantalum peaks in an unknown is all that is required to determine the copper concentration.

Sample preparation and experimental conditions

Sample preparation of the copper concentrates presented the greatest problem. Fused beads were prepared using a 12-22 flux pre-fused with 1.0% tantalum oxide (99.99%) as the internal standard with 12.8% sodium nitrate added to the flux post fusion to ensure complete oxidation of all components, particularly sulphides. The fusion method used (e.g. electric, gas, manual or automatic) is irrelevant to the results of this technique, provided standards and samples are treated in the same way.

Table with sample preparation parameters

	Sample weight	Flux weight
Nominal weights	0.6 g (0.3 or 0.1 g)	8 g
Oxidising temperature	700ºC	
Oxidising time	15 minutes	
Fusion device	Rocking furnace	
Fusion temperature	1050ºC	
Fusion time	15 minutes	
Releasing agent	NH_4I pellets	Added 1 to 2 min before casting
Alternative release method	Iodine caps over mould	During cooling
Cooling time	6 minutes	

Higher Cu concentrations have 2 effects on the melt:

1. Decreases the viscosity significantly and makes the melt very fluid
2. Causes the melt to strongly adhere to the platinum ware and not pour cleanly

Using a releasing agent such as ammonium iodide (NH_4I) tablets increases the surface tension of the glass melt and clean beads can be produced without cracking. Cleaning of the crucibles takes a long time without the use of ammonium iodide tablets. It should be noted that the possibility exists that iodine can also form a volatile copper iodide (CuI) compound (melting point 605ºC) and Cu could in this instance possibly escape from the melt causing lower intensities and thus lower concentrations.

For Cu-concentrates (Cu > 20%) the following different approaches were tried to produce good quality fused beads with varying degrees of success:

1. Sample weight was reduced to 0.3 g or 0.1 g
2. Reduced sample weight with or without NH_4I
3. Reduced sample weight using an iodine cap over cooling mould

Some difficulties encountered:

a. When initially using NH_4I, the intensities seem to be too low indicating possible loss of Cu through formation of CuI.
b. If no NH_4I is used the melt spreads out over the edges of the mould and when the bead is cooling it cracks into two pieces at best or it can shatter completely.
c. If the NH_4I pellet is added too close to the casting (about 1 minute) the melt doesn't spread out completely in the mould and forms a half-moon. The mould needs to be kept inside the furnace until the surface tension lowers again and the melt fills the mould. It's possible that more Cu might be lost during that time.

Instrumentation and measuring program

The instrument used for the study was a PANalytical PW2400 WD-XRF spectrometer with a 3 kW tube. Two sets of channels were set up, one using the scintillation counter and another one using the flow counter (for details see table on page 4). An added bonus of using the flux with an internal Ta standard is that Ta also has two lines near the Si K-alpha line. The Ta M-alpha (to the right of Si K-alpha peak) was used for a ratio correction of Si.

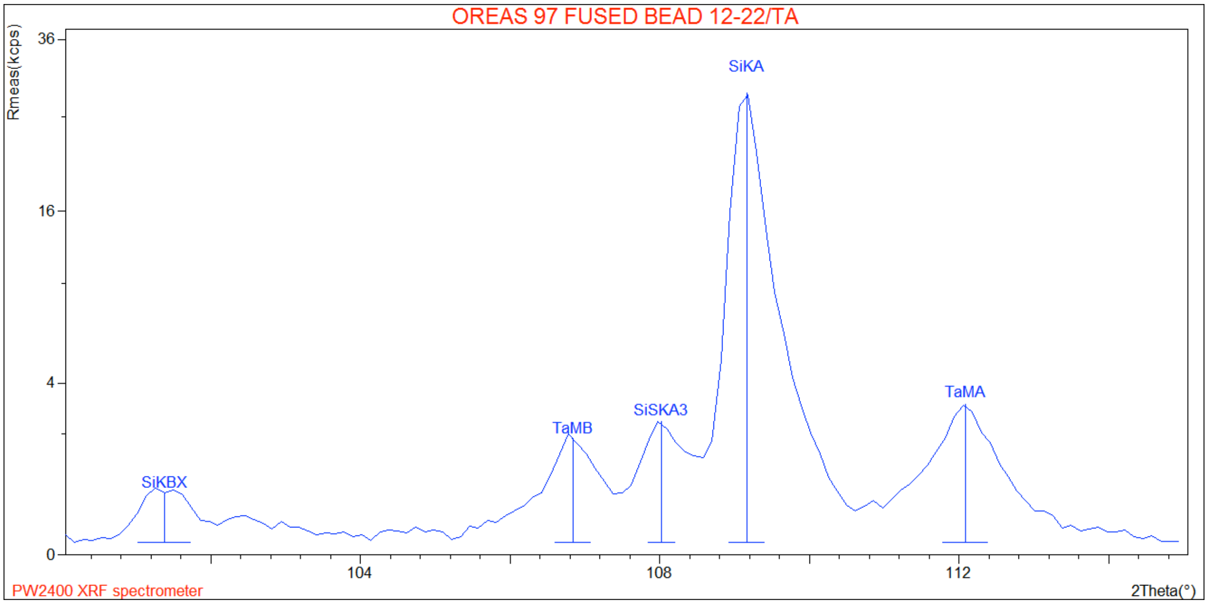


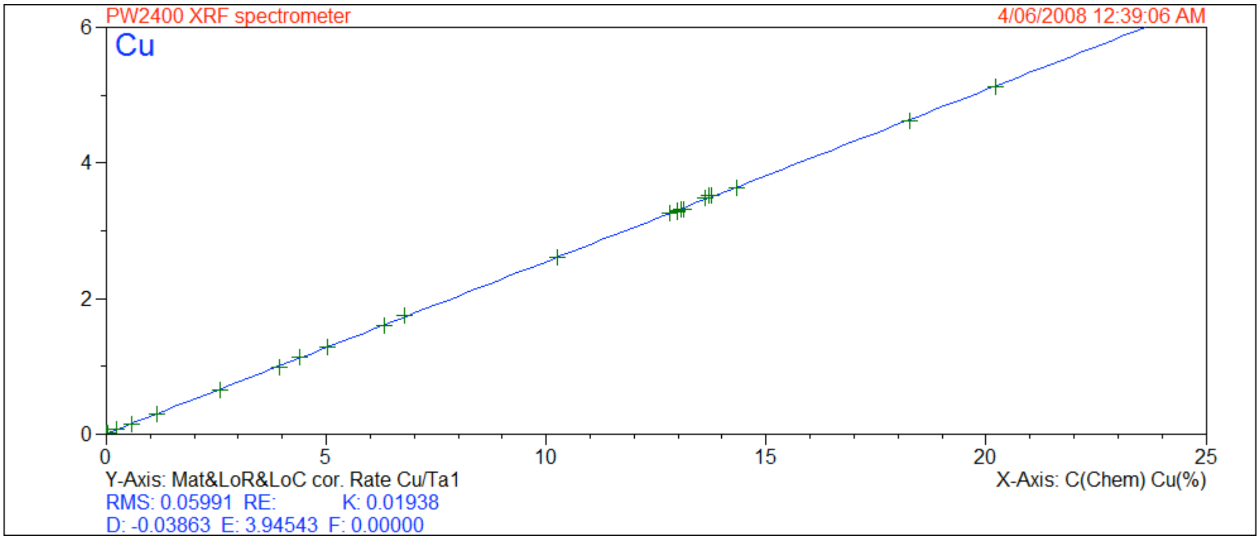
Table with channel settings (PW2400)

Channel	Line	X-tal	Collimator	Detector	kV	mA	Angle (°2T)	Offset Bg1 (°2T)	PHD1 LL	PHD1 UL
Cu	KA	LiF 220	150 µm	Scint.	60	50	65.5012	0.9508	24	75
Ta1	LA	LiF 220	150 µm	Scint.	60	50	64.5888		23	75
Cu1	KA	LiF 200	150 µm	Flow	60	50	45.0106	1.0304	23	63
Ta2	LA	LiF 200	150 µm	Flow	60	50	44.4006		23	63
Si	KA	PE 002	700 µm	Flow	25	120	109.1714		31	69
Ta3	MA	PE 002	700 µm	Flow	25	120	112.088		34	74

The total measuring time was 120 s but in practice only one set of channels (Cu and Ta) would be used and the measuring time would be reduced to 30 s. The intensities obtained were similar – Cu1in the above table being about 20% higher than Cu and Ta2 about 5 to 6% higher than Ta1 (actual intensities are shown in the table). The choice of the actual channel settings will depend on the spectrometer used and the sample preparation recipe.

Calibration

A few (high-Cu) standards (10 out of 33) were excluded from the calibration below because of Cu lost in the fusion. Most of those are replicates of the same CRM where various ways were tried to improve the fusion and cooling process to obtain good quality beads. The remaining CRMs form an excellent wide-range regression line (0 to 40% Cu) with a very small overall error (RMS) of 0.06%. There are no samples displayed at 40% because when the software applies the dilution factor a “half-weight” 40% sample appears at 20%.

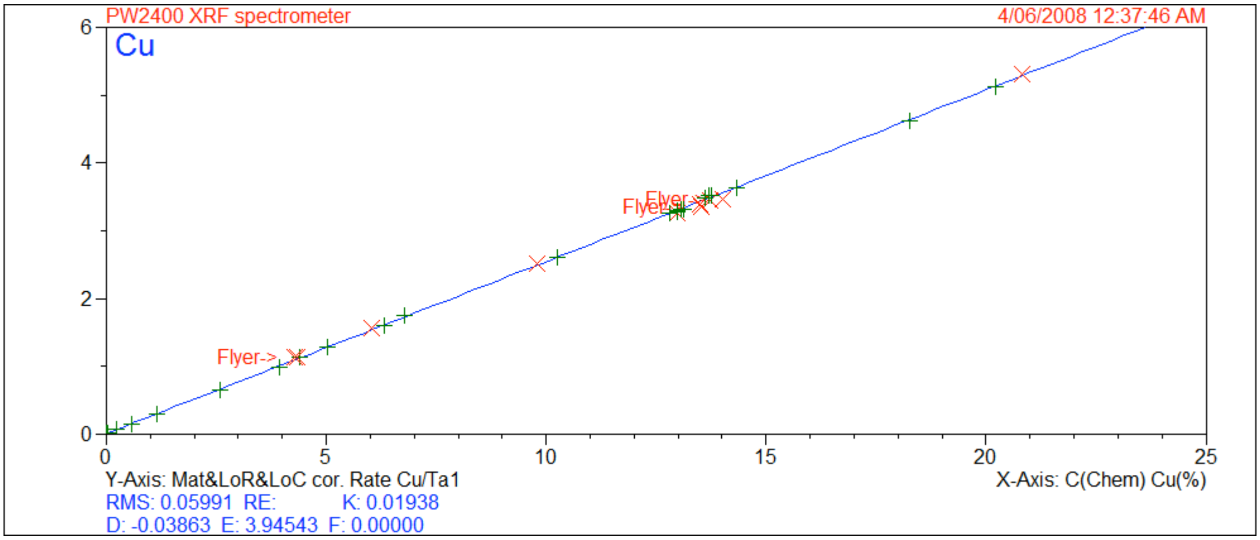


Complete range of standards/CRMs (excluded standards hidden)
The overall error is very small – RMS = 0.0599 – excellent.

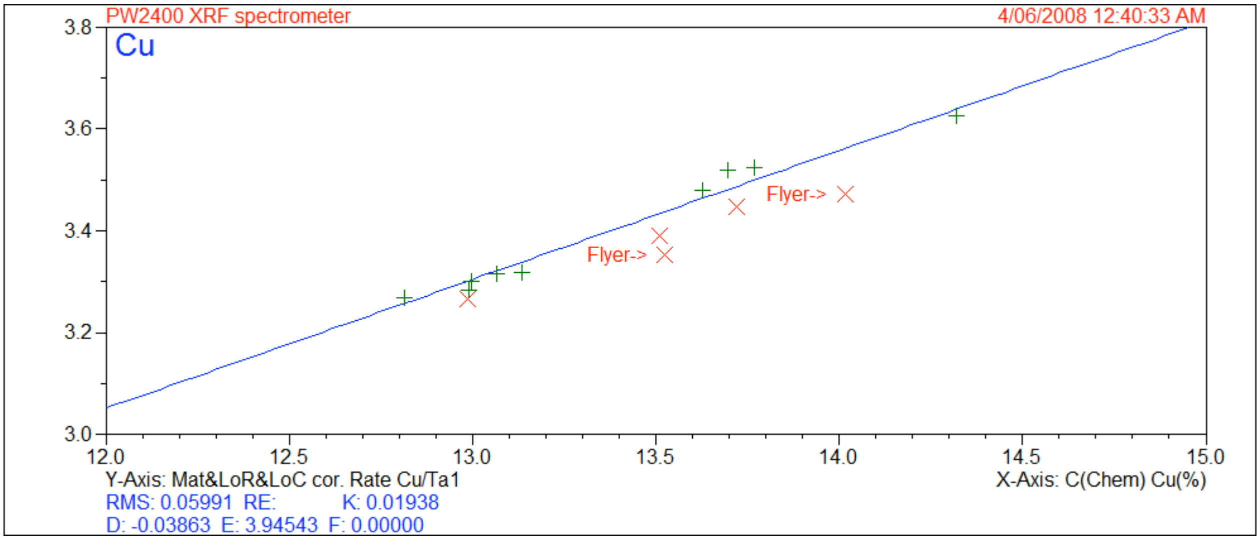
Table with calibration data (using channels Cu and Ta L alpha – scintillation counter)

Standard	**Ex.**	**C(Calc)**	**C(Chem)**	**Diff(C)**	**Gross rate**	**Net rate**	**Matrix**	**Ratio rate**	**Release aid**
		(%)	**(%)**	**(%)**	**(kcps)**	**(kcps)**		**(kcps)**	
BGS 100 A		35.74	35.90	-0.1566	522.790	518.559	1.021	114.666	NH4I
BGS 100 C	X	36.25	35.90	0.3496	345.602	341.914	1.011	137.384	NH4I
BGS 100 D	X	36.65	35.90	0.7462	241.946	238.552	1.007	152.728	none
BGS 100 E	X	36.12	35.90	0.2149	575.225	570.831	1.024	109.857	none
BGS 100 F		35.86	35.90	-0.0396	560.525	556.166	1.023	110.890	IC
CCU-1c		25.52	25.62	-0.1016	372.693	369.356	1.016	103.543	NH4I
CCU-1c B		25.60	25.62	-0.0220	352.053	348.694	1.015	107.202	NH4I
CCU-1c E		25.73	25.62	0.1112	367.129	363.813	1.015	106.204	none
CCU-1c F		25.71	25.62	0.0905	354.421	351.070	1.015	108.947	IC
OREAS 90 A		0.0150	0.0112	0.0040	3.706	1.751	1.000	127.294	NH4I
OREAS 91 A		0.0280	0.0265	0.0017	4.180	2.188	1.000	129.074	NH4I
OREAS 92 A		0.2260	0.2294	-0.0035	10.723	8.772	1.000	125.607	NH4I
OREAS 93 A		0.5700	0.5817	-0.0113	21.597	19.593	1.001	127.347	NH4I
OREAS 94 A		1.12	1.14	-0.0166	39.076	36.991	1.001	125.266	NH4I
OREAS 95 A		2.53	2.59	-0.0562	79.263	77.064	1.003	118.448	NH4I
OREAS 96 A		3.89	3.93	-0.0417	116.362	114.028	1.004	115.069	NH4I
OREAS 97 A		6.31	6.31	-0.0053	178.109	175.588	1.007	109.932	NH4I
OREAS 98 A		14.79	14.80	-0.0101	288.982	285.907	1.012	110.949	NH4I
OREAS 99 A	X	25.23	25.89	-0.6638	368.064	364.698	1.016	106.742	NH4I
OREAS 99 B	X	25.61	25.89	-0.2780	353.294	349.941	1.015	108.747	NH4I
OREAS 99 C	X	26.55	25.89	0.6584	171.066	168.138	1.005	148.209	NH4I
OREAS 99 D	X	26.72	25.89	0.8263	170.806	167.820	1.005	148.903	none
OREAS 99 E		25.85	25.89	-0.0384	360.085	356.757	1.015	109.178	none
OREAS 99 F		25.75	25.89	-0.1452	359.534	356.207	1.015	110.073	IC
OTML CON A	X	25.68	26.00	-0.3243	366.153	362.784	1.015	108.621	NH4I
OTML CON B		25.84	26.00	-0.1635	362.056	358.717	1.015	109.741	NH4I
OTML CON C		26.09	26.00	0.0858	168.959	165.987	1.005	147.860	NH4I
OTML CON D		26.21	26.00	0.2061	190.282	187.350	1.006	145.531	none
OTML CON E		26.19	26.00	0.1895	377.967	374.546	1.016	107.908	none
OTML CON F		26.28	26.00	0.2807	380.684	377.225	1.016	108.888	IC
VS 2891-84 A	X	39.4	40.4	-0.9967	479.325	474.881	1.015	143.796	NH4I
VS 2891-84 B	X	39.9	40.4	-0.4632	483.236	478.799	1.016	141.042	NH4I
VS 2891-84 C		40.8	40.4	0.3953	280.657	277.023	1.008	160.116	none

C(Chem) is the recommended concentration (certificate)
C(Calc) – concentration calculated from the regression line
Ratio Rate – Tantalum intensity
NH_4I – Ammonium Iodide
IC – Iodine Caps



Graph showing the complete range of standards/CRMs (excluded standards displayed)



The graph above shows an enlarged section of the regression line encompassing the range from 25 to 36%. High Cu samples appear at lower 'apparent concentrations' because of catch weights. They are mostly 'half-weights' and therefore a 26% sample appears at 13%. Some of the high Cu samples lie significantly below the calibration line. Some material was lost during the fusion either adhering to the wall of the crucible because of 'splattering' from the addition of the NH_4I tablets or due to formation of a volatile CuI compound. However, a few specimens also lie above the regression line. It is difficult to decide which samples should be used if there is any uncertainty about the sample preparation.

Table with fusion parameters and effects/observations

	No releasing aid	NH_4I tablets	Iodine caps
Crucible clean	No	Yes	No
Bead release	Beads crack or shatter	Excellent	Excellent
Problems		If added too late formation of half-moon, further, Cu can evaporate via formation of CuI	

Conclusion

The new Ta internal standard method for the XRF analysis of copper has demonstrated excellent Cu results similar to other methods that use an Internal Standard (Ni/Tm and Fe/Tb) over a wide calibration range of up to 40% copper. The only potential difficulty lies in the area of sample preparation/fusion of high Cu samples because of the adhesive tendencies of the Cu-rich melt.

Release agents such as NH_4I solve the problem by increasing the surface tension of the melt but the formation of a low melting phase (CuI) and subsequent possible escape of Cu is potentially counter-productive. Bromide release agents would give a similar result because of the possible formation of CuBr with the associated low melting temperature (760 to 777º C) and some copper could potentially be lost.

Iodine caps work well with respect to the release of the bead from the mould, however, the crucibles retain some melt and are therefore difficult to clean. A solution, although somewhat time consuming, would be to return the crucibles back to the furnace and add an NH_4I pellet just for cleaning and pour the remaining melt out.