

Development and Application of a Thulium[®] Based Internal Standard Method for High Accuracy Nickel Analysis

Shane J. Reeves^a, David Brown^b and Jorg Metz^c

^a*BHP Billiton, Nickel West, Leinster Nickel Operation, Leinster, Western Australia, 6437.
Now with Energy Resources of Australia, Ranger Mine, Locked Bag 1, Jabiru, NT, 0886, Australia*

^b*X-Ray Flux P.L., 88 Guthrie St., Osborne Park, Perth, Western Australia, 6017.*

^c*XRF Scientific Ltd, 24/200 Canterbury Rd, Bayswater, Victoria 3153, Australia. www.xrfscientific.com*

Abstract

Nickel analysis in high sample volume laboratories has historically been performed by acid digest AAS or ICP-OES, fused glass disc XRF or powder pellet XRF. Highest quality nickel analysis has been performed using the expensive and technically complex technique of nickel dimethylglyoximate (DMG) precipitation. Recently, concerns have been raised about the limitations of DMG analysis with the technique having been demonstrated to be prone to overestimation due to Cu, Co or Fe co-precipitation, to be sensitive to reagent quality, and to be dependant on skilled analysts (Williamson, 2006). Further, it is inherently less safe than XRF in that it requires the use of hazardous chemicals such as hydrofluoric acid and is labour intensive and slow, with a typical DMG assay turnaround of 2 days.

We present a new, relatively inexpensive technique using a thulium (Tm) internally doped flux (type 12:22 SRT) developed by X-Ray Flux P.L., and tested and confirmed at the Nickel West, BHP Billiton, Leinster Analytical Laboratory, which has the potential to revolutionise currently used methods of quality control as well as high quality shipment grade nickel analysis. A calibration created from reliable nickel standards and tested using well characterised samples outside the calibration has shown excellent results, with precision significantly better than either conventional XRF or the DMG technique and applicable down to sub % levels. The technique is intrinsically safer than either AAS or DMG analysis, is significantly faster (fusion followed by a 70 second count time in the Tm method), is much less reliant on technical expertise, is amenable to high sample throughput and is significantly cheaper than DMG. Whilst the analysis is an X-ray technique, it is independent of conventional α -correction X-ray procedures, relying only on the ratio of the Ni K_{α} to Tm L_{α} peaks and has significant advantages over conventional fused glass disc XRF analysis for nickel, including insensitivity to problems associated with glass disc curvature and variation in XRF cup quality.

January 2006

© X-Ray Flux Pty Ltd. All rights reserved.

Keywords: Nickel, Thulium, XRF, internal standard method

Corresponding authors. E-mail: shane.reeves@bhpbilliton.com; david.brown@iinet.net.au

Introduction

Nickel analysis, particularly in mining operations, requires rapid turnaround, high throughput and high accuracy data for the metallurgical optimisation of the concentration process. Historically, this has been accommodated by acid digest atomic absorption spectrometry (AAS) or optical emission spectrometry (ICP-OES), powder pellet X-ray fluorescence (XRF) or fused glass disc X-ray fluorescence.

In the AAS and ICP-OES techniques, the procedures involve the use of hazardous chemicals, such as hydrofluoric acid, are prone to underestimation if refractory minerals are present, may require complex matrix corrections and are usually heavily diluted and limited to low concentration analysis.

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 (e.g. Haukka and Thomas, 1977; Potts, 1987). Matrix correction is typically carried out by analysing all major elements likely to be encountered, using extensive standard suites for all elements, and by generating α correction factors using fundamental, empirical or regression methods or a combination of these approaches. The technique is sensitive to variation in glass disc flatness due to moulds becoming convex over time, and to variation in cup quality. Both of these factors lead to decreased precision.

The powder pellet XRF technique is typically used for low level trace element analysis (e.g. As) with matrix correction by reference to the tube Compton peak (Chappell, 1991). The technique is unsuitable for elements lighter than Fe due to diffraction, mineralogical and penetration depth effects (Mori et al., 2000).

Limitations and concerns with the DMG technique

In practice, the technical expertise required to produce high quality fused glass disc XRF Ni data is such that shipment quality is usually judged on the basis of the gravimetric technique dimethylglyoxime (DMG) precipitation of nickel dimethylglyoximate. This technique, however, is time consuming, labour intensive, expensive and not amenable to high sample throughput. Recent work (Williamson, 2006) has shown that Cu co-precipitation with DMG causes erroneously high Ni-DMG assays (approximately 25% of the contained copper will co-precipitate), that Co can co-precipitate unpredictably and also that Fe co-precipitation can cause errors in excess of 0.3% absolute. Reagent quality and degradation is also of concern and unless a specialist analyst is employed, significant variation in quality is observed in practice. In a recent round robin analysis of 40 Ni concentrate samples (averaging 15.5% Ni) three separate experienced DMG laboratories returned an average range of 0.26% absolute or 1.7% relative (Appendix 1). The three laboratories returned an average 3σ assay variation of 0.41%, indicating that DMG assay at the 99.7% confidence level was at best +/- 0.41% absolute or 2.7% relative.

Thulium Oxide Internal Standard Technique

The use of internal standards in XRF to matrix correct for a single element analysis is well known (Norrish and Fritz). This method corrects for matrix by comparing the analytical line to that of a known addition that has a line near to the analytical line. In the case of Fe the method compares FeK_{β} (1.756A) to CoK_{α} (1.788), a known amount of Co having been added to the sample. The ratio of the 2 intensities will be linearly related to concentration provided that no absorption edges occur between the lines.

For the analysis of Ni, scientists at X-Ray Flux P.L. opted to dose conventional 12:22 flux (33.3% lithium tetraborate: 66.7% lithium metaborate) with thulium in the form of thulium oxide (provisional patent 2006900048), as the L_{α} peak of thulium and the K_{α} peak of Ni do not suffer from any intervening absorption edges and Tm will not be present in the unknown sample in other than insignificant sub-ppm levels. Because of this the ratio method is applicable [Tm L_{α} (1.732A) and Ni K_{α} (1.659A)]. In addition, thulium oxide is commercially available in high purity and fuses extremely well with 12:22, lithium tetraborate and other ratios of lithium tetraborate/lithium metaborate flux.

The technique uses the count rate measured for Ni (R_{Ni}) and Tm (R_{Tm}) given by,

$$R_{Ni} = K_1 * C_{Ni} * A_{Ni} \quad \text{and} \quad R_{Tm} = K_2 * C_{Tm} * A_{Tm}$$

Where

- R_{Ni} = count rate of Ni K_{α}
- R_{Tm} = count rate of Tm L_{α}
- C_{Ni} = concentration of Ni in the sample
- C_{Tm} = concentration of Tm in the sample
- A_{Ni} = mass absorption coefficient of the sample for Ni K_{α}
- A_{Tm} = mass absorption coefficient of the sample for Tm L_{α}

Rearranging;

$$R_{Ni} / R_{Tm} = K_3 * C_{Ni} * A_{Ni} / C_{Tm} * A_{Tm}$$

Therefore;

$$C_{Ni} = K_3 * C_{Tm} * [R_{Ni} / R_{Tm}] * A_{Tm} / A_{Ni} = K_4 * [R_{Ni} / R_{Tm}]$$

where K_4 is a constant (C_{Tm} is also constant).

Therefore the concentration of nickel is linearly related to the ratio of the 2 peak intensities. The constant can be determined by using a suite of standards and the ratio of the Ni and Tm peaks in an unknown is all that is required to determine the nickel concentration.

The obvious benefit of the technique is that, unlike conventional XRF analysis, it does not require robust alpha correction factors for all contained elements above 500 ppm and only very short counting times are required (70 seconds). Norrish and Fritz have previously shown that for Fe analysis, using the internal standard method, both target element and internal reference lines will be similarly affected by glass disc shape and proximity to the X-ray tube, thus eliminating the potentially significant error due to disc curvature.

Experimental conditions

The glass discs for X-ray fluorescence measurement were prepared using 9.500g of X-ray Flux P.L. 12:22 flux + 20% $NaNO_3$ with Tm_2O_3 and 0.3600g of sample. Fusion was in platinum crucibles and onto platinum moulds using a Phoenix VFD/6000 fusion machine. By using a fused glass disc, particle size effects are eliminated. Sodium nitrate is added to the flux to ensure complete oxidation of all components, particularly sulphides. Sodium nitrate is used only for the purposes of oxidation of the sulphides and this new technique is equally applicable to pure lithium tetraborate flux, or any of the common fluxes. In addition, 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 similarly.

Instrument conditions were as in Table 1.

	<i>Thulium</i>	<i>Nickel</i>
Line	L _α	K _α
Crystal	LiF200	LiF200
Collimator	Fine 0.15	Fine 0.15
Detector	Scintillation and Flow counter	Scintillation and Flow counter
Voltage	60	60
Current	50	50
Mask	34mm	34mm
Count time	30 seconds	30 seconds

Table 1: Instrument conditions

Results and Discussion

A small initial calibration was created to determine what level of thulium oxide was required in the flux. Table 2 lists the standards used to create the calibration using the Ni/Tm method.

	Std Ni %	3 s.d
S18	0.36	+/- 0.01
S 6	1.63	+/- 0.02
S 5	4.66	+/- 0.05
S 8	9.9	+/- 0.10
S27	13.5	+/- 0.10
S26	19.67	+/- 0.10

Table 2: Standards used to test the technique with accepted values and 3 standard deviation confidence limits (WMC Series standards verified by XRF, DMG and ICP-OES)

Three separate pre-fused fluxes were produced by X-Ray Flux P.L. containing 1% Tm₂O₃, 5% Tm₂O₃ and 9.8% Tm₂O₃, in order to determine the minimum concentration of Tm₂O₃ required in the conventional 12:22 + 20% NaNO₃ flux (all were made with 99.99 grade Tm). Standards were fused in duplicate for each of the 3 fluxes, to produce 3 separate calibrations. Tables 3-5 present the raw data for all the standards analysed.

Tm₂O₃ 1%			
Sample	Tm L _α kCps	Ni K _α kCps	Ni K _α /Tm L _α
S18	25.5	7.14	0.280
S 6	25.3	23.9	0.946
S 5	21.0	54.5	2.59
S 8	19.8	105.0	5.31
S27	19.3	140.3	7.26
S26	20.2	212.6	10.53

Table 3: Data for Tm (L_α) and Ni (K_α) for the standard set, average of duplicates, using 1% Tm₂O₃ in 12:22 +20% NaNO₃ flux.

Tm₂O₃ 5%			
Sample	Tm L _α kCps	Ni K _α kCps	Ni K _α /Tm L _α
S18	78.1	5.46	0.070
S 6	77.4	17.4	0.225
S 5	68.7	40.6	0.591
S 8	65.3	78.8	1.21
S27	64.1	106.5	1.66
S26	66.4	159.0	2.40

Table 4: Data for Tm (L_α) and Ni (K_α) for the standard set, average of duplicates, using 5% Tm₂O₃ in 12:22+20% NaNO₃ flux.

Tm₂O₃ 9.8%			
Sample	Tm L _α kCps	Ni K _α kCps	Ni K _α /Tm L _α
S18	112.0	4.50	0.040
S 6	111.5	13.0	0.116
S 5	102.6	31.3	0.305
S 8	98.4	60.9	0.619
S27	97.0	81.7	0.842
S26	99.1	121.4	1.23

Table 5: Data for Tm (L_α) and Ni (K_α) for the standard set, average of duplicates, using 9.8% Tm₂O₃ in 12:22+20% NaNO₃ flux.

The Ni K_α/Tm L_α ratios were obtained for each of the standard concentrations and plots obtained (Figs. 1-3). All 3 figures showed exceptionally good correlation coefficients (>0.999). The very good peak count rates for 1% Tm₂O₃ in 12:22 flux indicates that this is a sufficient dosing level.

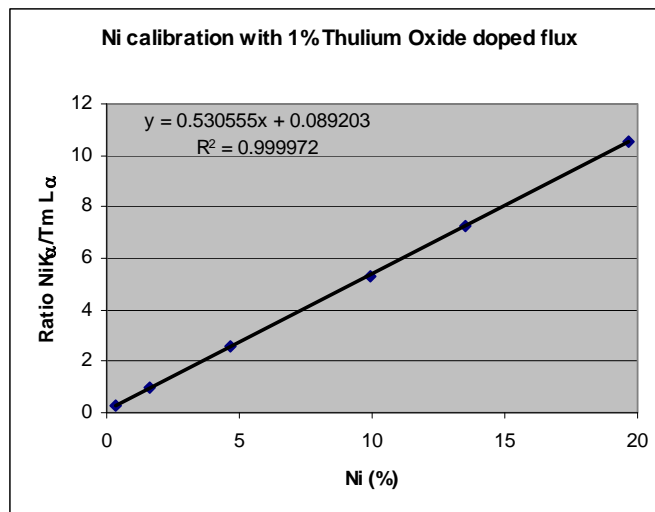


Figure 1: Ni K_α/Tm L_α versus Nickel concentration (%) for the standard set using 1% Tm₂O₃ in normal 12:22 flux with 20% NaNO₃

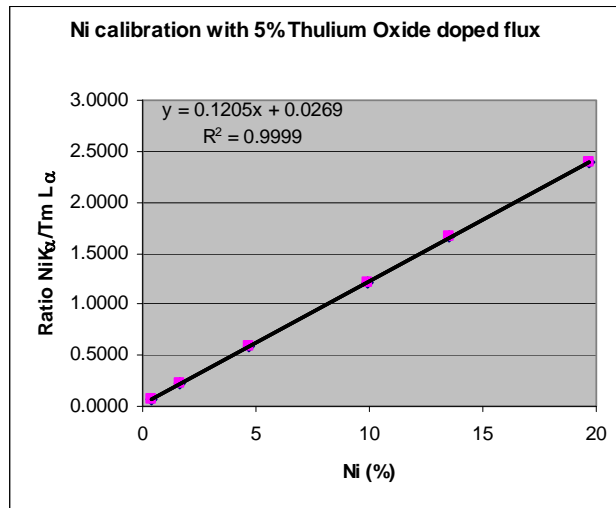


Figure 2: Ni K_α/Tm L_α versus Nickel concentration (%) for the standard set using 5% Tm₂O₃ in normal 12:22 flux with 20% NaNO₃

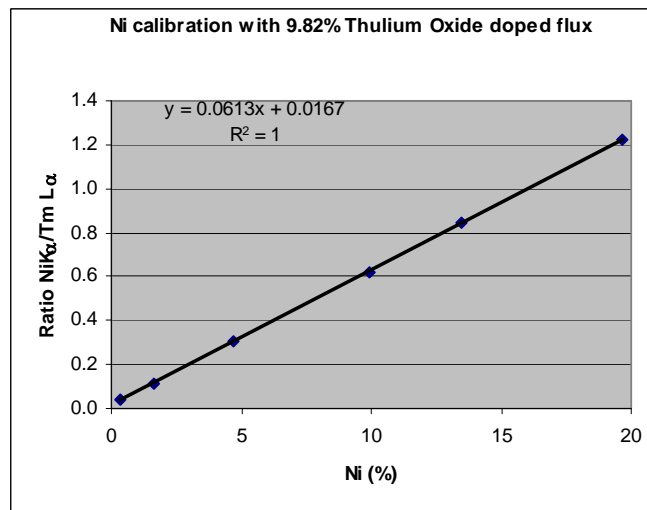


Figure 3: Ni K_α/Tm L_α versus Nickel concentration (%) for the standard set using 9.8% Tm₂O₃ in normal 12:22 flux with 20% NaNO₃

To test the robustness of the technique, a more elaborate calibration was constructed using a wide range of nickel standards in triplicate (Table 6). Conditions were as in Table 1, using 1% 99.99 grade Tm₂O₃ 12:22 + 20% NaNO₃ flux. The full details of the calibration are presented in Appendix 2.

The Ni K_α/Tm L_α ratio was plotted against Ni (%) for all standards and the results presented in Figure 4. Again, a very strong positive correlation ($r^2 > 0.999$) was achieved. Note that the data does not pass through the origin. This is because no background correction was put in place for the nickel line. For analysis at very low levels a background correction should be implemented.

Standard Name	Ni (%)
WMC18	0.36
WMC4	0.51
WMC15	0.61
WMC23	0.67
WMC24	0.69
WMC9	0.73
WMC20	1.47
WMC6	1.63
WMC19	2.10
WMC1	2.45
WMC7	4.51
WMC5	4.66
WMC25	7.82
WMC12	9.27
WMC8	9.90
WMC27	13.50
WMC13	14.96
WMC2	15.63
DMG	17.41
WMC26	19.67

Table 6: Complete standard set used to test the technique (WMC Series standards verified by XRF, DMG and ICP-OES)

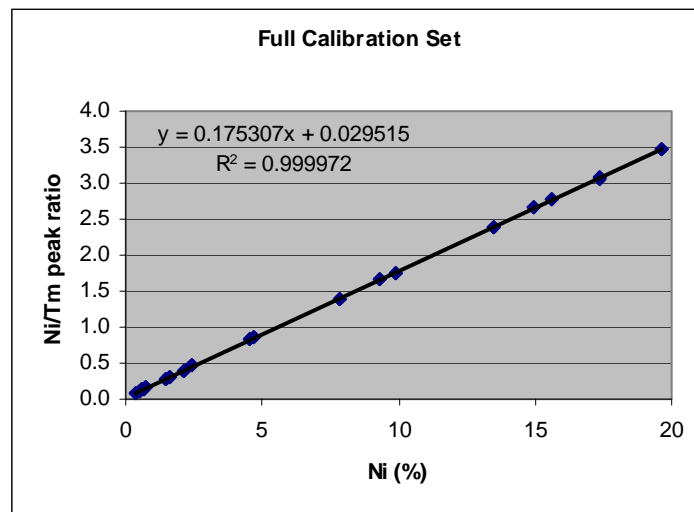


Figure 4: Ni K_{α} /Tm L_{α} versus Nickel concentration (%) for the complete standard set using 1% Tm₂O₃ in normal 12:22 flux with 20% NaNO₃

A selection of samples from Appendix 1 in which all three DMG laboratories obtained close results were then used to test the accuracy of the calibration, along with new standards fused multiple times to test precision. The results are presented in Table 7. This table clearly shows the very good replication possible using this technique, which effectively negates any imprecision due to glass disc curvature and cup variation. Average 1 standard deviation precision is 0.04%, as compared to 0.14% for DMG from the 3 laboratories, or 0.25% relative for the thulium method compared to 0.9% for DMG. Average accuracy for all samples tested, was <0.03% absolute and <0.2% relative. Bias was -0.02% absolute.

The robustness of the technique to glass disc and cup variation is exemplified by the range of Ni K α intensities for a single standard such as DMG1-6 (Table 7) which would have resulted in a concentration range of 17.23-17.44% by conventional α - correction XRF, but in the thulium method the range, using the same Ni K α intensities the range is only 17.32-17.36% because the Tm L α reference peak has corrected for bead variation.

	Ni	Tm	Ratio	Ni % Accepted	Ni % Calculated	Average	Calc Precision	1 st dev % rel
DMG1	185.2	60.4	3.07	17.36	17.34	17.34	0.02	0.09
DMG2	184.3	60.0	3.07		17.36			
DMG3	183.5	59.8	3.07		17.33			
DMG4	183.0	59.7	3.07		17.32			
DMG5	183.8	59.8	3.07		17.36			
DMG6	184.0	60.0	3.07		17.32			
4811a	194.1	58.7	3.31	18.80	18.70	18.76	0.05	0.29
4811b	193.8	58.3	3.32		18.78			
4811c	195.8	58.9	3.33		18.80			
4814a	192.3	58.8	3.27	18.54	18.49	18.54	0.04	0.24
4814b	192.1	58.5	3.28		18.57			
4814c	194.1	59.1	3.28		18.56			
4831a	187.9	58.4	3.22	18.14	18.18	18.12	0.06	0.34
4831b	187.3	58.4	3.21		18.12			
4831c	188.6	59.0	3.20		18.06			
4837a	175.0	58.1	3.01	17.04	17.03	16.99	0.03	0.20
4837b	174.5	58.1	3.00		16.96			
4837c	176.0	58.5	3.01		16.99			
4862a	181.8	59.1	3.08	17.42	17.38	17.40	0.06	0.34
4862b	182.0	58.9	3.09		17.46			
4862c	181.7	59.2	3.07		17.34			
S26a	215.0	62.0	3.47	19.67	19.63	19.64	0.04	0.18
S26b	215.0	62.0	3.47		19.61			
S26c	215.6	62.0	3.48		19.67			
S2a	161.5	58.2	2.77	15.63	15.66	15.66	0.02	0.14
S2b	162.4	58.4	2.78		15.68			
S2c	163.7	59.1	2.77		15.64			
S1a	34.3	75.0	0.46	2.45	2.44	2.45	0.01	0.40
S1b	34.2	74.3	0.46		2.46			
S1c	34.0	74.1	0.46		2.45			
Averages							0.04	0.25

Table 7: Samples and standard used to test the accuracy and precision of the Tm technique

Validation of Flux Types and Optimisation of Tm Concentration and Grade

Additional work was done to confirm that the technique is applicable to other flux compositions, and also to assess if lower levels and grades of Tm₂O₃ could be used, to make the technique less costly.

Figure 5 shows the correlation obtained for a series of standards, using 0.5% Tm₂O₃ in normal 12:22 flux with 20% NaNO₃ and a 99.99% grade Tm₂O₃. Data quality is as good as the 1% Tm₂O₃ equivalent which will enable an approximately 50% price reduction in the cost of the thulium oxide used.

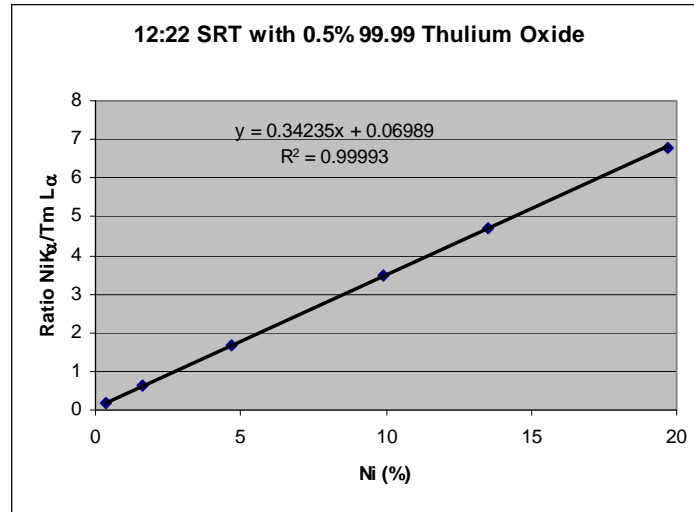


Figure 5: Ni K_α/Tm L_α versus Ni (%) using 0.5% Tm₂O₃ in normal 12:22 flux with 20% NaNO₃

The use of pure lithium tetraborate flux is prevalent in nickel producing countries other than Australia, and it is important to demonstrate that the technique is applicable to this flux composition, as well as to the eutectic mixture 12:22. Figure 6 illustrates the correlation obtained for a series of standards, using 1% Tm₂O₃ in pure lithium tetraborate flux with a 99.99 grade Tm₂O₃. Data obtained is of similar quality to that using the 12:22 flux and illustrates that the technique can be applied to any commercial flux compositions.

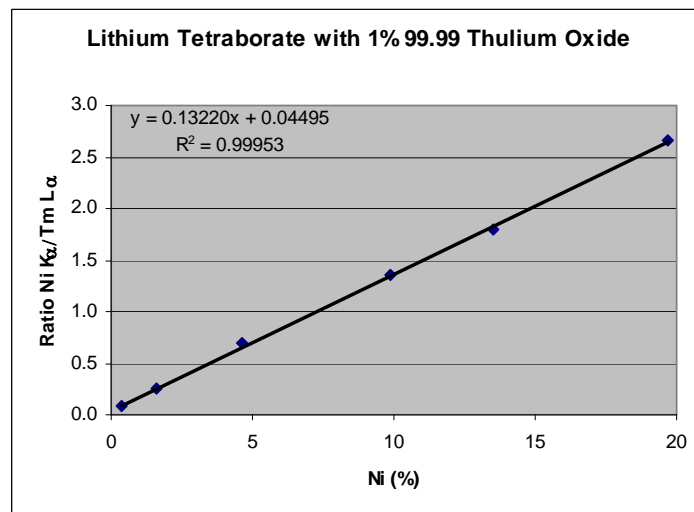


Figure 6: Ni K_α/Tm L_α versus Nickel concentration (%) using 1% Tm₂O₃ in Lithium Tetraborate flux

Finally, cheaper 99.9 grade Tm_2O_3 was used for both 12:22+20% $NaNO_3$ and for lithium tetraborate flux. Figures 7 and 8 illustrate the $Ni K_{\alpha}/Tm L_{\alpha}$ versus nickel concentration (%) for these two flux compositions and show that similar high quality data is obtained to those fluxes that use the 99.99 grade Tm_2O_3 , and that therefore the Tm reference method for Ni analysis can be made economically more attractive.

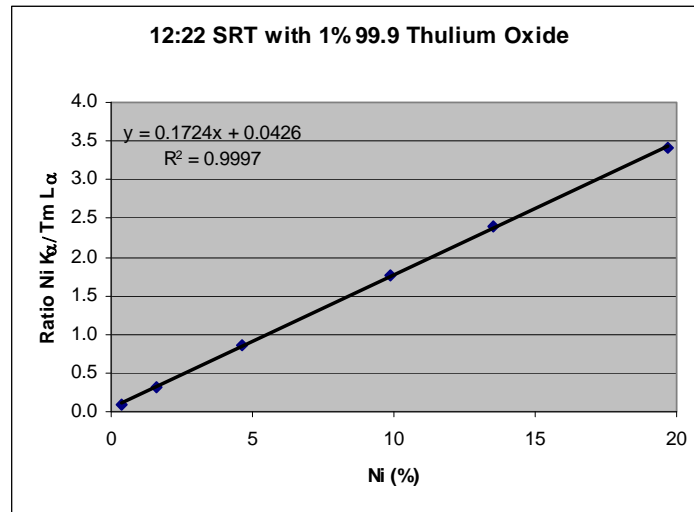


Figure 7: $Ni K_{\alpha}/Tm L_{\alpha}$ versus Ni (%) using 1% 99.9 grade Tm_2O_3 in normal 12:22 flux with 20% $NaNO_3$

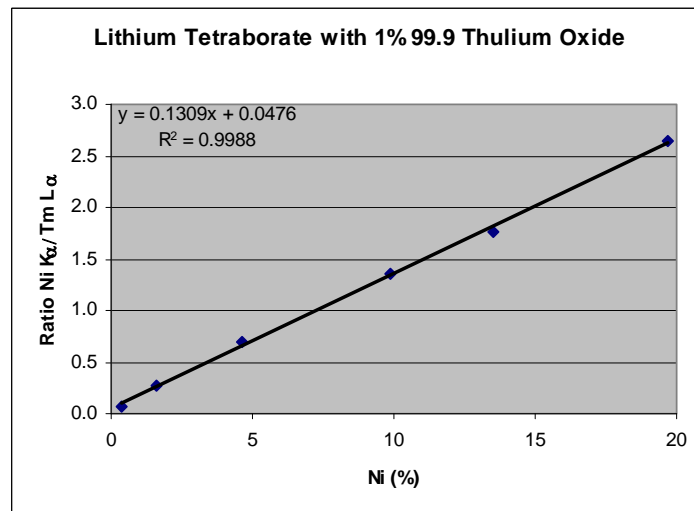


Figure 8: $Ni K_{\alpha}/Tm L_{\alpha}$ versus Nickel (%) using 1% 99.9 grade Tm_2O_3 in Lithium Tetraborate flux

Financial Justification

The addition of the thulium internal standard is likely to increase the cost of a single XRF analysis at Leinster by an estimated maximum of \$US0.40c, assuming a 0.5% Tm₂O₃ of 99.99 grade, and as low as \$US0.20c, assuming a 0.5% Tm₂O₃ of 99.9 grade. DMG analysis commercially costs around \$US60, so the additional cost is negligible when compared to DMG analysis. It should be emphasised that an analytical error of 0.1% absolute in a typical Leinster concentrate can result in a calculated recovery error of 0.5% absolute and reconciliation errors of up to two Ni tonnes per day based on current production. Therefore, the cost of adopting this technique for routine run-of-mine assays is negligible in comparison to the very real financial benefits, and the added confidence in the analytical data.

Conclusions

The new Tm internal standard method has demonstrated excellent results against reliably known samples not included in the calibration with considerably better precision than DMG analysis. The method shows great promise as a replacement technique for DMG analysis with significant advantages in terms of safety, labour, cost, throughput and quality.

In addition, the Tm dosed flux technique (at 0.5% Tm₂O₃) can easily be used in regular quality control as an internal check for Ni quality and machine drift in routine α – corrected fused glass disc calibrations. This technique, apart from validating nickel determined by conventional α matrix correction, enables a high quality primary nickel assay to be obtained together with all other elements of interest.

The internally doped Tm method is not sensitive to the fusion method used (gas, electric, manual or auto) and is demonstrably applicable to any flux combination of lithium tetraborate: lithium metaborate, or with 100% lithium tetraborate, with or without flux modifiers such as sodium nitrate.

Acknowledgements

The authors gratefully acknowledge the support of X-Ray Flux P.L., and the technical skills of Jeff Brown, Magid Sawiris, Damien Phelan, Seranica Williamson, Jayson Bramwell, Andrew Smethurst, Mai Thao Le, Moqadisa Noor and Eric Okomuniewski.

References

Chappell B. W. 1991. Trace element analysis of rocks by X-ray spectrometry. *Advances in X-ray Analysis*, **34**:263-276.

Haukka M. T. and Thomas I. L. 1977. Total X-ray fluorescence analysis of geological samples using a low-dilution lithium metaborate fusion method. Matrix corrections for major elements. *X-ray Spectrometry*, **6**:204-211.

Leinster Nickel Operation Analytical Laboratory. Procedures for DMG analysis of Nickel. BHP Billiton Nickel West Leinster, W. A., 6437.

Mori, P., Reeves, S. J., Correia, C., and Haukka, M., 2000. Development of a fused glass disc XRF facility and comparison with the pressed powder pellet technique at Instituto de Geociencias, Sao Paulo University. *Revista Brasileira de Geociencias*.

Norrish K., and Fritz M. Technical Report ISO/TC 102/SC2 N1572 E for the Committee for Chemical Analysis of Iron Ores, available from Standards Australia.

Potts P. J. 1987. *A handbook of silicate rock analysis*. Blackie, Glasgow and London.

Williamson, S., 2006. A study of the limitations of the DMG gravimetric method for nickel analysis. BHP Billiton Leinster Nickel Operation, analytical laboratory Technical Note TN_General_003.

Appendix 1: Comparative Ni (%) assay results, by Ni DMG, of three experienced Ni-DMG laboratories, illustrating the very large range of assays obtained.

Sample No.	Lab 1	Lab 2	Lab 3	1 σ	3 σ	Min	Max	Range
1	14.49	14.33	14.25	0.12	0.37	14.25	14.49	0.24
2	13.93	13.83	13.76	0.09	0.26	13.76	13.93	0.17
3	14.94	14.82	14.75	0.10	0.29	14.75	14.94	0.19
4	14.54	14.30	14.23	0.16	0.49	14.23	14.54	0.31
5	14.59	14.10	14.11	0.28	0.84	14.10	14.59	0.49
6	14.27	13.62	13.58	0.39	1.16	13.58	14.27	0.69
7	14.47	14.00	14.06	0.26	0.77	14.00	14.47	0.47
8	14.33	14.32	14.46	0.08	0.23	14.32	14.46	0.14
9	13.91	13.76	13.86	0.08	0.23	13.76	13.91	0.15
10	14.19	14.02	13.93	0.13	0.40	13.93	14.19	0.26
11	14.80	14.17	14.20	0.36	1.07	14.17	14.80	0.63
12	14.76	14.05	14.24	0.37	1.10	14.05	14.76	0.71
13	14.56	14.02	14.09	0.29	0.88	14.02	14.56	0.54
14	15.67	15.37	15.55	0.15	0.45	15.37	15.67	0.30
15	14.04	13.52	13.65	0.27	0.81	13.52	14.04	0.52
16	13.70	13.63	13.73	0.05	0.15	13.63	13.73	0.09
17	14.47	14.30	14.38	0.09	0.26	14.30	14.47	0.17
18	13.64	13.52	13.66	0.08	0.23	13.52	13.66	0.14
19	14.74	14.39	14.47	0.18	0.55	14.39	14.74	0.35
20	13.81	13.59	13.68	0.11	0.33	13.59	13.81	0.22
21	13.77	13.87	14.03	0.13	0.39	13.77	14.03	0.26
22	14.12	14.04	14.04	0.05	0.14	14.04	14.12	0.08
23	17.85	17.85	17.74	0.06	0.19	17.74	17.85	0.11
24	18.95	19.06	19.08	0.07	0.21	18.95	19.08	0.13
25	18.28	18.46	18.41	0.09	0.28	18.28	18.46	0.18
26	18.82	18.81	18.76	0.03	0.10	18.76	18.82	0.06
27	18.55	18.56	18.51	0.03	0.08	18.51	18.56	0.05
28	18.83	18.39	18.28	0.29	0.87	18.28	18.83	0.55
29	16.87	17.02	16.97	0.08	0.23	16.87	17.02	0.15
30	18.11	18.18	18.13	0.04	0.11	18.11	18.18	0.07
31	16.37	16.40	16.34	0.03	0.09	16.34	16.40	0.06
32	17.04	17.05	17.02	0.02	0.05	17.02	17.05	0.03
33	16.61	16.57	16.52	0.05	0.14	16.52	16.61	0.09
34	16.42	16.56	16.43	0.08	0.23	16.42	16.56	0.14
35	15.82	16.00	15.90	0.09	0.27	15.82	16.00	0.18
36	16.23	15.95	16.00	0.15	0.45	15.95	16.23	0.28
37	17.44	17.40	17.42	0.02	0.06	17.40	17.44	0.04
38	16.60	16.04	16.05	0.32	0.96	16.04	16.60	0.56
39	15.05	14.84	14.80	0.13	0.40	14.80	15.05	0.25
40	16.89	16.67	16.61	0.15	0.44	16.61	16.89	0.28
Averages				0.14	0.41	2.67		0.26

Appendix 2: Full calibration set data. RMC.Qan Leinster Analytical Laboratory.

<i>Standard Name</i>	<i>Ni (%)</i>	<i>Ni Kα Intensity</i>	<i>Tm Lα intensity</i>	<i>Ratio</i>
Std18a	0.36	6.95	77.92	0.089
Std18b	0.36	6.86	77.47	0.089
Std18c	0.36	6.91	78.09	0.088
Std4a	0.51	9.01	77.15	0.117
Std4b	0.51	9.20	76.51	0.120
Std4c	0.51	8.97	76.92	0.117
Std15a	0.61	8.18	60.47	0.135
Std15b	0.61	8.00	60.08	0.133
Std15c	0.61	8.05	60.29	0.134
Std23a	0.67	12.48	84.40	0.148
Std23c	0.67	12.45	84.65	0.147
Std24a	0.69	12.20	83.92	0.145
Std24b	0.69	12.23	83.37	0.147
Std24c	0.69	12.07	82.70	0.146
Std9a	0.73	11.79	76.29	0.155
Std9b	0.73	11.76	75.92	0.155
Std9c	0.73	11.77	76.06	0.155
Std20a	1.47	23.87	83.87	0.285
Std20b	1.47	23.59	82.49	0.286
Std20c	1.47	24.06	84.60	0.284
Std6a	1.63	23.89	76.07	0.314
Std6b	1.63	23.94	76.23	0.314
Std6c	1.63	23.90	76.36	0.313
Std19a	2.10	29.56	74.20	0.398
Std19b	2.10	29.74	74.07	0.402
Std19c	2.10	29.61	74.17	0.399
Std1a	2.45	33.90	73.67	0.460
Std1b	2.45	34.15	74.08	0.461
Std1c	2.45	34.23	74.33	0.461

**Appendix 2 continued: Full calibration set data.
RMC.Qan Leinster Analytical Laboratory.**

<i>Standard Name</i>	<i>Ni (%)</i>	<i>Ni Kα Intensity</i>	<i>Tm Lα intensity</i>	<i>Ratio</i>
Std7a	4.51	54.06	65.51	0.825
Std7b	4.51	54.14	65.27	0.829
Std7c	4.51	54.21	65.26	0.831
Std5a	4.66	55.39	65.05	0.852
Std5b	4.66	55.15	64.62	0.853
Std5c	4.66	55.38	65.01	0.852
Std25a	7.82	86.16	61.84	1.393
Std25b	7.82	85.90	61.32	1.401
Std25c	7.82	86.99	62.17	1.399
Std12a	9.27	112.41	67.56	1.664
Std12b	9.27	113.17	67.95	1.666
Std12c	9.27	112.69	67.46	1.671
Std8a	9.90	106.67	60.89	1.752
Std8b	9.90	107.19	60.96	1.758
Std8c	9.90	106.69	60.52	1.763
Std27a	13.50	142.17	59.33	2.396
Std27b	13.50	142.37	59.37	2.398
Std27c	13.50	141.71	59.28	2.391
Std13a	14.96	175.89	66.12	2.660
Std13b	14.96	174.92	65.68	2.663
Std13c	14.96	174.34	65.56	2.659
Std2a	15.63	162.19	58.49	2.773
Std2b	15.63	163.11	58.79	2.774
Std2c	15.63	162.43	58.53	2.775
StdDMGa	17.36	182.17	59.34	3.070
StdDMGb	17.36	184.17	59.98	3.070
StdDMGc	17.36	184.14	60.09	3.064
Std26a	19.67	212.99	61.53	3.461
Std26b	19.67	214.71	61.84	3.472
Std26c	19.67	213.90	61.61	3.472