FINDING A NEEDLE IN A HAYSTACK: PERFORMANCE EVALUATION OF PORTABLE XRF INSTRUMENTS FROM THREE MANUFACTURERS

Brand N. W[1] and Brand CJ[1]

[1]Portable XRF Services Pty Ltd. Suite 1, 5 Colin Street, West Perth, Australia, 6005
nwbrand@pxrfs.com.au & cjbrand@pxrfs.com.au

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Introduction

The advancement over the past decade in handheld XRF instruments following the inclusion of a silicon drift detector by Bruker (Bruker Press Release 25/06/2008) marked a step change in 'off-the-shelf' handheld XRF technology allowing for real time 'fit for purpose' data to be collected. On-going hardware and software developments have prompted an increasing number of manufacturers to introduce handheld XRF instruments with geochemical applications into the market.

To evaluate their geochemical capability, this study evaluated three 'off the shelf' portable XRF instruments from three manufacturers: the Bruker Titan 800, the Thermo-Niton XL3t and the Olympus Delta Premium 6000. This work differs from other comparative portable XRF studies in that a batch of over 900 'real world' surface samples were analysed to ascertain the instruments' capability in reproducing known geological trends within the sample data-set and in identifying a key sample adjacent to a significant nickel-sulphide deposit, the 'Needle-in-the-Haystack' sample.

Studies comparing different portable XRFs instruments include: Vanhoof *et al.* 2004, Goodale *et al*. 2012, Brand and Brand 2014 and Hall *et al*. 2011, 2014. Brand and Brand (2014) evaluated a Thermo-Niton XL3t and an Olympus Delta Premium DP6000c using a single sample (NIST 2709a) and showed large variation within and between the manufacturers' instruments and concluded that each portable handheld XRF instrument is uniquely individual, including the data it generates. Hall *et al.* (2011, 2014) analysed 41 certified reference materials utilising the Thermo-Niton XL3t, Olympus Delta Premium 6000 and Bruker Turbo handheld portable XRF instruments and noted the inconsistency in performance between manufacturers and the large variation in accuracy for many elements with no one instrument doing well across the element range.

Methodology

For this study, the Titan 800 (Bruker), XL3t GOLDD+ (Thermo-Niton) and Delta Premium (Olympus Innov-X) were used 'as received' from the manufacturers (Table 1) to enable 'off-the-shelf' evaluations and comparisons and minimise factors affecting accuracy and precision with the operator only having control of the duration of the measurement and the sample presented to each instrument. The instruments were run on the batteries in their portable bench stands as provided by the manufacturers. All samples were analysed in 'Soil Mode' for a two minute duration with all beam times symmetrical.

Regional regolith sample pulps collected over the Fraser Range by the Geological Survey of Western Australia (GSWA) were used for this study with 5-10 grams transferred into plastic cups contained by a Mylar film. The GSWA Fraser Range samples are an Open File sample data-set that are geochemically well characterised (Morris *et al.* 2000) and have been analysed by a variety of conventional laboratory assay methods. Quality control sample OREAS 45d was utilised to monitor the performance of the instrument during this study.

Table 1: Specifications of pXRF instruments used in this study.

Manufacturers	Bruker	Olympus Innov-X	Thermo-Niton
pXRF instrument	Titan 800	Delta Premium 6000	XL3t 950s GOLDD+
Report abbreviation	B	O	N
Anode	Rh	Rh	Ag
Tube voltage (kV_{max})	45	40	50
Tube power (μA_{max})	400	400	200
Resolution (eV)	147 eV @ 40,000 Cps	*c.* 156 eV @ 40,000 cps	<185 eV @ 60,000 cps
Detector area	25 mm^2 SDD	30 mm^2 SDD	25 mm^2 SDD
Power source used	Generic Li-ion batteries		Niton Li-ion batteries
Element range	Mg (Z12) and greater		
Application modes used	Soil Mode		
Windows	Propylene3		

Results

A suite of 16 reliable elements are common to each portable XRF instrument and include As, Ca, Cr, Cu, Fe, K, Mn, Ni, Pb, Rb, S, Sr, Ti, V, Zn and Zr; Table 2 shows the summary statistics for this study.

Each portable XRF instrument was able to reproduce known geological trends within the sample data-set for all 16 reliable elements. Figure 1 shows a nickel image from the three manufacturers along with the original GSWA data-set for comparison. Correlation between GSWA Ni data and results obtained by the portable XRF instruments are generally very good for Bruker (r^2 = 0.93) and Olympus (r^2 = 0.94) with Niton having an r^2 of only 0.73 (Figure 2). All portable XRF instruments correctly identified the Needle-in-the-Haystack sample (red dot, Figure 1) with concentrations reported by Morris *et al*. (2000) of 271 ppm Ni, 90 ppm Cu and 594 pm Cr. The low range KeV spectra for this critical sample from each instrument are shown in Figure 3. The data have been normalised to allow comparison and show the peaks for elements detected in the range 1 to 9 KeV including Ni, Cu and Cr.

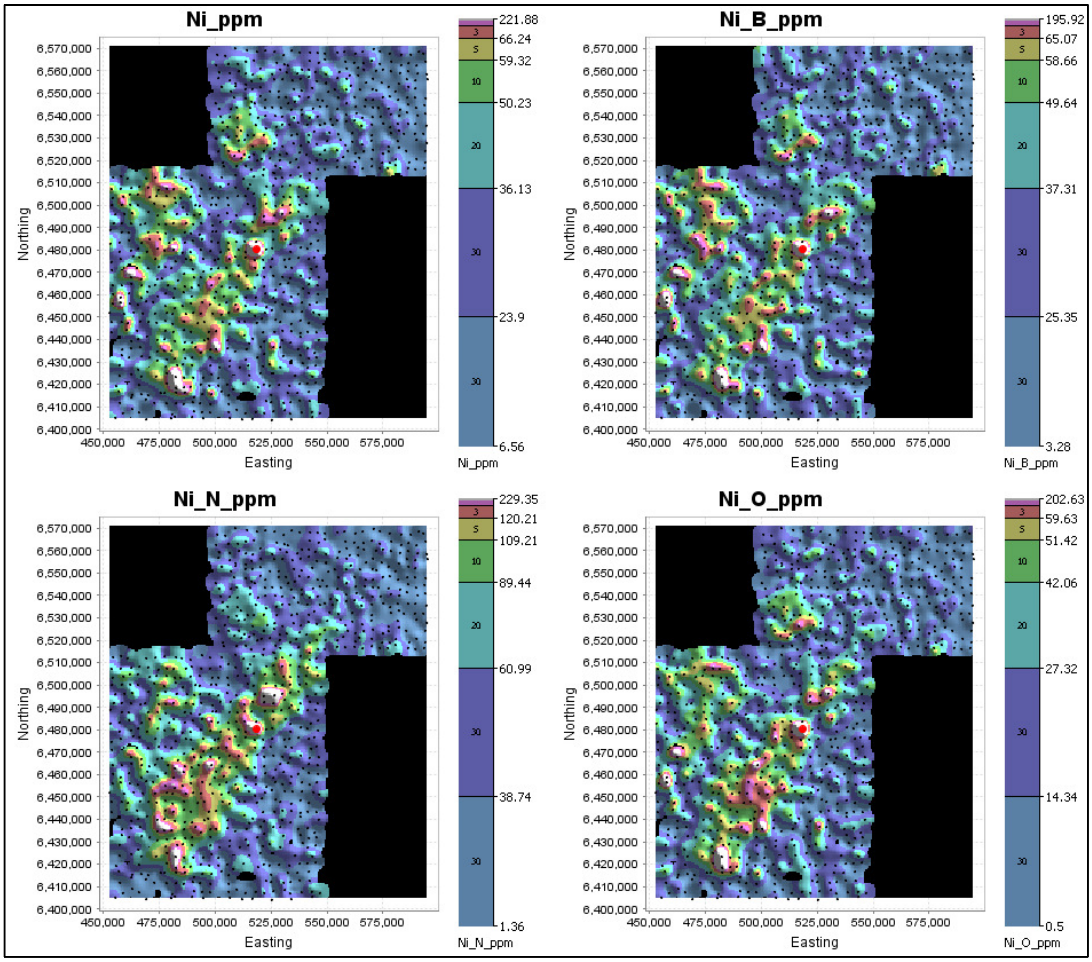

Figure 1: Correlation between GSWA data and results obtained by the portable XRF instruments Bruker (B), Niton (N), Olympus (O).

Table 1: Summary of statistics for GSWA and the Bruker, Niton and Olympus portable XRF results.

Element	Source	N	Min	Max	Mean	Median	Sdev	CV	50%ile	75%ile	95%ile	98%ile	Correlation with GSWA (R^2)
As	GSWA	918	0.5	61	5	4	6	107	4	7	17	25	1
	Bruker	692	2	61	7	6	5	71	6	8	14	20	0.76
	Niton	918	0.005	62.25	6	5	6	93	5	8	17	25	0.86
	Olympus	914	0.1	64.6	6	5	5	89	5	7	16	22	0.87
Ca	GSWA	918	357.5	253038	24172	13939	31931	132	13939	33595	80843	112938	1
	Bruker	918	545	164526	22464	12084	27445	122	12084	30515	79007	115364	0.94
	Niton	918	1179.63	218869.5	27587	14796	33639	122	14796	37272	95412	145288	0.96
	Olympus	917	19	335331	30763	13461	45123	147	13461	41446	120004	175565	0.98
Cr	GSWA	918	1	703	77	53	76	98	53	95	216	287	1
	Bruker	911	5	405	79	62	61	77	62	113	188	240	0.86
	Niton	918	0.09	712.68	104	87	79	76	87	148	243	292	0.88
	Olympus	918	3	615	93	78	61	66	78	124	198	233	0.91
Cu	GSWA	918	3	90	21	21	10	47	21	26	40	48	1
	Bruker	918	6	82	21	20	9	40	20	26	38	44	0.85
	Niton	918	0.02	84.5	20	18	13	66	18	28	46	53	0.73
	Olympus	918	0.15	74	19	17	10	52	17	24	37	43	0.85
Fe	GSWA	918	2098	268531	43315	31469	34102	79	31469	60839	107692	131636	1
	Bruker	918	3595	249134	43463	32488	32519	75	32488	59764	104856	126349	0.99
	Niton	918	2068	458989.81	38598	23516	42566	110	23516	50167	113450	149845	0.95
	Olympus	918	2	523788	44128	26631	49343	112	26631	58163	131717	172008	0.96
K	GSWA	918	415	34855	8735	7469	5277	60	7469	10788	19087	23751	1
	Bruker	918	276	32280	8698	7692	5190	60	7692	11053	18783	23151	0.96
	Niton	918	938.36	31358.51	9241	8389	4977	54	8389	11764	18624	22854	0.94
	Olympus	918	247	32219	8442	7696	4859	58	7696	11130	17509	20722	0.95
Mn	GSWA	918	193.5	10922	540	194	625	116	194	697	1549	2091	1
	Bruker	905	1	10627	482	281	615	128	281	642	1484	2051	0.97
	Niton	918	10.02	11733.04	488	284	644	132	284	603	1502	2283	0.95
	Olympus	918	2	9042	406	269	476	117	269	523	1153	1577	0.97
Ni	GSWA	918	3	271	35	30	24	66	30	49	75	93	1
	Bruker	916	1	238	36	32	22	62	32	47	76	88	0.93
	Niton	918	0.055	267.56	61	53	39	64	53	86	136	156	0.73
	Olympus	908	0.5	248	27	22	24	91	22	41	69	83	0.94
Pb	GSWA	918	0.5	186	11	10	8	74	10	15	22	28	1
	Bruker	174	13	96	19	17	7	39	17	20	30	36	0.86
	Niton	918	0.06	176.29	10	10	8	75	10	13	21	25	0.9
	Olympus	918	0.15	180	10	9	8	82	9	13	20	24	0.91
Rb	GSWA	918	4.3	694	40	35	33	82	35	50	89	109	1
	Bruker	913	6	637	40	35	31	77	35	50	89	105	0.97
	Niton	918	3.71	576.29	34	30	27	78	30	43	72	90	0.96
	Olympus	918	2.7	670	39	34	31	79	34	49	82	103	0.98
S	GSWA	918	0.05	20.6	0	0	2	473	0	0	1	6	1
	Bruker	472	1	304798	9624	293	39635	412	293	1199	36212	216413	0.97
	Niton	918	0.92	210801.75	3807	252	20251	532	252	511	8609	55885	0.98
	Olympus	913	0.5	140326	2011	25	12043	599	25	119	3651	26549	0.98
Sr	GSWA	918	6	1330	129	97	126	97	97	149	342	542	1
	Bruker	916	1	1143	129	102	118	92	102	147	361	498	0.96
	Niton	918	3.45	1140.81	111	84	102	92	84	133	309	418	0.97
	Olympus	918	2.7	1252	123	94	114	93	94	148	347	464	0.98
Ti	GSWA	918	150	22302	4196	3237	3259	78	3237	5336	11220	12987	1
	Bruker	918	241	21705	4279	3624	2913	68	3624	5717	9852	11695	0.96
	Niton	918	85.61	16546.72	3688	3131	2399	65	3131	5002	8316	10039	0.92
	Olympus	918	5	17983	3321	2690	2410	73	2690	4491	8249	9671	0.97
V	GSWA	918	5	738	96	71	81	85	71	129	252	321	1
	Bruker	911	1	521	95	72	75	79	72	138	237	286	0.93
	Niton	918	10.17	607.62	123	101	79	64	101	162	269	328	0.9
	Olympus	918	1.35	211	53	46	33	62	46	72	115	133	0.82
Zn	GSWA	918	1	191	26	21	20	77	21	37	64	82	1
	Bruker	902	1	184	27	23	19	69	23	38	59	75	0.91
	Niton	918	0.03	154.78	31	26	21	66	26	44	69	83	0.9
	Olympus	918	0.3	164	29	25	20	67	25	41	64	82	0.94
Zr	GSWA	918	6	792	113	104	56	49	104	145	207	234	1
	Bruker	918	56	4162	616	597	246	40	597	722	993	1142	0.78
	Niton	918	7	830.03	132	125	60	45	125	164	225	264	0.87
	Olympus	918	1	751	123	120	54	44	120	152	210	247	0.92

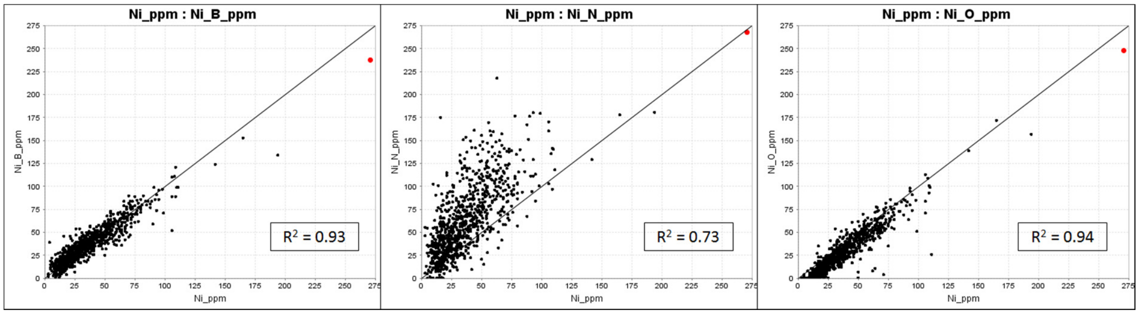

Figure 2: Correlation between GSWA data and results obtained by the portable XRF instruments Bruker (B), Niton (N), Olympus (O).

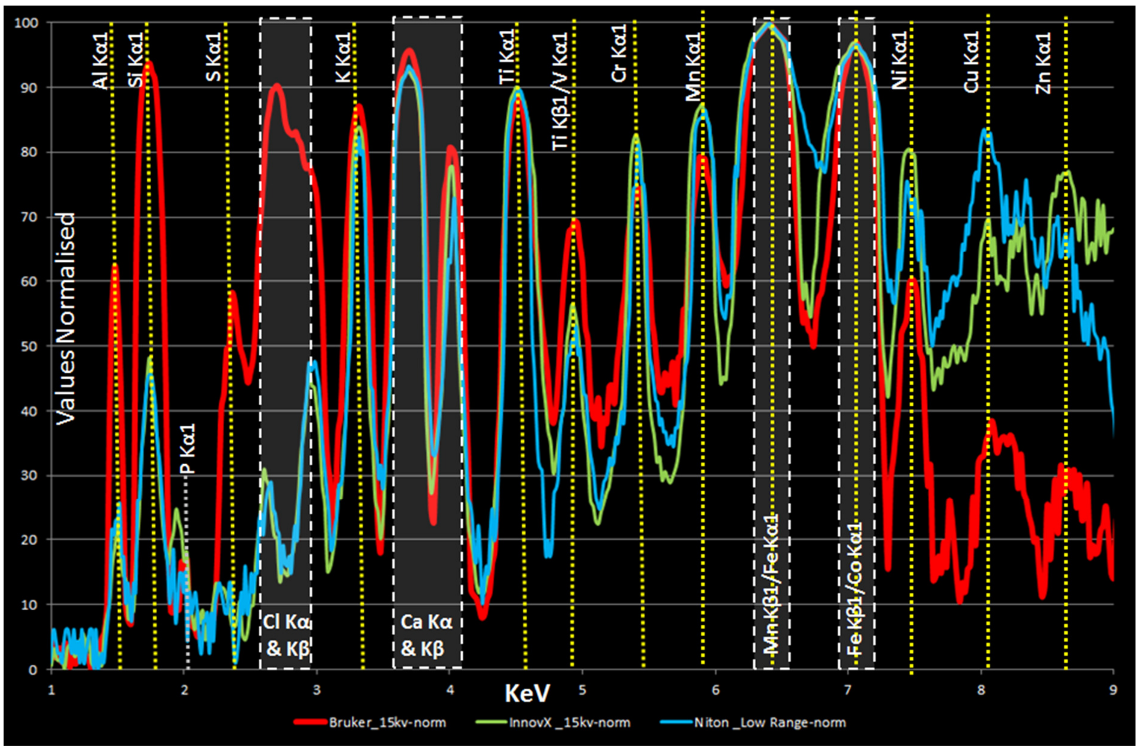

Figure 3: Low range filter spectra from each instrument from the Needle-in-the-Haystack sample, normalised to allow comparison.

One of the major challenges for portable XRF instruments has been to obtain reliable data for light elements (Mg, Al, Si) when using the Soil Mode. Bruker is the only manufacturer to offer the Soil Mode inclusive of Mg, Al and Si. Results obtained for Al (Z13) and Si (Z14) during this study show excellent correlation with the GSWA data (Table 3 and Figure 4) whilst those for Mg (Z12), the lightest element that can be determined by a portable XRF instrument, show promise at best (Figure 5).

Table 3: Summary statistics of Al, Mg and Si obtained by the Bruker Titan 800 in soil mode and compared with GSWA data.

Element	Source	N	Min	Max	Mean	Median	Sdev	CV	50%ile	75%ile	95%ile	98%ile	Correlation with GSWA (R2)
Al	GSWA	918	3176	124934	43969	39704	24220	55	39704	60879	85760	103028	1
	Bruker	918	4251	155283	43731	40653	23226	53	40653	59765	83356	100658	0.95
Mg	GSWA	918	301.5	77201	7981	6031	7656	96	6031	10856	21743	29928	1
	Bruker	918	400	72872	5702	4151	6407	112	4151	6481	17803	23821	0.76
Si	GSWA	918	22546	457492	325921	331611	70366	22	331611	382809	430249	439934	1
	Bruker	918	40194	447675	323098	323899	68078	21	323899	378991	424899	432541	0.95

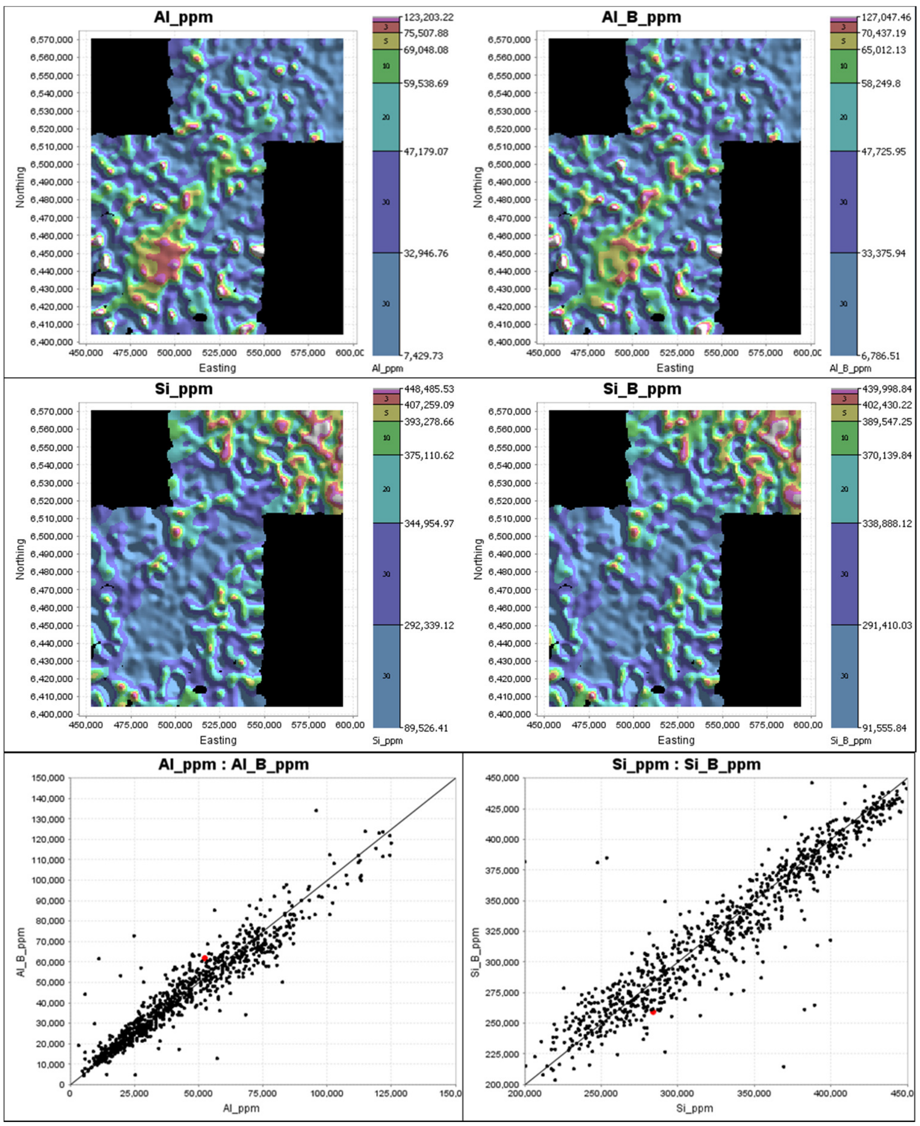

Figure 4. Images and correlations for Al and Si comparing the original GSWA data to those obtained using the Bruker (B) Titan 800.

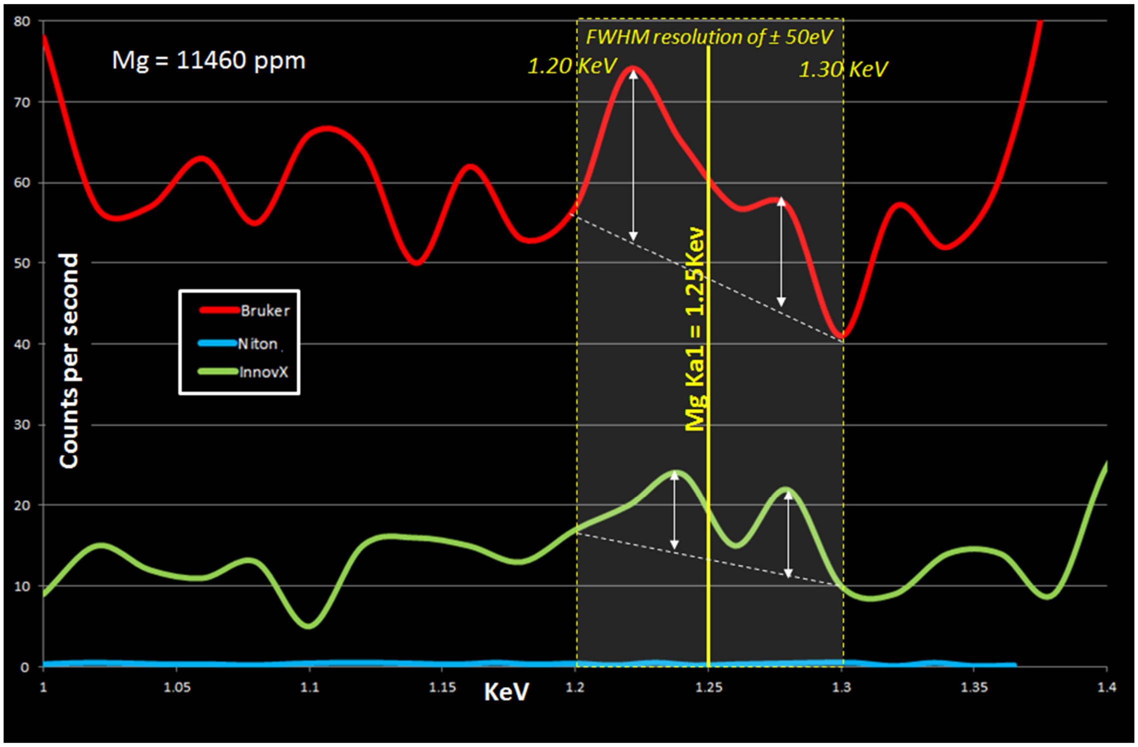

Figure 5: Low range filter spectra over the Mg Kα1 peak showing counts per second for a sample containing 11460 ppm Mg as analysed by fusion XRF.

Discussion

With the advancement in ‘off-the-shelf’ handheld XRF technology and the introduction of new models into the market place offering geochemical applications it is always worthwhile ensuring the instruments can perform as specified and are ‘fit for purpose’ This study used an Open File data-set containing over 900 surface samples in which one sample contained slightly anomalous geochemistry (271 ppm Ni, 90 ppm Cu and 594 pm Cr.) adjacent to a significant nickel-sulphide deposit. All three manufacturers’ instruments tested identified the Needle-in-the-Haystack sample and reproduced geological trends observed in the original GSWA laboratory assayed data.

One instrument (Bruker’s Titan 800) obtained light element results for Al and Si with excellent correlation with the GSWA data. Obtaining reliable data for these light elements (Z12-Z14) in soil mode has been a major challenge for pXRF instruments and demonstrates the on-going advancement of this technology.

Conclusions

All three manufacturers’ instruments (Bruker Titan 800, Thermo-Niton XL3t and Olympus Delta Premium 6000) correctly identified the Needle-in-the-Haystack sample and generated ’fit for purpose’ data that replicated known geological trends.

Bruker's Titan 800 instrument obtained light element results for Al and Si with excellent correlation with the GSWA data.

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