



*The JBS Journey from Environmental to Exploration
And
The Evolution of Handheld XRF Instrumentation*

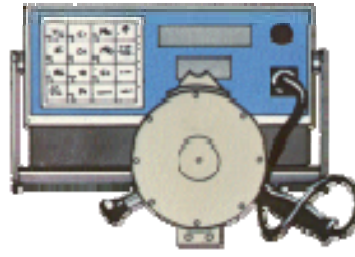
Prepared for:
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Discussion Forum, 6th November 2009

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40 Years of Portable X-Ray Fluorescence (XRF) History



1967:TN 9200
1st commercial field portable XRF; used non-dispersive scintillation detectors with x-ray filters



1975:TN 9266 Alloy Analyzer
1st portable XRF with dedicated application calibrations for alloy analysis; non-dispersive detectors; x-ray filters



1978:Outokumpu X-MET 740
1st portable XRF with energy dispersive gas-filled proportional counter detectors; stored (externally created) calibrations; used early microprocessors



1984:Outokumpu X-MET 880
1st portable XRF with data storage and internally generated calibration curves; used better microprocessors and limited electronic memory



1994:NITON XL-309
1st one piece, handheld XRF with real-time digital signal processing and silicon PIN diode detectors



2002:NITON XLt
1st handheld with x-ray tube source



2002: Innov-X Alpha
1st handheld with x-ray tube source

Both claim to be first. Let's call it a dead-heat.

Real Advance was Si-PIN Detector

Detectors are the main component that impact XRF performance

Si PIN-diode

- Very good resolution
- Excellent reliability and stability
- Long service life



JBS's XRF Journey From Environmental To Interactive Exploration



1996

2000

2005

2009

QCT Quality Assurance Program

- Two soil / sediment / dust samples sent per month.
- JBS participation 1996 to 2000 using NITON XL (brick)
- Results compared to other laboratories using wet chemistry methods.

Element	Correlation	Slope & Intercept	Range ppm
Cu	r ² 0.9701	y=0.9649x + 5.28	5 to 5000
Zn	r ² 0.9769	y=1.0831x - 37.99	20 to 25000
Pb	r ² 0.9863	y= 1.0057x - 16.99	20 to 15000

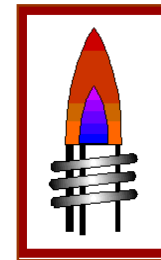
Strategies for the investigation of Contaminated Sites (CSIRO, 1999)



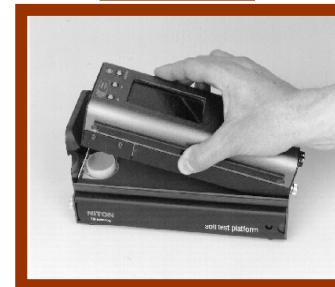
in-situ XRF USEPA
6200

Soil preparation

- drying
- homogenisation
- 250µm sieved fraction



USEPA 3050B

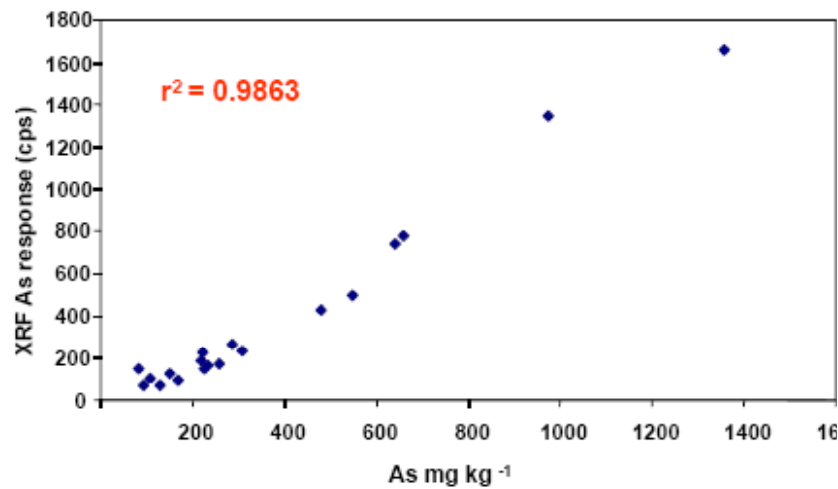


ex-situ XRF

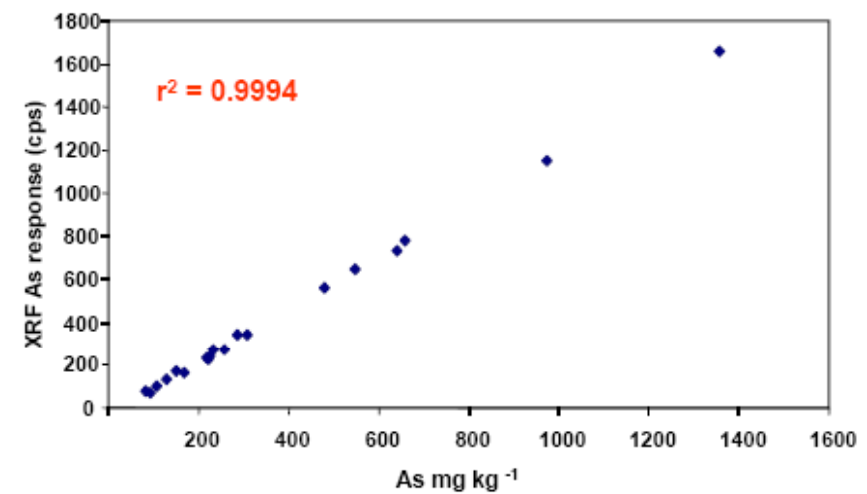
Strategies for the investigation of Contaminated Sites (CSIRO, 1999)



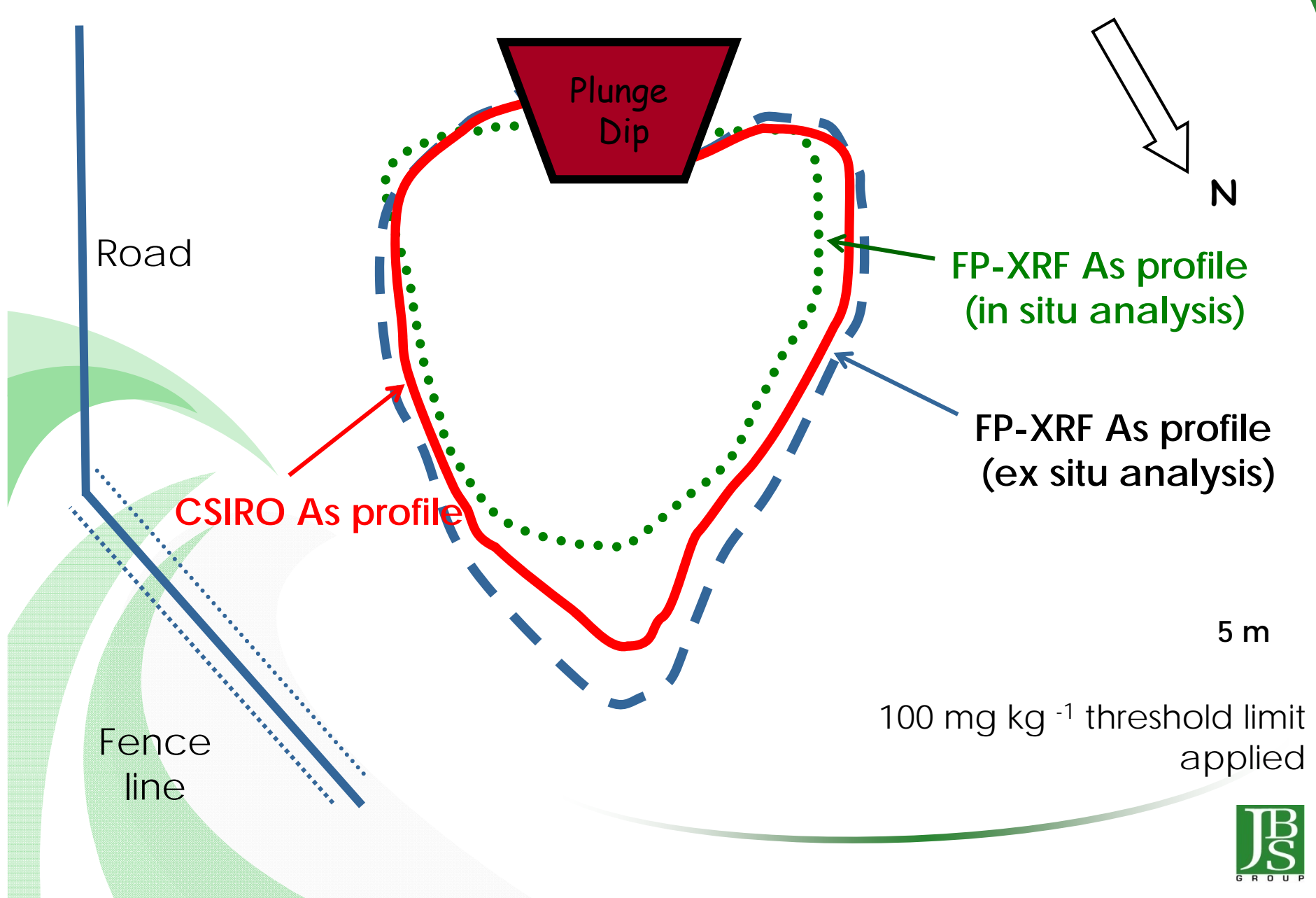
Plot of in-situ HH XRF vs. ICP



Plot of ex-situ HH XRF vs. ICP



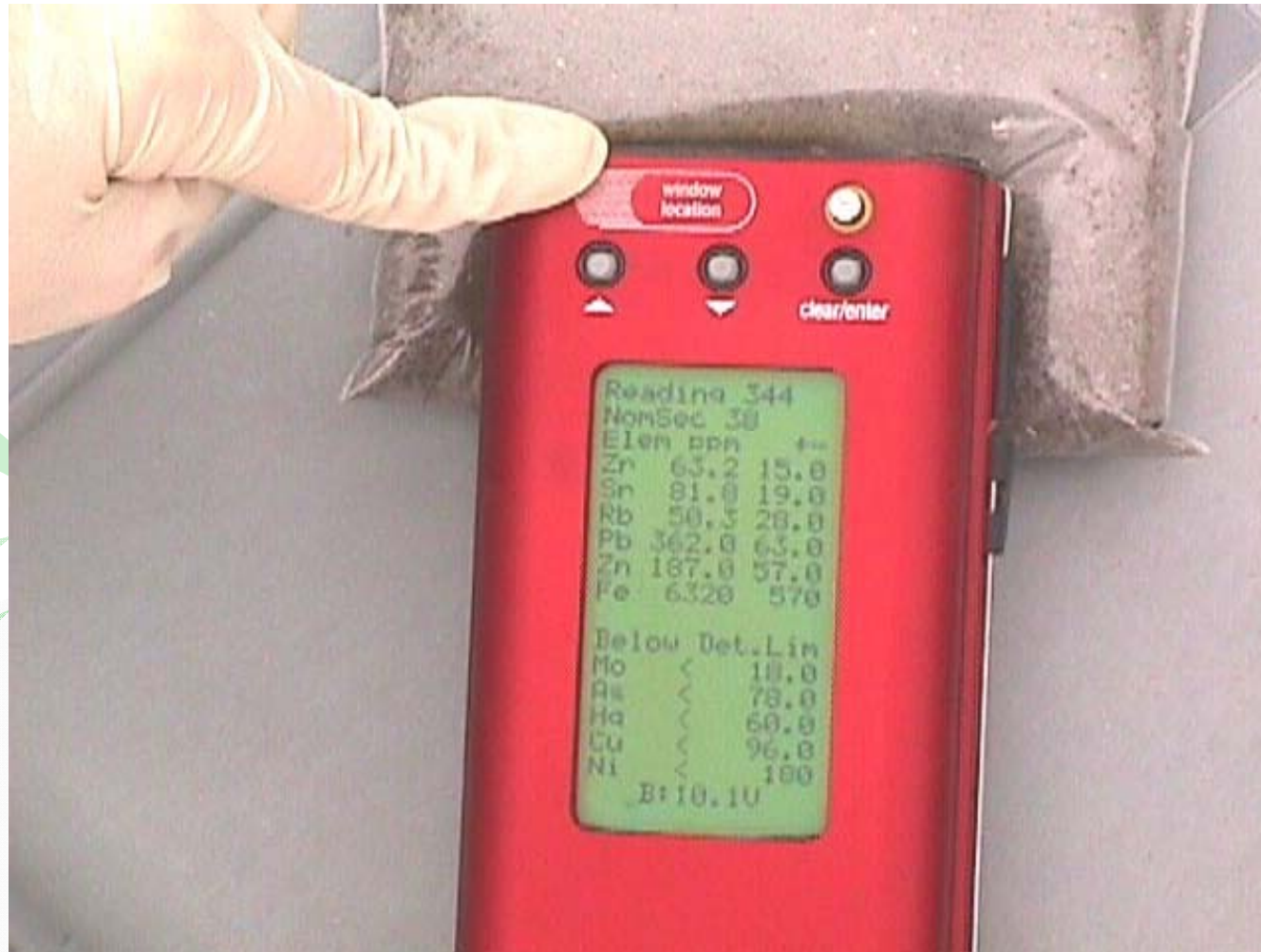
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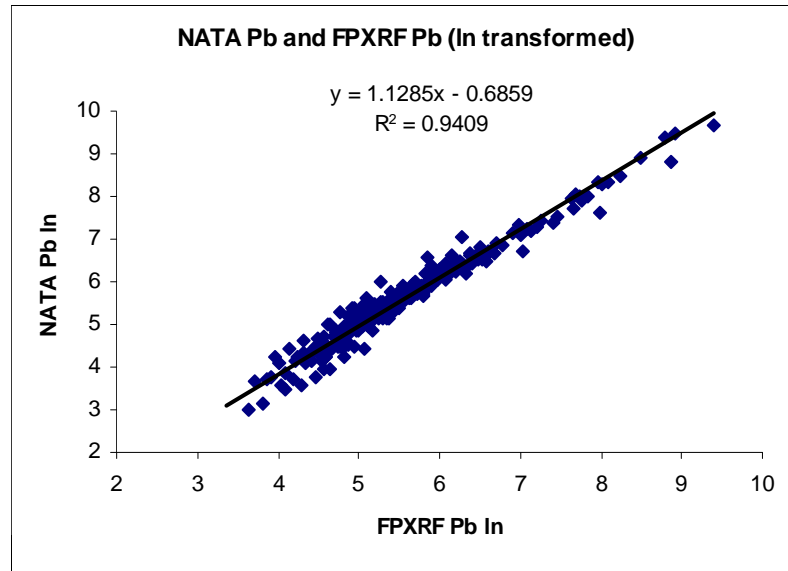
Broken Hill Baseline Soil Survey (Perilya, 2002)



Broken Hill Baseline Soil Survey (Perilya, 2002)



Broken Hill Baseline Soil Survey (Perilya, 2002)



Parameter	FPXRF Pb (mg/kg)	HNO ₃ /H ₂ O ₂ Pb (mg/kg)	HNO ₃ /HF Pb (mg/kg)
Geometric Mean	207	191	275
Median	162	170	228
Standard Error	4.08	5.45	3.98
Coefficient of Variation	1.24	1.33	1.25

JBS XRF Published Papers and Articles

T. Houlahan, S. Ramsay, D. Povey *Use of Field Portable XRF Analyzers for Grade Control – A Presentation Of Case Studies* 5th International Mining Geology Conference, **November 2003**

Bawden-Smith J. *Reducing Contaminated Soil Rehabilitation Costs – Review of Portable XRF Performance On Australian Soils.* Journal of the Australian Institute Of Mining and Metallurgy **6:17-19, 2001**

Bawden-Smith J. *Managing Metal Contaminated Soils. What's New in Waste Management* **62:44-46, 2000**

Davis, J., Bawden-Smith, J. *Management of lead contaminated soil from 67 Residential Properties using field portable XRF. Proceedings of the Australian and New Zealand Institute of Waste Management Annual Conference. 2000.*

Ridings M, Shorter AJ, Bawden-Smith J. *Strategies for the Investigation of Contaminated Sites Using Field Potable X-Ray Fluorescence Techniques. Commun. Soil Sci. Plant Anal, 31:11-14, 2000.*

Summary of Overall Findings

Sample Issues Greatly Influence Data

Soil type, particle size, heterogeneity, mineral dissemination and moisture
Allows for semi-quantitative data and trends if samples not homogenised.

Detection Limits Higher Than Lab

Good results for base metals

DL's too high for precious metals and some path finders(Hg, Sb, Te, Tl etc)
Light (whole rock) elements not possible (New SDD changes this)

Elemental Overlap in Some matrices

E.g. Fe/Co overlap gave erroneous Co data, requires matrix matched calibrations

Like all with all geochemistry programs you require good QA/QC procedures to achieve reliable data

Non- trained and in-experienced users = Poor Data

Evolution of Handheld XRF Technology

Decade	Weight	Source	Count Rate & Resolution	Lightest Element
1980s	13 kg	Isotope	1000 eV 1000 cps	Ti
1990s	7 kg	Isotope	500 eV 1000 cps	Ti
2000/8	1.2 - 2.2 kg	Isotope & Tube	200 eV 2000 to 10,000 CPS	Mg 3%
Today	< 1.2 kg	Tube	140 eV 50,000 to 200,000 CPS	Mg 0.5% now...

Key Advancements in SDD

Better Resolution

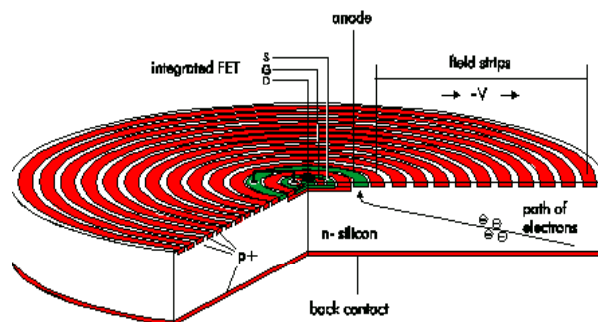
Silicon Drift Detectors operate at $<150\text{eV}$ resolution allowing better separation of difficult elements/peaks.

Higher Count Rates

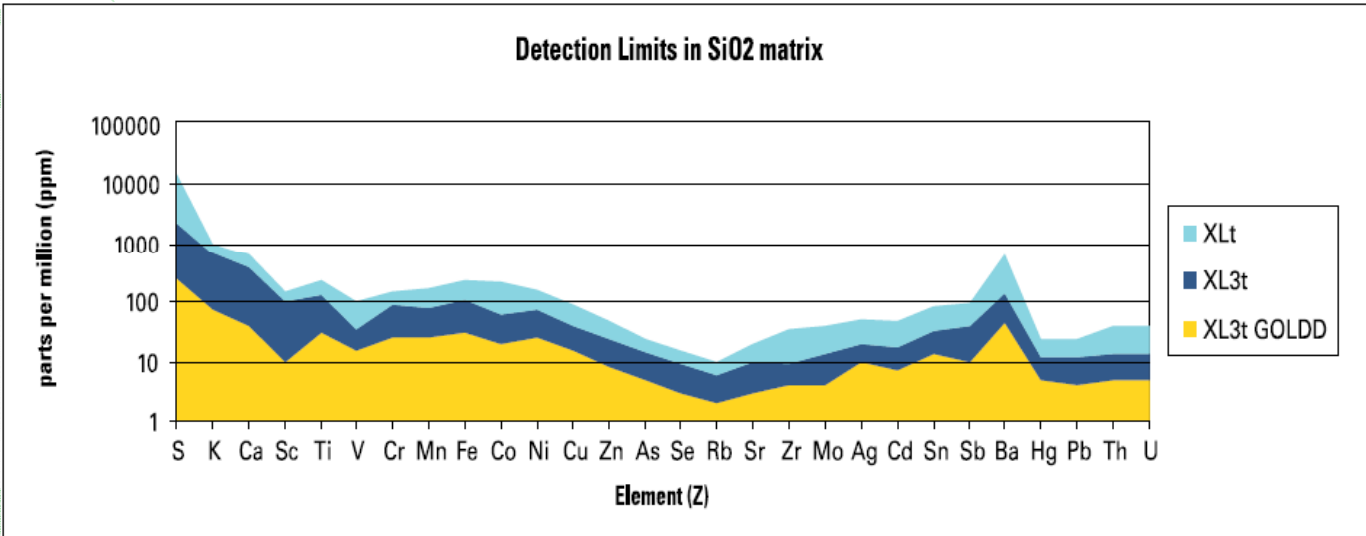
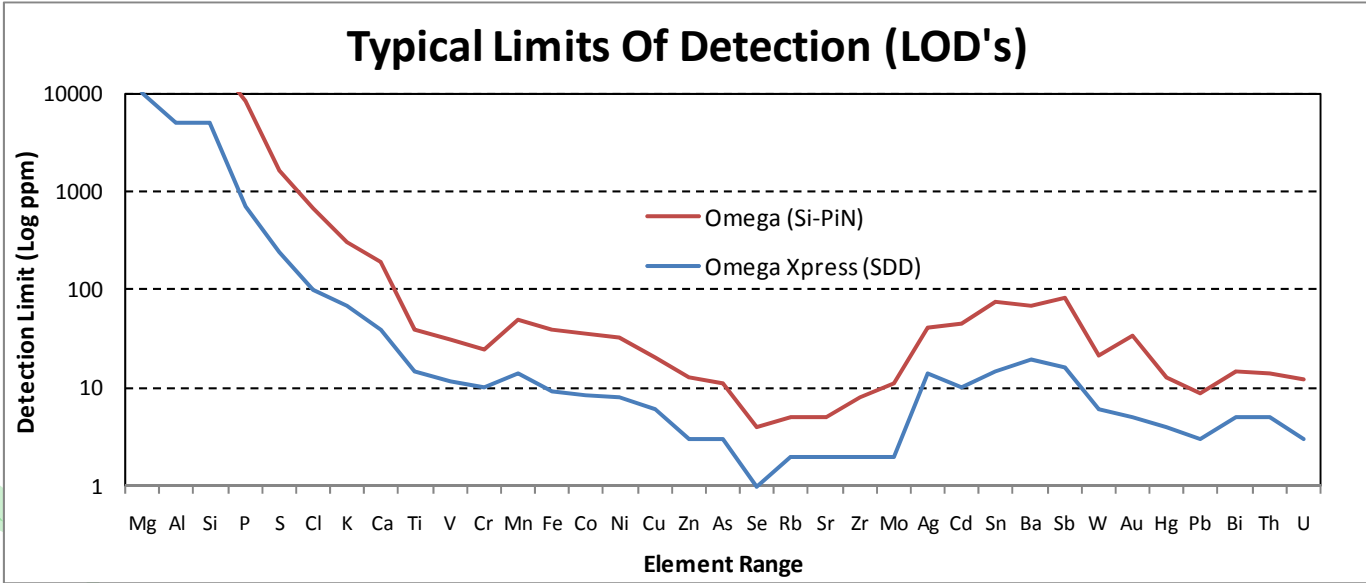
SDD can sustain up to 100,000 cps without loss of resolution compared to 10-15,000 cps for SiPIN improving LOD's and analyzing Light Elements

Better Peak-to-Background

Less background noise to mask elements/peaks improving analysis of complex matrices and applications requiring the highest levels of precision and analytical confidence.



Si-PIN vs. SDD For INNOV-X AND NITON



SDD Improves Light Elements

H 1	IIA																He 2																																
0.05 Li 3	0.11 Be 4															0.18 B 5	0.28 C 6	0.39 N 7	0.52 O 8	0.68 F 9	0.85 Ne 10																												
1.04 Na 11	Superior In-Air LOD's with NEW High Performance SDD																1.56 Al 13	1.74 Si 14	1.84 P 15	2.01 S 16	2.14 Cl 17	2.26 Ar 18	2.82 K 19	2.96 Ca 20	3.19 Sc 21																								
3.31 K 19	3.59 Ca 20	3.69 Sc 21	4.01 Ti 22	4.09 V 23	4.46 Cr 24	4.51 Mn 25	4.93 Fe 26	4.95 Co 27	5.43 Ni 28	5.41 Cu 29	5.95 Zn 30	5.9 Ga 31	6.49 Ge 32	6.4 As 33	7.06 Se 34	6.93 Br 35	7.65 Kr 36	7.48 Rb 37	8.26 Sr 38	8.05 Y 39	8.91 Zr 40	8.64 Nb 41	9.25 Mo 42	10.26 Tc 43	9.89 Ru 44	10.98 Rh 45	10.54 Pd 46	11.73 Ag 47	11.22 Cd 48	12.5 In 49	12.5 Sn 50	11.92 Sb 51	13.29 Te 52	12.65 I 53	14.11 Xe 54														
13.4 Rb 37	14.96 Sr 38	14.17 Y 39	15.84 Zr 40	14.96 Nb 41	16.74 Mo 42	15.78 Tc 43	17.67 Ru 44	16.62 Rh 45	18.62 Pd 46	17.48 Ag 47	18.37 Cd 48	20.62 In 49	18.37 Sn 50	20.62 Sb 51	19.28 Te 52	21.66 I 53	20.22 Xe 54	22.72 Cs 55	21.18 Ba 56	22.82 La 57	22.16 Ce 58	24.94 Pr 59	23.17 Nd 60	26.1 Pm 61	24.21 Sm 62	27.28 Eu 63	25.27 Gd 64	28.49 Tb 65	26.36 Dy 66	29.73 Ho 67	27.47 Er 68	31 Tm 69	28.61 Yb 70	32.29 Lu 71	29.78 Hf 72	33.62 Ta 73	29.78 W 74	33.62 Re 75	29.78 Os 76	33.62 Ir 77	29.78 Pt 78	33.62 Au 79	29.78 Hg 80	33.62 Tl 81	29.78 Pb 82	33.62 Bi 83	29.78 Po 84	33.62 At 85	29.78 Rn 86
1.69 Fr 87	1.75 Ra 88	1.81 Ac 89	1.87 Th 90	1.92 Pa 91	2 U 92	2.04 Np 93	2.12 Pu 94	2.17 Am 95	2.26 Cm 96	2.29 Bk 97	2.39 Cf 98	2.42 Es 99	2.54 Fm 100	2.56 Md 101	2.88 No 102	2.56 Lr 103	2.88 La 57	2.88 Ce 58	2.88 Pr 59	2.88 Nd 60	2.88 Pm 61	2.88 Sm 62	2.88 Eu 63	2.88 Gd 64	2.88 Tb 65	2.88 Dy 66	2.88 Ho 67	2.88 Er 68	2.88 Tm 69	2.88 Yb 70	2.88 Lu 71	2.88 Hf 72	2.88 Ta 73	2.88 W 74	2.88 Re 75	2.88 Os 76	2.88 Ir 77	2.88 Pt 78	2.88 Au 79	2.88 Hg 80	2.88 Tl 81	2.88 Pb 82	2.88 Bi 83	2.88 Po 84	2.88 At 85	2.88 Rn 86			

Lanthanides
57-71

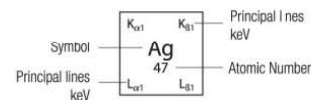
33.44 La 57	37.8 Ce 58	34.72 Pr 59	39.26 Nd 60	36.03 Pm 61	40.75 Sm 62	37.36 Eu 63	42.27 Gd 64	38.72 Tb 65	43.83 Dy 66	40.12 Ho 67	45.41 Er 68	41.54 Tm 69	47.04 Yb 70	43 Lu 71
4.85 4.85	5.04 5.04	4.84 4.84	5.26 5.26	5.03 5.03	5.49 5.49	5.23 5.23	5.72 5.72	5.43 5.43	5.96 5.96	5.64 5.64	6.21 6.21	5.85 5.85	6.46 6.46	6.06 6.06

Actinides
89-103

90.88 Ac 89	102.85 Th 90	93.35 Pa 91	105.61 U 92	95.87 Np 93	108.43 Pu 94	98.44 Am 95	111.3 Cm 96	101.00 Bk 97	114.18 Cf 98	103.65 Es 99	117.15 Fm 100	106.35 Md 101	120.16 No 102	109.10 Lr 103
12.65 12.65	15.71 15.71	12.97 12.97	16.2 16.2	13.29 13.29	16.7 16.7	13.61 13.61	17.22 17.22	13.95 13.95	17.74 17.74	14.28 14.28	18.28 18.28	14.62 14.62	18.83 18.83	14.96 14.96

Alloy Elements and Detection Limit Guidelines:
 Elements Detected Magnesium (Mg, Z=12) through Silicon (Si, Z=14) and Titanium (Ti, Z=22) through Plutonium (Pu, Z=94) typically 0.1% - some elements as low as 0.01%

Low-Density Sample Types
 (Soils, powders, liquids)



Requires vacuum, LOD 0.2 - 3%
 LOD 1% - 5%

250 - 2,500 ppm
 10 - 100 ppm

50 - 150 ppm
 Not Measured



High End vs. Low End Models

Innov-X

High Performance (SDD)



Omega Xpress

Mid Level (Si PIN)



Omega

Lower End (Si PIN)



Alpha

Thermo



XL3 GOLDD



XL3



XL2

Key Purchasing Parameters For End-Users

Detector

SDD performance outweighs price differential when compared to Si-PIN.

Features

End user specific. Live streaming of data important for soil geochem and data management.

Price

Get quotes from 3 suppliers with comparable specs (especially detector).

Service and support

Local service centres, geologists on staff, back-up XRF's, etc.



Buyers Market USD45K (approx.) for High End XRF (SDD)



Innov-X Xpress



NITON GOLDD



Oxford 5100



Bruker S1 Turbo



Sky Ray (Si PIN)