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The validation of the determination of trace elements by energy dispersive polarised x-ray fluorescence spectrometry

Laboratory Operations

Internal Report OR/07/012

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LABORATORY OPERATIONS

INTERNAL REPORT OR/07/012

The validation of the determination of trace elements by energy dispersive polarised x-ray fluorescence spectrometry

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PANalytical PW5000 Energy Dispersive Polarised X-Ray Fluorescence Spectrometer.

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Foreword

The BGS Analytical Geochemistry Laboratories are accredited by the United Kingdom Accreditation Service (UKAS Testing Laboratory 1816). The methods under this accreditation include the determination of trace elements by Energy Dispersive Polarised X-Ray Fluorescence Spectrometry (Technical Procedure AGN 2.1.6).

This report describes the validation of this method and includes additional validation of this method undertaken to meet the requirements of the MCERTS Standard.

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Summary

This report describes the validation of method AGN 2.1.6 Analysis of Pressed Powder Pellets by Energy Dispersive Polarised X-Ray Fluorescence Spectrometry for its accreditation under UKAS.

It includes additional validation carried out on soil samples undertaken to meet the requirements of the MCERTS Standard for submission of data to the Environment Agency.

1 Introduction

Technical Procedure AGN 2.1.6 defines the method for the analysis of geological and allied materials prepared as pressed powder pellets for the determination of trace elements by energy dispersive polarised X-Ray fluorescence spectrometry (ED(P)-XRFS). X-ray Fluorescence Spectrometry is widely used as an analytical technique in the field of geology and environmental monitoring. Energy dispersive systems have an extensive elemental range, and as they acquire data simultaneously, they can analyse solid materials rapidly. This documents details the method validation undertaken to comply with the requirements of UKAS and MCERTS accreditation.

2 Theory

All energy dispersive systems have an X-ray source, a sample holder and a detector. In a system with 2-dimensional optics, the X-ray source irradiates the sample directly and the detection system measures the fluorescence emitted by the sample. The instrument used in this validation study has 3-dimensional or Cartesian geometry, defined by three orthogonal axes. The primary beam from the X-ray tube irradiates a polarising target placed along the first axis. The X-rays are scattered at 90° irradiating the sample placed along the second axis. The spectrum of the sample is recorded by the detector, which is placed along the third axis. Polarised 3-D optics almost eliminates the tube spectrum. This reduces the continuum (often known incorrectly as spectral background), increases the peak to background ratio and lowers the limit of detection dramatically when compared to 2-D systems.

3 Scope

Technical Procedure AGN 2.1.6 covers the determination of trace elements Ag, Cd, In, Sn, Sb, Te, I, Cs, Ba, La and Ce by ED[P]-XRF (reported as ppm by weight) in geological and environmental samples prepared as pressed powder pellets.

AGN 2.1.6 also covers the submission of data for MCERTS accreditation and trace elements Cd, Sb and Ba reported in ppm by dry weight.

4 Method Validation

Method validation was carried out as a planned and documented activity, according to BGS Operating Procedure AGN 1.6, in preparation for accreditation of the analytical method by UKAS.

In order to meet the additional requirements of MCERTS, the results of the method validation were evaluated against the criteria specified in the Performance Standard for Laboratories Undertaking the Chemical Testing of Soil, version 2 (Environment Agency, 2003).

5 Instrumentation

The validation was performed solely on the Epsilon 5 ED [P]-XRF spectrometer, Serial No. DY605. Data handling was performed by PANalytical Epsilon 5 software v 1.0D.

6 Instrument Configuration

The Epsilon 5 ED[P]-XRF spectrometer uses a combination of secondary fluorescence and Barkla scatter targets to optimise excitation of the analyte of interest. Details of the instrument configuration are given in Table 1.

Table 1 Epsilon 5 instrument parameters for Ag to Ce analytes

Instrument	PANalytical Epsilon 5
Model	PW5000
Serial number	DY605
X-ray Tube	Side window gadolinium max power 600W
Detector	Germanium cooled by liquid nitrogen
Sample changer	Integrated X-Y sample changer Single sample loading mechanism with spinner
Targets used in Ag-Ce	Al_2O_3, CsI
Beam path	Vacuum
Software version	1.0D

7 Analytical Method

The overall suitability of the method was assessed from validation data covering a wide range of sample compositions including rocks, ores, soils, sludges, slags, lake and marine sediments, assessment of long term QC data and comparison with proficiency test results. The method of sample preparation is by pressed powder pellet as described in Technical Procedure SPN 2.1.8 and shown as a flowchart in Appendix 1. To produce a pressed powder pellet, the material is ground to ideally <30 µm and combined with 25% (by original sample weight) of a binder. The binder used is a styrene co-polymer with a polyethylene wax, (van Zyl, 1982). The material is then free pressed into a 40 mm diameter pellet at 25 tons load.

Descriptions of the CRMs used in this validation exercise are shown in Appendix 2. In order to comply with the performance requirements of MCERTS, certified reference materials relevant to the matrices and parameters under investigation were also analysed. For MCERTS, validation data were acquired for four certified soil reference materials; CMI 7002, CMI 7004, GSS-6 and NIST 2710. Descriptions of the matrices and certified values of these materials are shown in Appendix 3. A list of the reference material issuing organisations is shown in Appendix 4.

8 Analytical Application

The configuration of the Epsilon 5 instrument allows for a number of possible options when selecting suitable targets for use in an analytical application. Fifteen secondary targets are available to cover the elemental range from sodium to uranium.

In this validation exercise, the atomic numbers of the determinands are high, so the Al_2O_3 Barkla target was selected. Differences between the sample matrices were accounted for by Compton correction and for this, the CsI target was used. Correction is necessary as every sample has a unique matrix and the effects on the continuum vary widely; in geological and environmental samples, absorption is the predominant effect (Willis, 1989). The counts originating from the X-ray tube scatter from the CsI fluorescent target were measured using a region of interest (26.2 to 27.8 KeV), covering the continuum maximum (referred to as the I Kα Compton peak) as shown in Figure 1. The counts derived from deconvolution of the analyte peak were then corrected by the Compton scatter counts to give a relative net intensity. A brief explanation of the principles of deconvolution is described in Section 15.

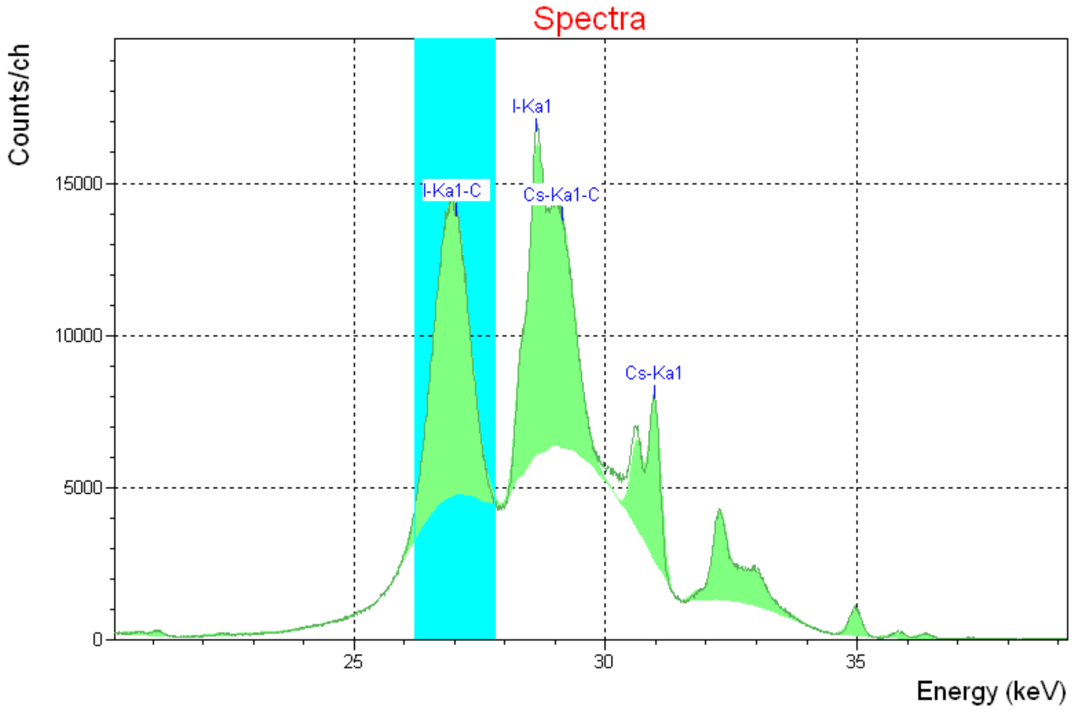

Figure 1 CsI target spectrum of a synthetic ProTrace standard containing 4000ppm Ba

Before the instrument can be used to measure standards and unknowns, several parameters require definition. The target condition list is shown in Table 2. In this condition list, software default values for the power settings were applied and 'Automatic mA adjustment' was used to optimise the measurement time. Sample preparation details are shown in Table 3 with application information in Table 4 and Table 5 Analytical application (2). Deconvolution parameters are listed in Table 6. The delta chi² (χ^2) value gives an indication of the goodness of spectral fitting; the lower the score, the better the fit; a score of 1.00 would indicate perfection. A region of fit (ROF) was applied to the CsI target.

Table 2 Ag-Ce condition list

Condition Name	kV	mA	Automatic mA adjustment	Requested Dead Time (%)	Detector Setting	Max Energy (keV)
Al_2O_3	100	1	Yes	50	Standard	80
CsI	100	1	Yes	50	Standard	80

Table 3 Sample preparation pressed powder

Finite Thickness	Diameter (mm)	Area (mm^2)	Initial Sample Wt (g)	Total Sample Wt (g)	Mass-Thickness (g/cm^2)	Binder Used	Binder Composition	Binder Weight (g)
Yes	40	1256.64	12	15	1.19	Yes	$C_{12}H_{13}N$	3

Table 4 Analytical application (1)

Element(s)	Condition	Report	Dec.	Measurement. Time (s)	Unit	Source
Ag	Al_2O_3	Yes	1	840	ppm	Analysis
Cd	Al_2O_3	Yes	1	840	ppm	Analysis
In	Al_2O_3	Yes	1	840	ppm	Analysis
Sn	Al_2O_3	Yes	1	840	ppm	Analysis
Sb	Al_2O_3	Yes	1	840	ppm	Analysis
Te	Al_2O_3	Yes	1	840	ppm	Analysis
I	Al_2O_3	Yes	1	840	ppm	Analysis
Ce	Al_2O_3	Yes	1	840	ppm	Analysis
Ba	Al_2O_3	Yes	1	840	ppm	Analysis
La	Al_2O_3	Yes	1	840	ppm	Analysis
Ce	Al_2O_3	Yes	1	840	ppm	Analysis
Cs (Compton)	CsI	No	1	120	ppm	Intensity only

Table 5 Analytical application (2)

Element	Line	Compton	Use ROI	Use background for ROI	ROI LL (keV)	ROI UL (keV)
Ag	Ka	No	No	No	-	-
Cd	Ka	No	No	No	-	-
In	Ka	No	No	No	-	-
Sn	Ka	No	No	No	-	-
Sb	Ka	No	No	No	-	-
Te	Ka	No	No	No	-	-
I	Ka	No	No	No	-	-
Cs	Ka	No	No	No	-	-
Ba	Ka	No	No	No	-	-
La	Ka	No	No	No	-	-
Ce	Ka	No	No	No	-	-
Cs (Compton)	Ka	Yes	Yes	Yes	26.2	27.8

Table 6 Deconvolution parameters Ag to Ce

Measurement condition:	Al_2O_3	CsI
Sum peaks	Yes	Yes
Escape peaks	Yes	Yes
Allow negative intensities	No	No
Max. iterations per pass	25	25
Max. delta chi² (χ^2)	0.001	0.001
Automatic ROF	Yes	No
ROF in keV	No	Yes
Minimum keV		2.282
Maximum keV		41.044
Compton fitting	Default	
Energy calibration	Default (Detector Calibration)	
Background fitting		
Filter pre-processing	Linear (none)	Linear (none)
Filter iterations	10	10

9 Calibration

The method was calibrated using a suite of synthetic multi-element pressed powder standards prepared from traceable, pure and stable chemical compounds; the element mixes were carefully designed to exclude all spectral line overlap interferences. The various compounds were ground to analytical fineness <30 μm in a planetary ball mill at 300 rpm (270 RPM for 500 ml jars). A binding agent (van Zyl, 1982) was added at a concentration of 25% and the powder was homogenised. The powders are pressed into pellets of 36 mm diameter at 25 kN. The pellets were glued into aluminium rings and coated with a resin to ensure robustness and durability.

The method was calibrated using calibration algorithms in the Epsilon 5 software.

10 Validation Calculations

Validation data were compiled into MS Excel spreadsheets from which measures of accuracy and precision were determined. An assessment of the fitness of purpose of the method for MCERTS was also included.

11 Acceptance Criteria (UKAS)

The method submitted for UKAS accreditation was validated by analysis of independent reference materials. To comply, the difference between known concentrations and the results of the calibration should be <15% relative except when the concentration was within an order of magnitude of the lower limit of reporting (LLR).

12 Acceptance Criteria (MCERTS)

For MCERTS accreditation, the method must be shown to be fit for purpose. This should be appropriate to the critical level of interest (CLI); this may be the soil guideline value (SGV) as published by the Department for Environment Food and Rural Affairs (DEFRA) or as agreed with the customer. Soil Guideline values are shown in Appendix 5.

The performance characteristics of the method submitted for MCERTS accreditation was determined from a minimum of 10 degrees of freedom using a combination of samples and replicate analyses.

The bias for the entire method was determined by the analysis of independent reference materials for specified matrices. The difference between certified values and the results of the calibration for Cd and Ba should be <10% relative and <15% relative for Sb.

The precision of the method, expressed as the standard deviation of the individual results determined for the entire method, should be < 5% for Cd and Ba and <7.5% for Sb.

13 Reporting Requirements (MCERTS)

For MCERTS accreditation, the reported data must be sufficient for a complete audit trail to be made. This requires information as to the location (and depth) of the sample site, date and time of sampling and sample preservation techniques, if used. Sample descriptions are recorded according to BGS UKAS Technical Procedure SPN 2.1.8.

14 Selectivity and Specificity

The specificity of an analytical method is its ability to distinguish one analyte from another. X-ray fluorescence as a technique is inherently specific since the fluorescent energies for each element are characteristic and of known value, enabling positive identification. To be selective, the method must also demonstrate that it can discriminate between analytes and avoid misidentification due, for example, to spectral interferences. In ED(P)-XRF applications this function is performed by deconvolution.

15 Deconvolution

The aim of deconvolution is to determine the number of counts that can be attributed to each x-ray line present in a given spectrum. Fixed parameters are used to model a theoretical spectrum and an algorithm adjusts variable parameters to fit the model as closely as possible with the 'real' spectrum.

Deconvolution provides the fitted continuum and fitted spectrum, the fitted energy calibration, fitted net peak areas (with standard deviations) and estimated peak backgrounds (for calculation of LLD).

The other major output values are the total number of iterations per pass and the final χ^2 (chi squared) value. The χ^2 value gives an indication of the goodness of fit. Low values show a good fit with a value of $\chi^2=1$ being perfect. Often the χ^2 value is high if one large peak is poorly fitted, particularly a large Compton peak.

Appendix 6 shows a fully deconvoluted spectrum of the analytes Ag to Ce.

16 Spectral Line Overlaps

The theory of deconvolution is that it accounts for all line-overlap interferences and background effects but known exceptions are found in practice. During the calibration of the Ag-Ce application, incomplete modelling of the Ba peak 'shelf' at the Cs Kα energy was observed. Although no Ba lines are known to overlap Cs Kα, the application of a Ba correction factor to Cs, gave an improved calibration line fit (RMS).

17 Lower Limits of Detection

Lower limits of detection can be calculated using count rates obtained by deconvolution or from regions of interest (ROI). Solid materials in an iron-rich alumino-silicate matrix, e.g. synthetic ProTrace standards, are suitable as they reflect the matrix found in geochemical samples. High instrumental stability results in the practical detection limits for most elements in silicate matrices approaching the theoretical values. ProTrace standards were doped with multiple elements at concentrations of around 500 ppm to obtain peak count rates. Blanks of the same matrix were used to obtain background count rates; this enabled the sensitivity and lower limits of detection to be determined as shown in Equation 1.

For MCERTS accreditation, the limit of detection should be appropriate to the critical level of interest (CLI); this may be the soil guideline value (SGV) as published by the Department for Environment Food and Rural Affairs (DEFRA) or as agreed with the customer. The limit of detection is generally regarded as being 10% of the concentration regarded as the critical level of interest.

$$LLD = \frac{3}{m}\sqrt{\frac{R_b}{T_b}}$$

Where: m = sensitivity (counts per second per %)
R_b = the background count rate (counts per second)
T_b = the counting time on the background (s)

Equation 1 Calculation of LLD

Appendix 7 shows the spreadsheet of LLD calculations from the ProTrace standards and a summary of values (as calculated by the E5 software) is shown in Table 7. For the trace elements of interest, the LLDs are typically less than 0.5 ppm for Ag-I and <1ppm for Cs to Ce. The lower limit of detection for In was not determined using ProTrace standards as they do not contain this analyte.

Table 7 Limits of detection

Element(s)	LLD calculated by software (ppm)	ROI LL (KeV)	ROI UL (KeV)	LLD calculated from ROI (ppm)
Ag	0.47	21.85	22.30	0.54
Cd	0.55	22.84	23.32	0.55
Sn	0.51	24.90	25.42	0.60
Sb	0.50	25.96	26.51	0.63
Te	0.47	27.05	27.63	0.66
I	0.60	28.16	28.77	0.71
Cs	0.81	30.46	31.14	0.9
Ba	1.06	31.65	32.36	1.2
La	1.16	32.87	33.61	1.4
Ce	1.35	34.11	34.89	1.7

18 Matrix Correction

Accurate net peak intensities calculated from peak and continuum (background) measurements are essential for the analysis of trace analytes. If the composition of the major analytes is known, matrix correction models using fundamental parameters (FP) or theoretical alphas can be employed. Since the Ag to Ce application does not measure majors, the alternative method of Compton correction was used. Compton scatter is inversely proportional to the mass attenuation coefficient of the sample and matrix correction can be calculated empirically using Equation 2. When selecting a Compton peak, the most popular choice is usually the anode element of the X-ray tube (*Andermann & Kemp, 1958*) but in the case of polarised ED-XRF, radiation from the tube doesn’t reach the detector, whereas radiation from the secondary targets do, but their useful energy ranges are restricted. Since the energies of the Ag-Ce Kα lines are greater than those of the Fe Kα absorption edge at 7.11 KeV, or any other major element absorption edge, matrix correction using mass absorption coefficients (MACs) is unnecessary.

The Compton scatter from the CsI target was used for matrix correction in the Ag-Ce application. Appendix 6 shows the CsI target spectrum of a synthetic ProTrace standard containing 4000ppm Ba.

$$C = D + E\frac{R}{IR}$$

Where: C = concentration
D = concentration intercept by linear regression
E = 1/slope by linear regression
R = analyte line net count rate
IR = Compton count rate

Equation 2 Matrix correction using the Compton scatter internal ratio method

19 Calibration Range and Linearity

Appendix 8 shows the calibration details for the DY605 spectrometer. Calibration coefficients, intercept (D) and slope (E) for each analyte are listed along with the standards used for calibration with their certified values and measured values. The Root Mean Square (RMS) value indicates the goodness of fit of the regression. For the Ag-Ce application, weighted regressions were used for the analytes In and La but all other analyte regression lines were un-weighted.

20 Reporting Limits

The lower limits of reporting were based on the LLD. The upper reporting limits were determined from the highest concentration standard used on calibration or from the highest validation standard. The lower limits of reporting (LLRs), upper limits of calibration (ULCs) and upper reporting limits (URLs for trace analytes) are shown in Table 8.

Table 8 Reporting limits

Element(s)	LLR (ppm)	ULC (ppm)	URL (ppm)
Ag	0.5	1000	2000
Cd	0.5	1000	2000
In	0.5	1000	2000
Sn	0.5	1000	2000
Sb	0.5	1000	2000
Te	0.5	1000	2000
I	0.5	1000	2000
Cs	1	1000	3000
Ba	1	1000	5000
La	1	1000	2000
Ce	1	1000	2000

21 Accuracy and Bias (UKAS)

The accuracy of the calibration for each analyte was assessed by measuring a range of materials encompassing the scope of the method including, commercially available CRMs, RMs and BGS in-house materials whose elemental composition has been verified by other methods.

Over 200 reference materials, listed in Appendix 2, were measured as unknown samples each of which had reference concentration values for at least one analyte. For each analyte, the measured data were regressed against certified data; the slope and intercept for each analyte are shown in Table 9.

Table 9 Accuracy data from validation exercise

Analyte	No of RMs	Maximum concentration (ppm)	Regression slope	Regression intercept	Correlation coefficient
Ag	19	40.4	1.001	-0.410	0.998
Cd	32	470	0.992	-0.113	1.000
In	5	5.1	1.008	-0.107	0.905
Sn	114	370	0.974	-0.006	0.999
Sb	78	412	0.986	-0.218	1.000
Te	2	13	0.922	0.911	1.000
I	16	19.4	1.028	-0.295	0.987
Cs	112	107	0.970	0.070	0.994
Ba	163	4400	0.974	13.349	0.994
La	153	184	1.027	0.244	0.981
Ce	158	402	1.000	0.377	0.984

For the 11 analytes, the slopes are in the range of 1.000 ± 0.03 with the exception of Te which has only two validation standards. The correlation coefficients for all the analytes were at least 0.98 except for Indium, which has only five validation standards. Regression plots for each of the analytes are shown in Appendix 9 together with plots of absolute and relative difference of measured values from certified values.

22 Precision and Bias (MCERTS)

Four certified soil reference materials: CMI 7002, CMI 7004, GSS-6 and NIST 2710, were prepared as pressed powder pellets; four were used to give adequate coverage for the analytes of interest. To comply with the requirements of the MCERTS standard, it was necessary to prepare eleven pellets of each soil CRM. Each pellet was measured in duplicate at random intervals over a period of not less than 6 days and not more than 3 months. The testing commenced on 14/03/2005 and was completed by 24/05/2005. The calculation of precision and bias are shown in full in Appendix 10 and summarised in Table 10. No certified values were available for Sb in CRM CMI 7002 and 7004.

Table 10 Summary of MCERTS precision and bias test

Analyte	Required targets		CRM 1 CMI7004				CRM 2 CMI7002			
	Precision	Bias	Certified value	Mean	Precision	Bias	Certified value	Mean	Precision	Bias
Cd	* 0.20	* 0.40	1.52	1.74	0.24	0.22	0.31	0.32	0.18	0.01
Sb	* 0.25	* 0.50	N/A	2.81	0.29	N/A	N/A	1.47	0.26	N/A
Ba	26.8	56.8	568	536.6	2.3	31.4				
Ba	45.3	98.7					987	905.0	2.8	82

Analyte	Required targets		CRM 3 GSS-6 (NCS DC73324, GBW07406)				CRM 3 NIST 2710			
	Precision	Bias	Certified value	Mean	Precision	Bias	Certified value	Mean	Precision	Bias
Cd	* 0.20	* 0.40	0.13	0.15	0.13	0.02				
Cd	1.01	2.18					21.8	20.15	0.29	1.65
Sb	4.54	9.00	60	60.55	0.38	0.55				
Sb	2.47	5.76					38.4	32.90	0.24	5.50
Ba	5.3	11.8	118.0	105.7	0.7	12.3				

The method complies for all analytes except GSS-6, which fails the bias test for Ba. For this analyte the required target for bias was 10% but the bias obtained was 10.4%, which fell just outside the acceptable bias range.

In all, 163 RMs were analysed during the validation exercise, 26 of which were sediments and 18 were soils. The certified values, measured values, absolute difference and the relative difference for Ba in the soil RMs are shown in Table 11, from which it can be seen that 17 of the 18 soils analysed had a bias of less than 10%. This additional evidence demonstrates that the method is considered suitable for the determination of Ba.

Table 11 Barium validation data from soil RMs

Reference Material	Description	Certified value Ba (ppm)	Measured value Ba (ppm)	Absolute Difference Ba (ppm)	Relative Difference (%)
GSS-6	Soil, GBW07406	118	108	10.0	8.47
GSS-7	Soil, GBW07407	180	199	-19.0	10.56
GSS-4	Soil, GBW07404	213	214	-1.0	0.47
SO-3	Soil Sample	290	293	-3.0	1.03
GSS-5	Soil, GBW07405	296	306	-10.0	3.38
GSS-8	Soil, GBW07408	480	491	-11.0	2.29
GSS-1	Soil, GBW07401	590	583	7.0	1.19
SO-4	Soil Sample	700	711	-11.0	1.57
NIST2710	Montana Soil	707	723	-16.0	2.26
NCS DC 80301	Polluted farmland soil	724	718	6.0	0.83
NIST2711	Montana Soil	726	718	8.0	1.10
SO-1	Soil Sample	870	911	-41.0	4.71
GSS-2	Soil, GBW07402	930	868	62.0	6.67
NIST2709	San Joaquin Soil	968	917	51.0	5.27
SO-2	Soil Sample	1000	1021	-21.0	2.10
GSS-3	Soil, GBW07403	1210	1142	68.0	5.62
GXR-6	Soil	1300	1229	71.0	5.46
GXR-2	Soil	2240	2170	70.0	3.13

23 Repeatability

Repeatability is an assessment of precision under reproducible conditions, where independent test results are obtained by the same method on identical test items in the same laboratory by the same operator using the same equipment within short intervals of time. To demonstrate repeatability, three silica glass beads spiked with multiple analytes at different concentrations were analysed over a period of 18 months and the resulting data were charted. The charts cover two calibrations of the DY605 instrument, P-Ag-Ce Cal (October 2003 to January 2005) and

PC–Ag-Ce (January 2005 to April 2005). Some steps in the datasets were noted between the calibrations as shown graphically in Appendix 11.

All QC charts were prepared using SPSS QI Analyst software package in accordance with BGS AGN 1.7 and these Quality Control charts are a robust estimate of short to long-term precision. Iodine is not present in the high and low quality control standards; the QC status of this analyte is inferred from a spectrographically adjacent element. Summary data are shown in Table 12(QCBGS High), Table 13(QCBGS Low) and Table 14 (QCBGSMON).

The upper and lower limits are calculated as twice the standard deviation of the population of data points. The method specification limits are long-term control limits, based on the uncertainty of the method and set at approximately the target value ± 5% relative for QC High and QC Low. The limits for BGSMON are set up to 2x the lower limit of reporting (LLR) as this better represents the instrument noise at this concentration. No data outside these limits are accepted under normal circumstances.

Table 12 Summary of repeatability data for QCBGS High

Date from: 28/10/2003 to 19/04/2005, QCBGS High was analysed 240 times during this period

Analyte	Mean (ppm)	Standard deviation	Relative standard deviation (%)	Upper Specification Limit (ppm)	Lower Specification Limit (ppm)
Ag	266.5	2.70	1.01	279	251
Cd	400.9	5.05	1.26	440	380
In	-	-	-		
Sn	329.9	2.60	0.79	347	313
Sb	336.3	4.28	1.27	350	316
Te	289.2	3.57	1.23	304	274
I	-	-	-	-	-
Cs	358.0	4.81	1.34	373	337
Ba	374.2	4.10	1.10	390	354
La	351.2	3.76	1.07	367	331
Ce	350.2	5.92	1.69	365	329

Table 13 Summary of repeatability data for QC BGS Low

Date from: 28/10/2003 to 18/04/2005, QCBGS Low was analysed 239 times during this period

Analyte	Mean (ppm)	Standard deviation	Relative standard deviation (%)	Upper Specification Limit (ppm)	Lower Specification Limit (ppm)
Ag	30.5	0.41	1.34	32	29
Cd	44.9	1.31	1.31	47	43
In	-	-	-		
Sn	38.5	0.93	0.93	40.5	36.5
Sb	38.1	1.28	1.28	40	36
Te	32.1	1.54	1.54	33.4	30.5
I	-	-	-	-	-
Cs	41.0	1.53	1.53	43	39
Ba	62.8	1.21	1.21	66	60
La	41.3	1.75	1.75	43.5	39.5
Ce	36.9	2.00	2.00	39	35

The upper and lower warning limits are calculated as twice the standard deviation of the population of data points. The method specification limits are long-term control limits, based on the uncertainty of the method and set at approximately the target value ± 5% relative for QC High and QC Low. QCBGSMON limits are set up to 2x the lower limit of reporting (LLR) as this better represents the instrument noise at this concentration. No data outside these limits are accepted under normal circumstances.

Table 14 Summary of repeatability data for QCBGS BGSMON

Date from: 28/10/2003 to 20/04/2005, QCBGSMON was analysed 169 times during this period

Analyte	Mean (ppm)	Standard deviation	Upper Specification Limit (ppm)	Lower Specification Limit (ppm)
Ag	0.2	0.11	0.75	-0.75
Cd	0.2	0.12	1	-0.5
In	0.4	0.16	1.15	-0.35
Sn	0.5	0.15	1.2	-0.3
Sb	0.0	0.07	0.75	-0.75
Te	0.0	0.07	0.75	-0.75
I	0.0	0.04	0.75	-0.75
Cs	2.3	0.33	4	1
Ba	0.3	0.42	1.5	-1.5
La	0.6	0.63	3.65	-2.35
Ce	5.7	0.64	8	4

24 Reproducibility

Reproducibility is also described as intermediate precision or within laboratory reproducibility. It is an assessment of precision under conditions where independent test results are obtained with the same method on identical test items in the same laboratory by different operators using different equipment on different days. Within laboratory reproducibility was evaluated by analysing a selection of CRMs as check standards after calibration and every subsequent recalibration of the instrument.

To demonstrate reproducibility, a selection of GBASE bulk reference soil samples were prepared as pressed powder pellets. This test set was run at the start and end of every batch of 500 samples over a period of 16 months. These data were complied into QC charts prepared using SPSS QI Analyst software package in accordance with BGS AGN 1.7. These data are summarised in Table 15 to Table 20.

Table 15 Summary of reproducibility data GSD-3

Analyte	Certified value (ppm)	Mean (ppm)	Standard deviation	Relative Standard Deviation (%)
Ag	0.59 ± 0.07	<	-	-
Cd	0.1 ± 0.02	<	-	-
In	0.09 ± 0.02	<	-	-
Sn	3.4 ± 0.9	3.1	0.21	6.8
Sb	5.4 ± 0.8	6.3	0.19	3.0
Te	0.14 ± 0.03	<	-	-
I	#	2.0	0.30	14.6
Cs	7.8 ± 0.6	7.2	0.50	6.9
Ba	615 ± 63	608.3	5.67	0.9
La	39 ± 7	38.0	0.64	1.7
Ce	64 ± 6	65.4	0.80	1.2

These data are also shown graphically in Appendix 12. The # symbol indicates where no data were available and the < shows where the concentration was <LLR.

Table 16 Summary of reproducibility data GSD-7

Analyte	Certified value (ppm)	Mean (ppm)	Standard deviation	Relative Standard Deviation (%)
Ag	1.05 ± 0.09	0.9	0.31	33.5
Cd	1.05 ± 0.08	0.9	0.27	29.1
In	0.064 ± 0.012	<	-	-
Sn	5.4 ± 1.3	4.9	0.19	3.8
Sb	2.6 ± 0.3	2.8	0.27	10.0
Te	0.06 ± 0.02	<	-	-
I	#	<	-	-
Cs	5.9 ± 0.7	4.7	0.35	7.4
Ba	720 ± 70	734.6	6.69	0.9
La	45 ± 6	44.6	0.82	1.8
Ce	78 ± 7	80.5	1.14	1.4

Table 17 Summary of reproducibility data GSS-1

Analyte	Certified value (ppm)	Mean (ppm)	Standard deviation	Relative Standard Deviation (%)
Ag	0.35 ±0.07	<	-	-
Cd	4.3 ± 0.6	4.3	0.21	5.0
In	0.08 ± 0.02	<	-	-
Sn	6.1 ± 1	5.9	0.22	3.7
Sb	0.87 ± 0.32	<	-	-
Te	0.047	<	-	-
I	1.9 ± 0.4	1.9	0.24	12.9
Cs	9 ± 0.9	8.2	0.47	5.7
Ba	590 ± 50	582.9	4.41	0.8
La	34 ± 3	33.1	0.74	2.2
Ce	70 ± 5	67.2	0.84	1.3

Table 18 Summary of reproducibility data LKSD-1

Analyte	Certified value (ppm)	Mean (ppm)	Standard deviation	Relative Standard Deviation (%)
Ag	0.6	<	-	-
Cd	1.4	1.2	0.21	18.5
In	#	0.5	0.20	39.3
Sn	16	14.6	0.67	4.6
Sb	1.2	0.8	0.24	30.5
Te	#	<	-	-
I	#	1.6	0.26	16.5
Cs	1.5	1.2	0.24	20.3
Ba	430	392.7	4.01	1.0
La	16	0.64	0.64	4.6
Ce	27	24.8	0.80	3.2

Table 19 Summary of reproducibility data LKSD-4

Analyte	Certified value (ppm)	Mean (ppm)	Standard deviation	Relative Standard Deviation (%)
Ag	#	<	-	-
Cd	2	2.0	0.18	9.0
In	#	<	-	-
Sn	5	4.6	0.17	3.7
Sb	1.7	1.3	0.23	17.6
Te	#	<	-	-
I	#	9.4	0.25	2.6
Cs	1.7	1.7	0.24	13.8
Ba	330	260.1	2.65	1.0
La	26	20.4	0.57	2.8
Ce	48	37.1	0.80	2.2

Table 20 Summary of reproducibility data STSD-3

Analyte	Certified value (ppm)	Mean (ppm)	Standard deviation	Relative Standard Deviation (%)
Ag	#	0.6	0.35	58.9
Cd	1.1	0.9	0.20	23.9
In	#	<	-	-
Sn	4	3.1	0.18	5.8
Sb	4	3.5	0.31	8.7
Te	#	<	-	-
I	#	11.0	0.31	2.8
Cs	5.2	5.2	0.48	9.4
Ba	1490	1373.2	12.76	0.9
La	39	32.8	0.69	2.1
Ce	63	54.3	0.92	1.7

25 Proficiency Testing

Proficiency testing is an effective way for a laboratory to monitor its performance against the performance standards set by other participating laboratories. The scheme organisers distribute a sample of established homogeneity to participating laboratories. These laboratories analyse the sample using established techniques following their routine procedures and analytical conditions.

In the case of XRF analysis, direct comparison between laboratories is not always possible as several techniques are available for elemental analysis including ICP-AES, ICP-MS and AAS. Most proficiency testing schemes quote the methods used to generate the results. Consensus data invariably includes extraction techniques and therefore the data obtained for a particular element do not necessarily represent the total concentration.

For this validation study, data were submitted to two proficiency testing schemes, GeoPT and ISE WEPAL. The International Proficiency Test of Analytical Geochemistry Laboratories (GeoPT) is organised by the International Association of Geoanalysts (IAG) and is administered by the Department of Earth Sciences at the Open University, Milton Keynes. Results were submitted under GeoPT ‘Applied Geochemistry’ (Data Quality 2) which applies to high sample throughput laboratories who provide data for geochemical mapping or geochemical exploration programmes. The second scheme, the Wageningen Evaluating Programmes for Analytical

Laboratories (WEPAL) organisation is accredited for the organization of Inter-laboratory Studies by the Dutch Accreditation Council RvA since April 26, 2000 (registration number R002). The accreditation is based on the ILAC-requirements (Guidelines for the requirements for the competence of providers of proficiency testing schemes, ILAC-G13:2000). The accreditation covers the quality system of the organisation and the test parameters. Data for submission to proficiency testing schemes have been collected over long periods, during which time changes due to environmental conditions, different operators, preparation of standards, running of different sample types and instrument services have all taken place. These data are therefore a measure of how the system responds to these changes and shows that general day-to-day variations in operation do not significantly affect the performance of the method.

25.1 GEOPT PROFICIENCY TESTING SCHEME

Data from three samples analysed as part of the GeoPT Proficiency Testing Scheme, together with the assigned z-score, are presented in Table 21. Samples supplied as part of the GeoPT Proficiency Testing scheme distributions 14, 15 and 16 have been analysed. Z-scores for Sn, Sb, Cs, Ba, La and Ce are shown, no assigned values were returned and so no z-score could be calculated for Ag, Cd, In, Te and I over this period.

All z-scores for Sn, Ba and Ce fall within the acceptable range ($-2<z<+2$). Only one assigned value was returned for Sb with an associated z-score of 3.55, a measured value of 0.8 ppm (close to the 0.5 ppm LLD) compared with a provisional assigned value of 0.49 ppm. Two of the three z-scores for Cs and La are within the acceptable range. Cs in GeoPT 16 had a z-score of 92.43, the magnitude of which was grossly distorted by a measured value of 1.0 ppm (the LLR for this element) compared with an assigned value of 0.04 ppm. La in GeoPT 16 had a z-score of 3.39; a measured value of 7.4 ppm compared with an assigned value of 5.2 ppm.

Table 21 Z-scores for the GeoPT proficiency testing scheme (Nov 2004-Apr 2005).

Analyte	GeoPT14	GeoPT15	GeoPT16
Ag	#	#	#
Cd	#	#	#
In	#	#	#
Sn	0.07	-1.26	0.34
Sb	#	3.55	#
Te	#	#	#
I	#	#	#
Cs	-0.13	-0.65	92.43
Ba	0.71	0.74	1.92
La	1.83	1.23	3.39
Ce	1.05	0.19	0.38

25.2 ISE WEPAL PROFICIENCY TESTING SCHEME

For the purposes of this validation, data from the calibration were compared to WEPAL consensus values for real total inorganic chemical composition. WEPAL samples are distribution quarterly; each distribution is comprised of four samples.

The descriptions and sampling locations of the WEPAL materials analysed during the validation period are shown in Table 22.

Table 22 WEPAL materials, descriptions and sampling locations

WEPAL Material No.	Description	Sampling Location
921	River Clay-91	The Netherlands
930	Moist Clay	Ivory Coast
951	River Clay	The Netherlands
952	Clay	Africa
958	Sandy Soil	The Netherlands
961	Clay	The Netherlands
962	Sandy Clay	The Netherlands
965	Clay	The Netherlands
970	River Clay-95	The Netherlands
986	Sandy Soil	The Netherlands
989	River Clay	The Netherlands
992	Sandy Clay Soil	The Netherlands
995	Sandy Soil-90	The Netherlands
997	Sandy Soil	The Netherlands
998	Organic Ferrasol	Indonesia
999	Moist Clay	Ivory Coast

Z-scores reported are shown for six distributions covering the period from January 2004 to April 2005. No assigned values were returned and so no z-score could be calculated for In, Te, I and Cs over this period. The z-scores are shown in Table 23 to Table 28.

All z-scores returned for Sn, Sb, Ba and La all fell within acceptable limits ($-2<z<+2$). Ce in sample 4, Period 1, had a z-score of 4.02; a measured value of 40 ppm compared with an assigned value of 47.4 ppm. All remaining z-scores for Ce were within the acceptable range. Cd z-scores fell outside the acceptable range on two occasions; both were due to the assigned values being close to, or less than the LLD of 0.5ppm.

Table 23 Z-scores for the WEPAL PT scheme (Period 1, 2004)

Analyte	Sample 1	Sample 2	Sample 3	Sample 4
	965	989	970	992
Ag	<	#	#	<
Cd	9.8	0.61	-0.87	1.8
In	#	#	#	#
Sn	0.08	0.11	#	0.19
Sb	<	-0.67	-0.62	<
Te	#	#	#	#
I	#	#	#	#
Cs	#	#	#	#
Ba	0.08	-0.43	-1.00	-1.09
La	1.89	0.34	0.38	-1.07
Ce	-0.18	-0.59	-1.03	-4.02

Table 24 Z-scores for the WEPAL PT scheme (Period 2, 2004)

t	Sample 1 995	Sample 2 989	Sample 3 930	Sample 4 962
Ag	#	#	<	<
Cd	1.81	0.05	<	<
In	#	#	#	#
Sn	#	0.46	#	#
Sb	-1.17	-0.57	<	<
Te	#	#	#	#
I	#	#	#	#
Cs	#	#	#	#
Ba	-0.79	-0.22	-1.81	-0.67
La	-1.05	0.17	-0.61	1.57
Ce	#	-0.68	-0.41	-0.34

Table 25 Z-scores for the WEPAL PT scheme (Period 3, 2004)

Analyte	Sample 1 951	Sample 2 921	Sample 3 986	Sample 4 989
Ag	<	<	<	#
Cd	<	-0.99	<	-0.59
In	#	#	#	#
Sn	0.86	0.38	#	0.13
Sb	#	#	#	#
Te	#	#	#	#
I	#	#	#	#
Cs	#	#	#	#
Ba	-0.27	-0.85	-0.95	-0.64
La	0.90	-0.30	-0.90	-0.09
Ce	-0.48	-0.72	0.21	-0.76

Table 26 Z-scores for the WEPAL Proficiency Testing scheme (Period 4, 2004)

Analyte	Sample 1 958	Sample 2 995	Sample 3 998	Sample 4 989
Ag	<	#	<	#
Cd	<	1.05	<	-0.47
In	#	#	#	#
Sn	#	#	#	-0.12
Sb	#	-0.81	<	-0.89
Te	#	#	#	#
I	#	#	#	#
Cs	#	#	#	#
Ba	-0.87	-0.52	-0.44	-0.15
La	-0.81	-0.14	-0.71	-0.46
Ce	0.05	-0.40	#	-1.05

Table 27 Z-scores for the WEPAL Proficiency Testing scheme (Period 1, 2005)

Analyte	Sample 1 989	Sample 2 952	Sample 3 997	Sample 4 999
Ag	#	<	<	<
Cd	0.88	<	2.03	
In	#	#	#	#
Sn	#	#	-0.04	0.29
Sb	#	#	#	<
Te	#	#	#	#
I	#	#	#	#
Cs	#	#	#	#
Ba	-0.45	0.89	0.53	1.97
La	0.22	0.33	-0.47	0.78
Ce	-0.94	-0.14	-0.78	-0.50

Table 28 Z-scores for the WEPAL Proficiency Testing scheme (Period 2, 2005)

Analyte	Sample 1 961	Sample 2 989	Sample 3 986	Sample 4 992
Ag	<	#	<	<
Cd	-1.35	-0.02	<	<
In	#	#	#	#
Sn	#	0.03	#	#
Sb	#	#	#	#
Te	#	#	#	#
I	#	#	#	#
Cs	#	#	#	#
Ba	-1.17	-2.14	-0.47	-2.57
La	-1.25	-0.75	#	-1.00
Ce	-0.48	-0.9	#	-0.42

26 Measurement of Uncertainty

The calibrations cover wide concentration ranges and the uncertainty of measurement is dependant upon the analyte concentration in the specified sample. However an attempt has been made to calculate an overall uncertainty that applies to all analytes at approximately one order of magnitude above the LLD.

The method uncertainty can be estimated by incorporating components that can be attributed to data precision and bias. A measure of precision (the relative standard deviation) can be calculated from data that have been acquired from repeated analysis of two QC samples (Table 12 and Table 13) and six RMs (Table 15 to Table 20); a pooled standard deviation was calculated from those samples that had elements present at sufficiently high concentrations. A measure of bias can be taken from the regression charts plotted using validation data (Table 9). The difference of the slope from 1 is used as a relative standard deviation.

The combined uncertainty of the bias and the precision estimated in this way has been calculated as the square root of the sum of the squares of bias and standard deviation. This value has been used to represent the standard uncertainty and has been multiplied by a coverage factor of 2 to give an expanded uncertainty. The standard and expended uncertainties are shown in Table 29 and expanded uncertainties are depicted in Figure 2. The precision for In is estimated as the QC materials did not contain this element and it was present in the RMs at insufficiently high concentrations. The bias component for Te is high due to the very few RMs from which validation data could be obtained, so the tabulated value was halved for the purposes of this calculation. The precision component for I is high as it was calculated from materials with I concentrations at ~10 ppm, so the tabulated value was halved for the purposes of this calculation.

Table 29 Estimates of Measurement Uncertainty

Analyte	Bias	Precision	Standard uncertainty (%)	Expanded uncertainty (%)
Ag	0.1	1.7	1.7	3.4
Cd	0.8	2.7	2.8	5.6
In	0.8	*2.0*	2.2	4.3
Sn	2.6	1.7	3.1	6.2
Sb	1.4	3.1	3.4	6.9
Te	*3.9*	2.0	4.4	8.7
I	2.8	*3.8*	4.7	9.4
Cs	3.0	3.0	4.3	8.5
Ba	2.6	0.4	2.6	5.3
La	2.7	1.0	2.9	5.8
Ce	0.0	0.8	0.8	1.6

Precision for In and I and bias for Te estimated

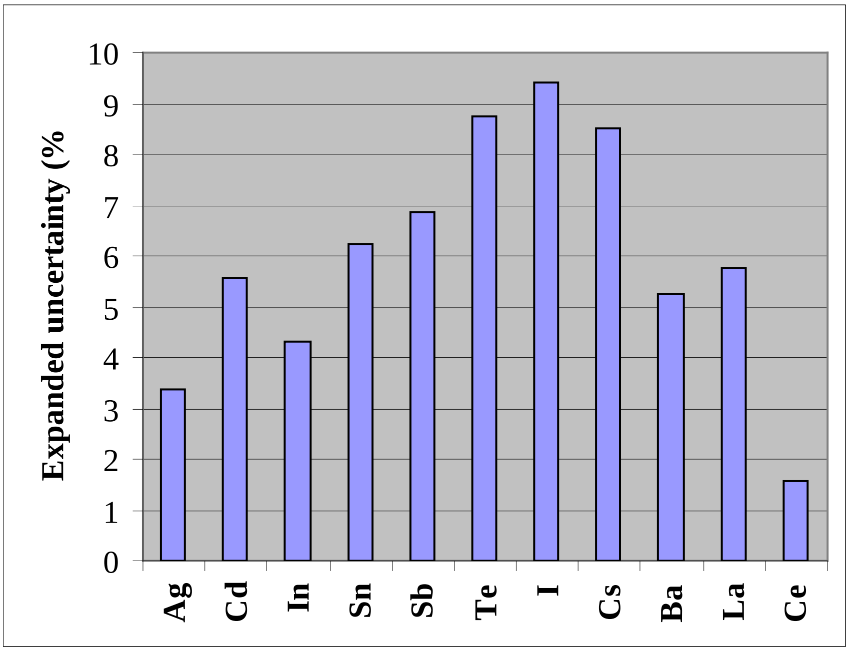

Figure 2 Measurement uncertainty plotted as expanded uncertainties

Glossary

Accuracy	The closeness of agreement between a test result and the true concentration or accepted reference value. The term accuracy, when applied to a set of results, involves a combination of random components and a common systematic error (bias component).
Bias	Bias characterises the systematic error in a given analytical procedure and is a measurement of the (positive or negative) deviation of the mean analytical result from the (known or assumed) true value.
Limit of Detection	The lowest amount of analyte that can be measured with reasonable statistical certainty
Precision	A statement of the closeness of agreement between independent test results obtained under stipulated conditions. Usually stated in terms of the standard deviation, the relative standard deviation or the standard deviation of the mean of a number of replicates. Precision depends only on the distribution of random errors and does not relate to the true value or specified value. Repeatability and reproducibility are measures of precision under particular sets of extreme conditions.
Repeatability	Precision under repeatability conditions, i.e. conditions where independent test results are obtained with the same method on identical test items in the same laboratory by the same operator using the same equipment within short intervals of time. In terms of this validation study, the same operator is considered to be the robotic arm of the instrument; the three silica glass beads remain on the sample loader at all times and are analysed automatically by the instrument at a pre-defined rate.
Reproducibility	Precision under reproducibility conditions, i.e. conditions where independent test results are obtained with the same method on identical test items in the same laboratory by different operators using different equipment on different days.
Selectivity	The ability of a method to determine accurately and specifically the analyte of interest in the presence of other compounds in a sample matrix under the stated conditions of the test.
Specificity	The ability of a method to measure only what it is intended to measure.

References

Most of the references and bibliography listed below are held in the Library of the British Geological Survey at Keyworth, Nottingham. Copies of the references may be purchased from the Library subject to the current copyright legislation.

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APPENDIX 1 – Sample Preparation

Section: SPN 1.2 Installation Date: 24 October 2005
Issue: 3.0 Status: Operational

Title: PREPARATION OF SAMPLES FOR GEOCHEMICAL ANALYSIS

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1.2.1 PURPOSE

To define the recommended routes for the preparation of solid samples for geochemical and mineralogical analysis.

1.2.2 SCOPE

Samples received by the Sample Preparation Facility for preparation prior to geochemical analysis, including soils submitted under the Environmental Agency's Monitoring Certification Scheme (MCERTS).

1.2.3 RESPONSIBILITIES

The supervision of sample preparation procedures and the control of sample preparation administration are the responsibility of the Sample Preparation Facility Manager or the designated deputy.

The correct application of this procedure is the responsibility of Sample Preparation Facility Technicians identified as having authorisation in their UKAS Training Records (see Operating Procedure AGN 1.2).

1.2.4 DEFINITIONS

1.2.5 FORMS

Sample Preparation Record Form – SPF/SPRF
Sample Registration Form – AGN/SRF
Sample Receipt and Transfer Form – AGN/SRTF
MCERTS Soils Description Form – SPN/SDF

1.2.6 REFERENCES

Operating Procedure AGN 1.2 – Training and Development
Operating Procedure AGN 1.8 – Sample Handling
Operating Procedure AGN 1.9 – Control of Laboratory Records

Operating Procedure SPN 1.1 – Quality Control of Sample Preparation and Testing Facility Equipment
Technical Procedure SPN 2.1 – Sub-sampling and Sieving
Technical Procedure SPN 2.2 – Operation of Manual Rock Splitters
Technical Procedure SPN 2.3 – Operation of Jaw Crushers
Technical Procedure SPN 2.4 – Operation of the Mixer-mill 2000
Technical Procedure SPN 2.5 – Operation of Disk Mills
Technical Procedure SPN 2.6 – Operation of Vibrating Cup (Tema) Mills
Technical Procedure SPN 2.7 – Operation of Planetary Ball Mills

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Section: SPN 1.2 | Installation Date: 24 October 2005
Issue: 3.0 | Status: Operational

Title: PREPARATION OF SAMPLES FOR GEOCHEMICAL ANALYSIS

Technical Procedure SPN 2.8 – Operation of the Herzog pellet Press
Technical Procedure SPN 2.9 – Operation of the Micronising Mill
Technical Procedure SPN 2.10 – Operation of the P14 Rotor Speed Mill
Technical Procedure SPN 2.11 – Operation of the Roller Crusher
Technical Procedure SPN 2.12 – Operation of the Cross-Beater Mill
Technical Procedure SPN 2.13 – Operation of the P7 Micro Mill
Technical Procedure SPN 2.14 – Operation of the Waring Blender

1.2.7 PROCEDURES

Outline

1. Solid samples are rendered into a suitable form for geochemical and mineralogical analysis using one of the standard preparation routes given in section 1.2.8 of this procedure where appropriate.

Equipment

2. Equipment used for the preparation of samples for analysis conforms to the requirements of Operating Procedure SPN 1.1.

3. All sample preparation equipment should be operated in accordance with the relevant technical procedures (SPN 2.1 – 2.14).

Records

4. Sample receipt is carried out according to Operating Procedure AGN 1.8. The laboratory or customer sample numbers, preparation processes required, number and type of sub-samples needed, any deviations from the required preparation and the unique identification number of the equipment used are recorded on the Sample Preparation Record Form, which is filed in the appropriate laboratory record file (AGN 1.9). Where samples are submitted for physical preparation only, the SPRF is filed in U115 on completion.

5. Where the Sample Registration Form states that the chemical testing of the samples is to be performed to MCERTS, the condition of the samples as received must be recorded using the MCERTS Soils Description Form.

6. *Screening of Samples Prior to Preparation*

All samples are screened for radioactivity using a radiation monitor, which is calibrated externally once every thirteen months. Results are recorded on the appropriate Sample Preparation Record Form. Samples reading over 3.5 times background activity are considered to be too hazardous for handling by the Sample

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Preparation Facility; no further work is carried out on these samples and the customer is informed.

Sample Description for MCERTS

7. Soils registered for analysis under MCERTS are described on an as received basis, prior to any sample preparation, including drying, using the key on the MCERTS Soil Description Form.

8. Sample colour is assessed using a Munsell Colour chart. Soil texture is assessed by comparison with a set of soils of known texture designated for this purpose, selected to be comparable with other soil descriptions in the BGS. Descriptions of moisture and size of sample are recorded for the benefit of the BGS Sample Preparation Facility only and are not reported to the customer.

Sample Hardness

9. To indicate the likely resistance of a sample to crushing/milling etc., hardness is broadly defined as follows:

Hard-tough	Igneous and highly metamorphosed rocks (highly resistant)
Hard	Most rocks, panned concentrates, concrete (resistant)
Hard-brittle	Mudstones (resistant to moderately-resistant)
Medium-tough	Micas (can be resistant)
Medium	Some sandstones and harder clays
Medium-brittle	Cooled plastics, circuit boards
Soft-flexible	Grasses, hairs, some plastics
Soft-brittle	Branches, leaves, clays (dried)

1.2.8 STANDARD PREPARATION ROUTES FOR GEOLOGICAL MATERIALS

Determination of sample preparation route

1. It is the responsibility of the Sample Preparation Facility Manager, or the designated deputy, to determine the preferred sample preparation route based on the information provided on the Sample Registration Form. The choice of the appropriate route is dependent upon the nature of the sample received, and the analytical requirements of the prepared sample or sub-samples. Where appropriate, the proposed route is agreed with the customer before preparation commences.

2. The appropriate points at which to enter the following flow diagrams will be dependant on the nominal particle size and hardness of the samples received and the analytical requirements. Deviations from the following preparation routes may be appropriate for non-routine samples.

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Sub-sampling

3. Riffle splitting, cone quartering or random sub-sampling may be used at any point in the following flow diagrams. The sub-sampling method used is at the request of the customer, the Sample Preparation Facility Manager or deputy.

Drying

4. Samples are processed on an ‘as received’ basis, unless preparation can only be carried out on dried material, or when a particular drying regime is specifically requested by the customer or the Sample Preparation Facility Manager or deputy.

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Alternative sample preparation routes

5. Rock samples for XRF pellets and fused beads

(Particle size >180 mm) Rock splitting (SPN 2.2)
↓ → Retain reference sample(s)
(Particle size <180 mm) Jaw crushing (SPN 2.3)
↓
Sub-sampling (SPN 2.1)
↓ → Retain excess crushed sample
Dry if necessary (SPN 2.1)
↓
(Particle size <5 mm) Agate Tema-milling (SPN 2.6)
↓
Sub-sampling (SPN 2.1)
↓ → Retain excess milled powder
Planetary ball-milling (SPN 2.7)
↓
Sub-sampling (SPN 2.1)
↓ → Retain sub-sample for fused bead preparation (if necessary) (AGN 2.1.2)
Pellet pressing (SPN 2.8)

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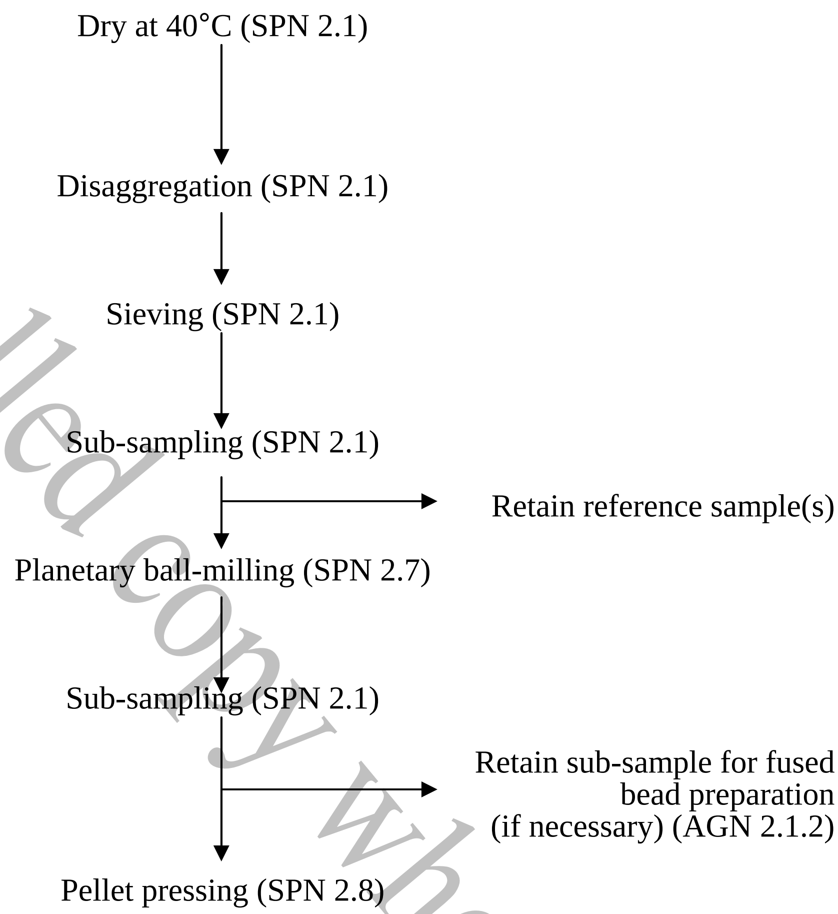
6. <u>Soils and stream sediments for XRF pellets and fused beads</u>



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APPENDIX 2 – Reference Materials

List of Reference Materials used for the validation exercise.

Reference Material name	Material type	Source of RM
AC-E	Granite	GIT-IWG
AGV-1	Andesite	USGS
AN-G	Anorthosite	GIT-IWG
BCR-1	Basalt	USGS
BCR-32	Moroccan phosphate rock	BCR
BCR 100	Beech leaves	BCR
BCR141	Calcareous loam soil	BCR
BCR 142	Light sandy soil	BCR
BCR144		BCR
BCR 144R	Sewage sludge	BCR
BCR 146	Sewage sludge	BCR
BCR 176	City waste incineration ash	BCR
BCS-174/1	Basic slag	BAS
BCS-175/1	Liberian iron ore	BAS
BCS-175/2	Nimba iron ore	BAS
BCS-176/1	Manganese ore	BAS
BCS-176/2	Manganese ore	BAS
BCS-267	Silica brick	BAS
BCS-269	Firebrick	BAS
BCS-301	Lincolnshire iron ore	BAS
BCS-301/1	Lincolnshire iron ore	BAS
BCS-302	Northamptonshire iron ore	BAS
BCS-302/1	Northamptonshire iron ore	BAS
BCS-303	Iron ore sinter	BAS
BCS-308	Grecian chrome ore	BAS
BCS-309	Sillimanite	BAS
BCS-313/1	High purity silica	BAS

Reference Material name	Material type	Source of RM
BCS-314	Silica brick	BAS
BCS-319	Magnesite	BAS
BCS-348	Ball clay	BAS
BCS-353	Sulphate-resisting Portland cement	BAS
BCS-354	White Portland cement	BAS
BCS-369	Magnesite-chrome	BAS
BCS-370	Magnesite-chrome	BAS
BCS-372/1	Ordinary Portland cement	BAS
BCS-375	Soda feldspar	BAS
BCS-376	Potash feldspar	BAS
BCS-381	Basic slag	BAS
BCS-382/1	Basic slag	BAS
BCS-388	Zircon	BAS
BCS-389	High purity magnesite	BAS
BCS-392	Fluorspar	BAS
BCS-393	Limestone	BAS
BCS-394	Calcined bauxite	BAS
BCS-395	Bauxite	BAS
BCS-396	Low silica magnesite-chrome	BAS
BCSS-1	Coastal marine sediment	NRCC
BE-N	Basalt	GIT-IWG
BHVO-1	Basalt	USGS
BIL-1	Baikal bottom silt	IGI
BIR-1	Basalt	USGS
BSK-1	Kesterson bottom sediment	
BX-N	Bauxite	ANRT
CAL-S	Calcite	
CRMPR 9472	Sewage sludge	

Reference Material name	Material type	Source of RM
DNC-1	Diabase	USGS
DR-N	Diorite	ANRT
DT-N	Kyanite	ANRT
DTS-1	Dunite	USGS
ECRM676-1	Iron ore sinter	BAS
ECRM681-1	Iron ore	
ECRM683-1	Iron ore sinter	BAS
ECRM776/1	Firebrick	BAS
ECRM877/1	Furnace dust	BAS
ECRM879/1	Basic slag	BAS
FER-1	Iron formation	CCRMP
FER-2	Iron formation	CCRMP
FER-3	Iron formation	CCRMP
FER-4	Iron formation	
FGD-1	Gypsum	DOMTAR
FGD-2	Gypsum	DOMTAR
FK-N	Potash feldspar	USGS
G-2	Granite	USGS
GA	Granite	CRPG
GBW07303	Stream sediment	
GBW07307	Stream sediment	
GBW07401	Soil	
GSD-1a	Stream sediment	
GSD-2	Stream sediment	IGGE
GSD-3	Stream sediment	IGGE
GSD-4	Pond sediment	IGGE
GSD-5	Pond sediment	IGGE
GSD-6	Stream sediment	IGGE
GSD-7	Stream sediment	IGGE
GSD-8	Stream sediment	IGGE
GSD-9	Stream sediment	IGGE
GSD-10	Stream sediment	IGGE
GSD-11	Stream sediment	IGGE
GSD-12	Stream sediment	IGGE
GSD-13	Limestone	IGGE
GSD-14	Granite gneiss	IGGE
GS-N	Granite	IGGE

Reference Material name	Material type	Source of RM
GSP-1	Granodiorite	USGS
GSR-1	Granite	IGGE
GSR-2	Andesite	IGGE
GSR-3	Basalt	IGGE
GSR-4	Sandstone	IGGE
GSR-5	Shale	IGGE
GSR-6	Carbonate	IGGE
GSR-7	Ijolite syenite	IGGE
GSR-8	Trachyte andesite	IGGE
GSR-9	Granodiorite	IGGE
GSR-10	Gabbro	IGGE
GSR-11	Rhyolite	IGGE
GSR-12	Dolomite	IGGE
GSR-13	Limestone	IGGE
GSR-14	Granite gneiss	IGGE
GSR-15	Amphibolite	IGGE
GSR-16		IGGE
GSR-17		IGGE
GSR-18		IGGE
GSS-1	Dark brown soil	IGGE
GSS-2	Chestnut soil	IGGE
GSS-3	Yellow brown soil	IGGE
GSS-4	Limy soil	IGGE
GSS-5	Yellow red soil	IGGE
GSS-6	Yellow red soil	IGGE
GSS-7	Laterite soil	IGGE
GSS-8	Loess	IGGE
GSS-9	Lake deposit	IGGE
GTS-1	Gold tailings	IGGE
GXR-1	Jasperoid	USGS-AEG
GXR-2	Soil	USGS-AEG
GXR-3	Hot spring deposit	USGS-AEG
GXR-4	Porphyry copper mill heads	USGS-AEG
GXR-6	Soil	USGS-AEG

Reference Material name	Material type	Source of RM
GYP-A	Gypsum rock	DOMTAR
GYP-B	Gypsum rock	DOMTAR
GYP-C	Gypsum rock	DOMTAR
GYP-D	Gypsum rock	DOMTAR
IF-G	Iron formation	GIT-IWG
JA-1	Andesite	GSJ
JA-2	Andesite	GSJ
JA-3	Andesite	GSJ
JB-1a	Alkali basalt	GSJ
JB-3	High-alumina basalt	GSJ
JCh-1	Chert	GSJ
JDo-1	Dolomite	GSJ
JF-1	Feldspar	GSJ
JF-2	Feldspar	GSJ
JG-1a	Granodiorite	GSJ
JG-2	Granite	GSJ
JG-3	Granodiorite	GSJ
JGb-1	Gabbro	GSJ
JLk-1	Lake sediment	GSJ
JLs-1	Limestone	GSJ
JP-1	Peridotite	GSJ
JR-2	Rhyolite	GSJ
JSd-1	Stream sediment	GSJ
JSd-2	Stream sediment	GSJ
JSd-3	Stream sediment	GSJ
JSl-1	Slate	GSJ
JSl-2	Slate	GSJ
LKSD-1	Lake sediment	
LKSD-2	Lake sediment	
LKSD-3	Lake sediment	
LKSD-4	Lake sediment	
MA-N	Granite	GIT-IWG
MAG-1	Marine mud	USGS
MESS-2	Estuarine sediment	NRCC
MESS-3	Marine sediment	NRCC
MB1		
MB2		

Reference Material name	Material type	Source of RM
MB3		
Mica-Mg	Phlogopite	CRPG
MRG-1	Gabbro	CCRMP
NBS-1a	Argillaceous limestone	NBS
NBS-25c	Manganese ore	NBS
NBS-27d	Mesabi ore	NBS
NBS-28a	Norrie iron ore	NBS
NBS-69a	Bauxite	NBS
NBS-76	Burnt refactory	NBS
NBS-77	Burnt refactory	NBS
NBS-78	Burnt refactory	NBS
NBS-88a	Dolomitic limestone	NBS
NbS-89	Lead Barium glass	NBS
NBS-92	Low Boron glass	NBS
NBS-93	Borosilicate glass	NBS
NBS-99a	Soda feldspar	NBS
NBS-103a	Chrome refractory	NBS
NBS-113	Zinc ore	NBS
NBS-120b	Phosphate rock	NBS
NBS-137	Tin ore	NBS
NBS-138	Tin ore	NBS
NBS-165	Glass sand	NBS
NBS-183	Lithium ores	NBS
NBS-1633a	Fly-ash	NBS
NBS-1633b	Coal fly ash	
NBS-165	Glass sand	NBS
NCS DC 74301		
NCS DC 80301	Polluted farmland soil	
NIM-D	Dunite	MINTEK
NIM-G	Granite	MINTEK
NIM-L	Lujavrite	MINTEK
NIM-N	Norite	MINTEK
NIM-P	Pyroxenite	MINTEK
NIM-S	Syenite	MINTEK

Reference Material name	Material type	Source of RM
NIST-690	Iron ore Canada	NIST
NIST-692	Iron ore Labrador	NIST
NIST-694	Western phosphate rock	NIST
NIST 2709	San Joaquin soil	NIST
NIST2710	Montana I soil	NIST
NIST2711	Montana II soil	NIST
Nod-A-1	Manganese nodule	USGS
Nod-P-1	Manganese nodule	USGS
PACS-1	Harbour marine sediment	NRCC
PACS-2	Marine sediment	NRCC
PCC-1	Peridotite	USGS
PM-S	Microgabbro	GIT-IWG
QL-O	Quartz latite	USGS
QC376W		
QC377W		
QC379W		
QC426W		
QC427W		
QC428W		
QC7821W		
QC7823W		
QCP450W		
RGM-1	Rhyolite	USGS
S13		
S13-32mm		
S15		
S15-32mm		
S24		
S24-32mm		
S26		
S26-32mm		
S3B		
S3B-32mm		
SARM-7	Pt ore	
SARM-32	Phosphate rock	MINTEK
SARM-46	Stream sediment	MINTEK

Reference Material name	Material type	Source of RM
SARM-51	Stream sediment	MINTEK
SCo-1	Shale	USGS
SDC-1	Mica schist	USGS
SDO-1	Shale	USGS
SG-3	Alkaline apatite granite	
SGR-1	Shale	USGS
SIEM-01	Granite	
SIEM-02	Cordierite gneiss	
SIEM-03	Peridotite	
SIEM-04	Nosean phonolite	
SIEM-05	Greywacke	
SIEM-06	Gabbro	
SIEM-07	Tonolite	
SIEM-08	Melilite basalt	
SIEM-09	Siltstone	
SIEM-10	Copper slate	
SL-1	Lake sediment	
SNS-2	Nephaline syenite	
SO-1	Regosolic soil	USGS
SO-2	Podzolic soil	USGS
SO-3	Calcareous soil	USGS
SO-4	Black chernozemic soil	USGS
ST-2	Trap	IGI
STSD-1	Stream sediment	
STSD-2	Stream sediment	
STSD-3	Stream sediment	
STSD-54	Stream sediment	
SY-2	Syenite	CCRMP
SY-4	Syenite	CCRMP
TDB-1	Diabase	
TIG-1	Gypsum	DOMTAR
TRACE-000	ProTrace Synthetic Standard	BGS
TRACE-001	ProTrace Synthetic Standard	BGS
TRACE-002	ProTrace Synthetic Standard	BGS

Reference Material name	Material type	Source of RM
TRACE-003	ProTrace Synthetic Standard	BGS
TRACE-004	ProTrace Synthetic Standard	BGS
TRACE-005	ProTrace Synthetic Standard	BGS
TRACE-006	ProTrace Synthetic Standard	BGS
TRACE-007	ProTrace Synthetic Standard	BGS
TRACE-008	ProTrace Synthetic Standard	BGS
TRACE-009	ProTrace Synthetic Standard	BGS
TRACE-010	ProTrace Synthetic Standard	BGS
TRACE-011	ProTrace Synthetic Standard	BGS
TRACE-012	ProTrace Synthetic Standard	BGS
TRACE-013	ProTrace Synthetic Standard	BGS
TRACE-014	ProTrace Synthetic Standard	BGS
TRMAC-001	ProTrace Synthetic Standard	BGS
TRMAC-002	ProTrace Synthetic Standard	BGS
TRMAC-003	ProTrace Synthetic Standard	BGS
TRMAC-004	ProTrace Synthetic Standard	BGS
TRMAC-005	ProTrace Synthetic Standard	BGS
TRMAC-006	ProTrace Synthetic Standard	BGS
UB-N	Serpentine	ANRT
W-2	Diabase	USGS
WGB-1	Gabbro rock	
WMG-1	Gabbro	
WPR-1	Peridotite	
WS-E	Dolerite	GIT-IWG
WT-H	City water treatment sludge	
WT-L	City water treatment sludge	
WT-M	City water treatment sludge	
X0201	Cement	Dillinger
X0202	Cement	Dillinger
X0202	Cement	Dillinger
X0203	Cement	Dillinger
X0204	Cement	Dillinger
X0205	Cement	Dillinger
X0206	Cement	Dillinger
X0207	Cement	Dillinger
X0208	Cement	Dillinger
ZEOLITE 1	Natural Slovak zeolite	
ZUK-1	Coal ash	IGI
ZW-C	Zinnwaldite	GIT-IWG

APPENDIX 3 – MCERTS
Certified Soil Reference Materials

MCERTS Certified Soil Reference Materials

CRM 1: CMI 7004. Loam with elevated analyte levels
CRM 2: CMI 7002. Light sandy agricultural soil with elevated levels of As and Cr
CRM 3: GSS-6. Red silty/sandy soil sample. A composite sample collected from the subtropical low hill region in Yangchun, Guagdong.
CRM 4: NIST 2710. Highly contaminated pasture land from Montana, USA, which periodically floods and deposits high levels of Cu, Mn and Zn

Certified Soil Reference Material	Element of interest and concentration (mg kg^{-1})														
	Cd	Sb	Ba	V	Cr	Co	Cu	Ni	Zn	As	Se	Mo	Tl	Pb	Hg
CMI 7004	1.52	-	(568)	126	82.2	20.0	183	33.3	227	49.6				93.4	0.223
CMI 7002	0.3	-	(987)	54.9	179	12.6	29.3	42	69	32.4	-	-	-	58.9	0.09
GSS-6 (GBW07406 or NCS DC 73324)	0.13	60	118	130	75	7.6	390	53	97	220	1.34	18	2.4	314	0.072
NIST 2710	21.8	38.4	707	76.6	(39)	(10)	2950	14.3	6952	626	-	(19)	(1.3)	5532	32.6

APPENDIX 4 – Reference Materials Issuing Organisations

Reference Material Issuing Organisations

Abbreviation	Issuing Organisation
ANRT	Association National de la Recherche Technique, France
BAS	Bureau of Analysed Standards Ltd, UK
BCR	Community Bureau of Reference, Brussels, Belgium
BGS	British Geological Survey. Formerly IGS, Institute of Geological Sciences, UK
CCRMP	Canadian Certified Reference Materials Project, Canada
CRPG	Centre de Recherches Petrographiques et Geochimiques, France
DILLINGER	AG Der Dillinger Huttenwerke, Germany
DOMTAR	Domtar Inc., Canada
GIT	Groupe International de Travail
IWG	International Working Group
GIT-IWG	Preferred designation of GIT and AWG
GSJ	Geological Survey of Japan
IGGE	Institute of Geophysical and Geochemical Exploration, Peoples Republic of China
IGI	Institute of Geochemistry, Irkutsk, Russia
MINTEK	Council for Mineral Technology. Formerly NIM, National Institute for Metallurgy, South Africa
NBS	National Bureau of Standards, USA
NIST	National Institute of Standards and Technology, USA. (formerly NBS)
NRCC	National Research Council of Canada
USGS	United States Geological Survey
USGS-AEG	Samples prepared and distributed by the USGS on behalf of the Association of Exploration Geochemists, USA

APPENDIX 5 – DEFRA Soil Guideline values

DEFRA Soil Guideline Values

The following tables show the soil guideline values as published by DEFRA for specified land usages).

Land Usage	Soil Guideline Value (mg kg^{-1} dry weight soil)					
	As	Cr	Pb	Ni	Se	Inorganic Hg
Residential with plant uptake	20	130	450	50	35	8
Allotments						
Residential without plant uptake	20	200	450	75	260	15
Commercial/industrial	500	5000	750	5000	8000	480

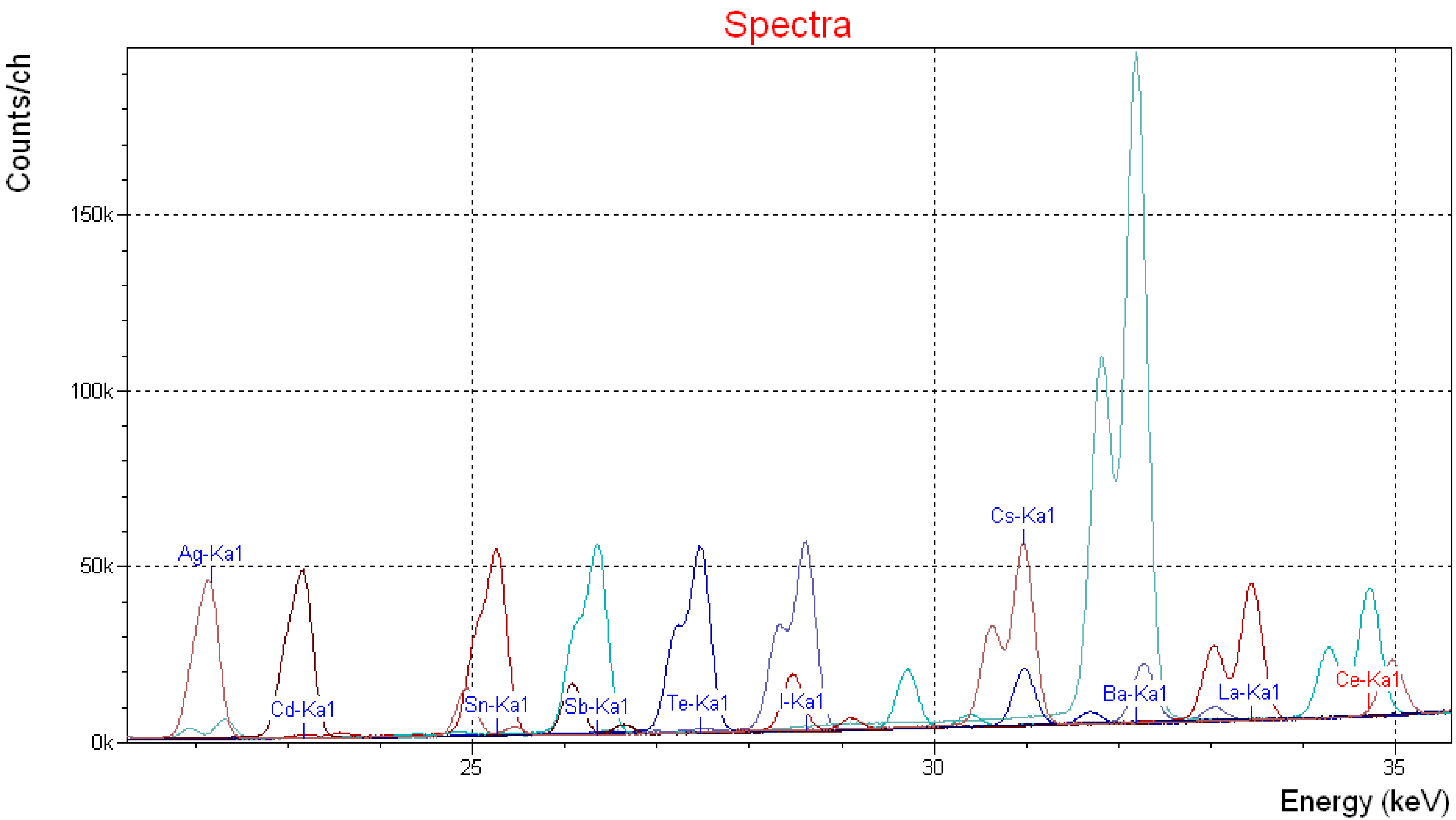
The soil guideline values for Cadmium are pH dependent as shown in the following table:

Land Usage	Soil Guideline Value (mg kg^{-1} dry weight soil)		
	pH 6	pH 7	pH 8
Residential with plant uptake	1	2	8
Allotments			
Residential without plant uptake	30		
Commercial/industrial	1400		

APPENDIX 6 – Deconvolution

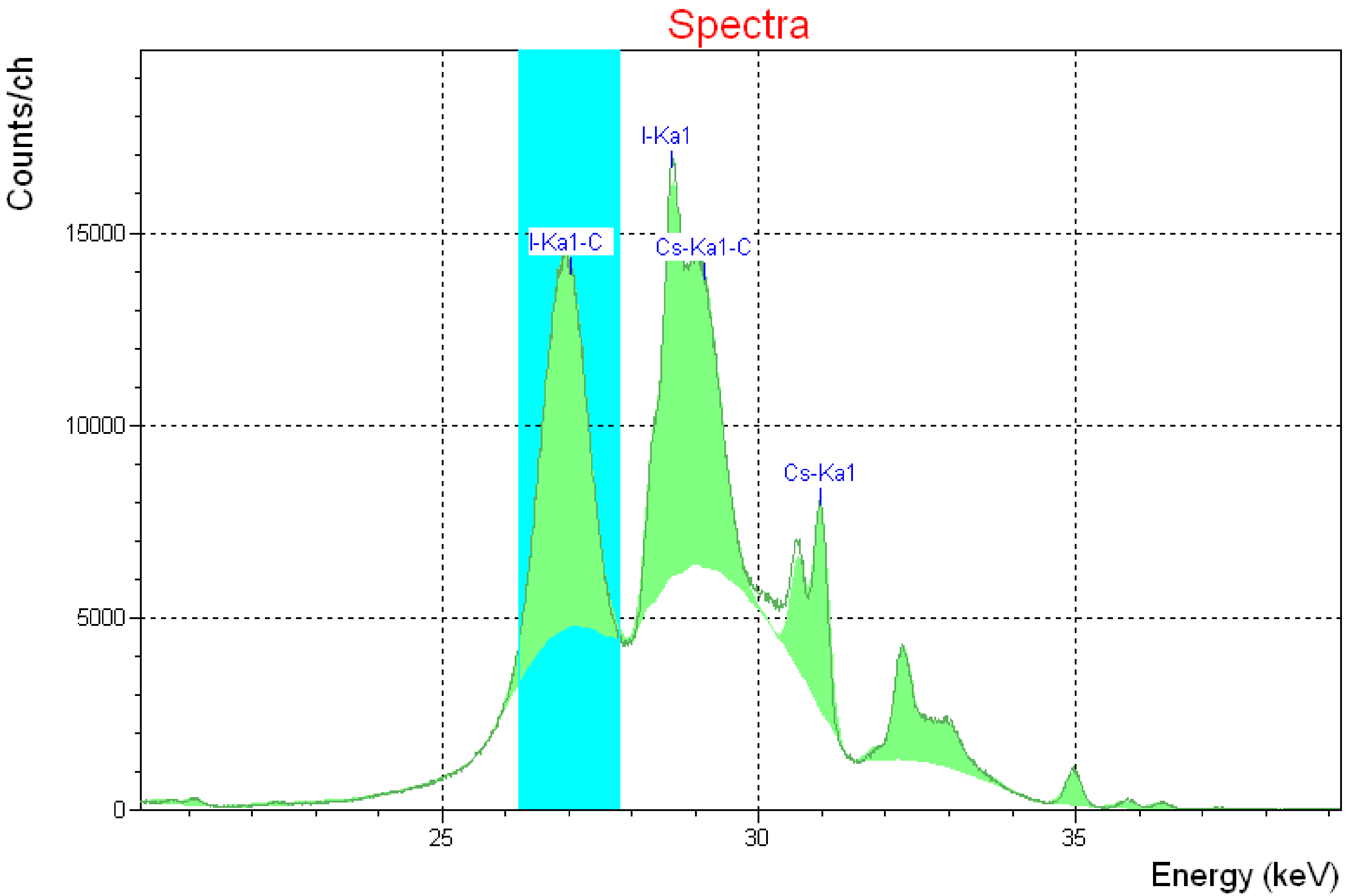
Deconvoluted spectrum for Ag to Ce elements

Synthetic ProTrace standards containing approximately 1000pm Ag, Cd, Sn, Sb, Te, I Cs, La and Ce in an iron-rich alumino-silicate matrix,. Barium concentration is 4000ppm.



Deconvoluted Spectrum of the CsI Fluorescence Target

The I Kα Compton scatter from the CsI target was used to matrix correct the Ag-Ce application. This picture shows the CsI target spectrum of a synthetic ProTrace standard containing 4000ppm Ba and the selected analytical Region of Interest (ROI).



APPENDIX 7 – Limits of Detection

ED-(P)XRFS

Lower Limits of Detection P Ag-Ce Cal LLD

Standard	Ag cps/mA	Cd cps/mA	Sn cps/mA	Sb cps/mA	Te cps/mA	I cps/mA	Cs cps/mA	Ba cps/mA	La cps/mA	Ce cps/mA
TRACE-000	14.342	17.788	30.995	38.454	37.216	52.106	83.426	148.128	120.777	158.355
TRACE-001		181.041								
TRACE-002				287.164						316.504
TRACE-003					231.624					
TRACE-004			226.625						288.354	
TRACE-005								984.067		
TRACE-006						268.117				
TRACE-007	163.194						299.772			
Peak (mA)	6	6	6	6	6	6	6	6	6	6
Bkgd (mA)	6	6	6	6	6	6	6	6	6	6

Analyte	**Ag**	**Cd**	**Sn**	**Sb**	**Te**	**I**	**Cs**	**Ba**	**La**	**Ce**
STD ID	TRACE-007	TRACE-001	TRACE-004	TRACE-002	TRACE-003	TRACE-006	TRACE-007	TRACE-005	TRACE-004	TRACE-002
STD Conc (ppm)	499	505	500	602	501	503	500	2002	499	499
Peak (cps) obtained from ROI	979.1640	1086.2460	1359.7500	1722.9840	1389.7440	1608.7020	1798.6320	5904.4020	1730.1240	1899.0240
Bkgd (cps) obtained from ROI	86.0520	106.7280	185.9700	230.7240	223.2960	312.6360	500.5560	888.7680	724.6620	950.1300
Bkgd live time (s)	840	840	840	840	840	840	840	840	840	840
Sensitivity (cps/ppm)	1.8	1.9	2.3	2.5	2.3	2.6	2.6	2.5	2.0	1.9
LLD (ppm) - 3s	**0.54**	**0.55**	**0.60**	**0.63**	**0.66**	**0.71**	**0.9**	**1.2**	**1.4**	**1.7**
For information										
E5 by deconvolution (software)	0.47	0.55	0.51	0.50	0.47	0.60	0.81	1.06	1.16	1.35

APPENDIX 8 – Calibration Range and Linearity

Element	Compound Ag - [ppm]	Compound Cd - [ppm]	Compound In - [ppm]	Compound Sn - [ppm]	Compound Sb - [ppm]	Compound Te - [ppm]	Compound I - [ppm]	Compound Cs - [ppm]	Compound Ba - [ppm]	Compound La - [ppm]	Compound Ce - [ppm]
Status											
K	0.0154	0.0111	0.0006	0.0161	0.0530	0.0024	0.0143	0.0255	0.5621	0.7738	0.1074
RMS	0.5497	0.3932	0.1414	0.5707	1.9089	0.0843	0.5066	0.9066	28.1627	2.3823	3.9430
Correlation	0.9990	0.9995	0.9908	0.9995	0.9986	0.9995	0.9971	0.9991	0.9986	0.9951	0.9986
Relative error	4.34E-04	3.11E-04	2.26E-06	4.52E-04	1.47E-03	6.74E-05	4.04E-04	7.20E-04	0.0116	1.3181	2.93E-03
Concentration range	0 - 40.4	0 - 54.7	0.033 - 5.1	0 - 72	0 - 171	0 - 13	0 - 19.4	0.17 - 107	0 - 2240	0 - 82.7	3.58 - 402
No. of standards	32	35	25	31	37	25	20	30	31	33	28
No. of coefficients	1	1	2	1	1	1	1	2	2	2	2
D	0	0	0.036	0.15	0	0	0	-1	-4.9512	-2.199	-2.667
E	7481.6	7510.7	8392.7	5557.4	5213.1	4331.1	4675.4	4986.2	5382.9	6166.8	7025.2
F	0	0	0	0	0	0	0	0	0	0	0
Error weighting type	Absolute	Absolute	Square root	Absolute	Absolute	Absolute	Absolute	Absolute	Absolute	Square root	Absolute
Error weighting constant			5							1.00E-05	
Ratio channel	Cs1	Cs1	Cs1	Cs1	Cs1	Cs1	Cs1	Cs1	Cs1	Cs1	Cs1
Matrix correction model	<None>	<None>	<None>	<None>	<None>	<None>	<None>	<None>	<None>	<None>	<None>
Elimination compound											
Line overlap1											
Channel	<None>	<None>	<None>	<None>	<None>	<None>	<None>	Ba	<None>	<None>	<None>
I or C								Intensity			
Factor								-4.83E-07			
Line overlap2											
Channel	<None>	<None>	<None>	<None>	<None>	<None>	<None>	<None>	<None>	<None>	<None>
I or C											
Factor											
Line overlap3											
Channel	<None>	<None>	<None>	<None>	<None>	<None>	<None>	<None>	<None>	<None>	<None>
I or C											
Factor											
Line overlap4											
Channel	<None>	<None>	<None>	<None>	<None>	<None>	<None>	<None>	<None>	<None>	<None>
I or C											
Factor											

Compound: Ag

Standard	Description	Date/Time	Included	Cchem. ppm	Ccalc. ppm	Diff(C) ppm
TRMAC-002	SiO2 100%	04/11/2003 18:10	Yes	0	0.00	0.00
TRACE-000	SiO2 75%: Al2O3 20%: Fe2O3 5%	04/11/2003 18:37	Yes	0	0.14	0.14
GSR-7	Ijolite Syenite, GBW - 07109	23/10/2003 18:35	No	0.033	0.00	-0.03
GSR-12	Dolomite, GBW - 07114	23/10/2003 20:46	Yes	0.044	0.00	-0.04
GSR-10	Gabbro, GBW - 07112	23/10/2003 19:54	Yes	0.052	0.37	0.32
GSS-2	Soil, GBW07402	23/10/2003 21:40	Yes	0.054	0.33	0.28
GSS-7	Soil, GBW07407	23/10/2003 23:23	Yes	0.057	0.06	0.00
GSS-8	Soil, GBW07408	23/10/2003 23:50	Yes	0.06	0.00	-0.06
GSR-9	Granodiorite, GBW - 07111	23/10/2003 19:29	No	0.066	1.19	1.12
GSS-4	Soil, GBW07404	23/10/2003 22:06	Yes	0.07	0.00	-0.07
GSR-2	Andesite, GBW07104	23/10/2003 18:08	Yes	0.071	0.60	0.53
GSR-11	Rhyolite, GBW - 07113	23/10/2003 20:20	Yes	0.076	0.00	-0.08
GSD-4	Stream Sediment, GBW07304	23/10/2003 15:31	Yes	0.084	0.01	-0.07
SO-1	Soil Sample	24/10/2003 03:26	Yes	0.1	0.00	-0.10
SO-4	Soil Sample	24/10/2003 09:08	Yes	0.12	0.00	-0.12
GSR-8	Trachyte Andesite, GBW - 07110	23/10/2003 19:01	Yes	0.17	0.13	-0.04
SO-2	Soil Sample	24/10/2003 03:52	Yes	0.19	0.19	0.00
GSS-6	Soil, GBW07406	23/10/2003 22:58	Yes	0.2	0.00	-0.20
GSD-10	Stream Sediment, GBW07310	23/10/2003 17:15	Yes	0.27	0.08	-0.19
GSS-1	Soil, GBW07401	23/10/2003 21:12	Yes	0.35	0.00	-0.35
GSD-5	Stream Sediment, GBW07305	23/10/2003 15:57	Yes	0.36	0.06	-0.30
GSD-6	Stream Sediment, GBW07306	23/10/2003 16:23	Yes	0.36	0.36	0.00
NIST2709	San Joaquin Soil	24/10/2003 01:13	Yes	0.41	0.53	0.12
GSD-7	Stream Sediment, GBW07307	23/10/2003 16:50	Yes	1.05	1.50	0.45
GSD-12	Stream Sediment, GBW07312	23/10/2003 17:42	Yes	1.15	0.19	-0.96
GXR-3	Deposit	24/10/2003 00:46	Yes	2.4	3.29	0.89
GSS-5	Soil, GBW07405	23/10/2003 22:32	Yes	4.4	3.83	-0.57
NIST2711	Montana Soil	24/10/2003 02:06	Yes	4.63	4.28	-0.35
WT-L	Sludge from city water treatment	24/10/2003 10:01	Yes	11.9	10.72	-1.19
GXR-2	Soil	24/10/2003 00:18	Yes	17	18.45	1.45
GXR-1	Jasperoid	23/10/2003 14:18	Yes	31	30.39	-0.61
NIST2710	Montana Soil	24/10/2003 01:40	Yes	35.3	34.30	-1.00
WT-H	Sludge from city water treatment	24/10/2003 09:35	Yes	38.4	39.53	1.13
WT-M	Sludge from city water treatment	24/10/2003 10:28	Yes	40.4	40.25	-0.15
SO-3	Soil Sample	24/10/2003 04:18	No		0.09	0.09
PACS-1	Marine Sediment	24/10/2003 02:33	No		1.88	1.88
SL-1	Lake Sediment	24/10/2003 02:59	No			

Compound: Cd

Standard	Description	Date/Time	Included	Cchem. ppm	Ccalc. ppm	Diff(C) ppm
TRMAC-002	SiO2 100%	04/11/2003 18:10	Yes	0	0.25	0.25
TRACE-000	SiO2 75%: Al2O3 20%: Fe2O3 5%	04/11/2003 18:37	Yes	0	0.23	0.23
GSR-2	Andesite, GBW07104	23/10/2003 18:08	Yes	0.061	0.00	-0.06
GSR-7	Ijolite Syenite, GBW - 07109	23/10/2003 18:35	No	0.066	0.00	-0.07
GSR-12	Dolomite, GBW - 07114	23/10/2003 20:46	Yes	0.07	0.22	0.15
GSS-2	Soil, GBW07402	23/10/2003 21:40	Yes	0.071	0.09	0.01
GSS-7	Soil, GBW07407	23/10/2003 23:23	Yes	0.08	0.00	-0.08
GSR-9	Granodiorite, GBW - 07111	23/10/2003 19:29	Yes	0.081	0.00	-0.08
GSR-10	Gabbro, GBW - 07112	23/10/2003 19:54	Yes	0.093	0.46	0.37
SO-3	Soil Sample	24/10/2003 04:18	Yes	0.12	0.19	0.07
GSS-6	Soil, GBW07406	23/10/2003 22:58	Yes	0.13	0.00	-0.13
GSS-8	Soil, GBW07408	23/10/2003 23:50	Yes	0.13	0.00	-0.13
SO-1	Soil Sample	24/10/2003 03:26	Yes	0.13	0.00	-0.13
SO-2	Soil Sample	24/10/2003 03:52	Yes	0.13	0.33	0.20
GSR-11	Rhyolite, GBW - 07113	23/10/2003 20:20	Yes	0.14	0.00	-0.14
GSD-4	Stream Sediment, GBW07304	23/10/2003 15:31	Yes	0.19	0.20	0.01
SL-1	Lake Sediment	24/10/2003 02:59	Yes	0.26	0.00	-0.26
SO-4	Soil Sample	24/10/2003 09:08	Yes	0.34	0.22	-0.12
GSS-4	Soil, GBW07404	23/10/2003 22:06	Yes	0.35	0.00	-0.35
NIST2709	San Joaquin Soil	24/10/2003 01:13	Yes	0.38	0.43	0.05
GSD-6	Stream Sediment, GBW07306	23/10/2003 16:23	Yes	0.43	0.00	-0.43
GSS-5	Soil, GBW07405	23/10/2003 22:32	Yes	0.45	0.15	-0.30
GSR-8	Trachyte Andesite, GBW - 07110	23/10/2003 19:01	Yes	0.61	0.36	-0.25
GSD-5	Stream Sediment, GBW07305	23/10/2003 15:57	Yes	0.82	0.72	-0.10
GSD-7	Stream Sediment, GBW07307	23/10/2003 16:50	Yes	1.05	1.03	-0.02
GSD-10	Stream Sediment, GBW07310	23/10/2003 17:15	Yes	1.12	1.40	0.28
GXR-3	Deposit	24/10/2003 00:46	No	1.8	0.13	-1.67
WT-L	Sludge from city water treatment	24/10/2003 10:01	Yes	1.97	1.97	0.00
PACS-1	Marine Sediment	24/10/2003 02:33	Yes	2.38	2.09	-0.29
GXR-1	Jasperoid	23/10/2003 14:18	Yes	3.3	2.31	-0.99
GSD-12	Stream Sediment, GBW07312	23/10/2003 17:42	Yes	4	3.66	-0.34
GXR-2	Soil	24/10/2003 00:18	Yes	4.1	3.42	-0.68
GSS-1	Soil, GBW07401	23/10/2003 21:12	Yes	4.3	4.36	0.06
WT-M	Sludge from city water treatment	24/10/2003 10:28	Yes	11.9	11.89	-0.01
NIST2710	Montana Soil	24/10/2003 01:40	Yes	21.8	20.34	-1.46
NIST2711	Montana Soil	24/10/2003 02:06	Yes	41.7	42.36	0.66
WT-H	Sludge from city water treatment	24/10/2003 09:35	Yes	54.7	54.84	0.14

Compound: In

Standard	Description	Date/Time	Included	Cchem. ppm	Ccalc. ppm	Diff(C) ppm
TRMAC-002	SiO2 100%	04/11/2003 18:10	No	0	0.50	0.50
TRACE-000	SiO2 75%: Al2O3 20%: Fe2O3 5%	04/11/2003 18:37	No	0	0.42	0.42
GSR-2	Andesite, GBW07104	23/10/2003 18:08	Yes	0.033	0.04	0.00
GSS-8	Soil, GBW07408	23/10/2003 23:50	Yes	0.044	0.19	0.14
GXR-3	Deposit	24/10/2003 00:46	No	0.058	0.76	0.70
GSR-12	Dolomite, GBW - 07114	23/10/2003 20:46	Yes	0.066	0.32	0.25
GSD-10	Stream Sediment, GBW07310	23/10/2003 17:15	Yes	0.067	0.31	0.25
GSR-9	Granodiorite, GBW - 07111	23/10/2003 19:29	Yes	0.08	0.04	-0.04
GSS-1	Soil, GBW07401	23/10/2003 21:12	Yes	0.08	0.21	0.13
GSD-7	Stream Sediment, GBW07307	23/10/2003 16:50	Yes	0.081	0.10	0.02
GSD-4	Stream Sediment, GBW07304	23/10/2003 15:31	Yes	0.085	0.11	0.02
GSS-2	Soil, GBW07402	23/10/2003 21:40	Yes	0.09	0.04	-0.05
GSR-11	Rhyolite, GBW - 07113	23/10/2003 20:20	Yes	0.091	0.04	-0.06
GSS-7	Soil, GBW07407	23/10/2003 23:23	Yes	0.1	0.04	-0.06
SO-1	Soil Sample	24/10/2003 03:26	Yes	0.1	0.04	-0.06
SO-3	Soil Sample	24/10/2003 04:18	Yes	0.1	0.21	0.11
SO-4	Soil Sample	24/10/2003 09:08	Yes	0.1	0.11	0.01
GSR-8	Trachyte Andesite, GBW - 07110	23/10/2003 19:01	Yes	0.11	0.04	-0.07
GSR-10	Gabbro, GBW - 07112	23/10/2003 19:54	Yes	0.12	0.35	0.23
GSS-4	Soil, GBW07404	23/10/2003 22:06	Yes	0.12	0.04	-0.08
GSD-5	Stream Sediment, GBW07305	23/10/2003 15:57	Yes	0.13	0.04	-0.09
GSD-6	Stream Sediment, GBW07306	23/10/2003 16:23	Yes	0.14	0.18	0.04
GSR-7	Ijolite Syenite, GBW - 07109	23/10/2003 18:35	Yes	0.15	0.04	-0.11
GXR-2	Soil	24/10/2003 00:18	Yes	0.252	0.35	0.10
GXR-1	Jasperoid	23/10/2003 14:18	No	0.77	1.38	0.61
GSS-6	Soil, GBW07406	23/10/2003 22:58	Yes	0.84	0.66	-0.18
GSD-12	Stream Sediment, GBW07312	23/10/2003 17:42	Yes	0.96	0.66	-0.30
NIST2711	Montana Soil	24/10/2003 02:06	Yes	1.1	0.90	-0.20
GSS-5	Soil, GBW07405	23/10/2003 22:32	No	4.1	4.64	0.54
NIST2710	Montana Soil	24/10/2003 01:40	Yes	5.1	5.13	0.03
SO-2	Soil Sample	24/10/2003 03:52	No		0.04	0.04
WT-H	Sludge from city water treatment	24/10/2003 09:35	No		0.04	0.04
WT-L	Sludge from city water treatment	24/10/2003 10:01	No		0.16	0.16
SL-1	Lake Sediment	24/10/2003 02:59	No		0.17	0.17
NIST2709	San Joaquin Soil	24/10/2003 01:13	No		0.22	0.22
WT-M	Sludge from city water treatment	24/10/2003 10:28	No		0.26	0.26
PACS-1	Marine Sediment	24/10/2003 02:33	No		4.17	4.17

Compound: Sn

Standard	Description	Date/Time	Included	Cchem. ppm	Ccalc. ppm	Diff(C) ppm
TRMAC-002	SiO2 100%	04/11/2003 18:10	Yes	0	0.64	0.64
TRACE-000	SiO2 75%: Al2O3 20%: Fe2O3 5%	04/11/2003 18:37	Yes	0	0.32	0.32
GSR-12	Dolomite, GBW - 07114	23/10/2003 20:46	Yes	0.53	0.69	0.16
GSR-2	Andesite, GBW07104	23/10/2003 18:08	Yes	0.79	0.58	-0.21
GSR-10	Gabbro, GBW - 07112	23/10/2003 19:54	Yes	0.89	1.03	0.14
SO-3	Soil Sample	24/10/2003 04:18	Yes	0.97	0.73	-0.24
GSD-10	Stream Sediment, GBW07310	23/10/2003 17:15	Yes	1.4	1.89	0.49
GSR-9	Granodiorite, GBW - 07111	23/10/2003 19:29	Yes	1.44	1.19	-0.25
GXR-2	Soil	24/10/2003 00:18	Yes	1.7	1.72	0.02
GXR-3	Deposit	24/10/2003 00:46	Yes	1.7	1.23	-0.47
SO-4	Soil Sample	24/10/2003 09:08	Yes	2.5	1.42	-1.08
SO-1	Soil Sample	24/10/2003 03:26	Yes	2.6	1.88	-0.72
SO-2	Soil Sample	24/10/2003 03:52	Yes	2.6	1.76	-0.84
GSD-6	Stream Sediment, GBW07306	23/10/2003 16:23	Yes	2.8	3.08	0.28
GSS-8	Soil, GBW07408	23/10/2003 23:50	Yes	2.8	2.38	-0.42
GSS-2	Soil, GBW07402	23/10/2003 21:40	Yes	3	2.03	-0.97
GSR-8	Trachyte Andesite, GBW - 07110	23/10/2003 19:01	Yes	3.12	2.47	-0.65
GSR-11	Rhyolite, GBW - 07113	23/10/2003 20:20	Yes	3.35	3.37	0.02
GSS-7	Soil, GBW07407	23/10/2003 23:23	Yes	3.6	3.48	-0.12
GSD-4	Stream Sediment, GBW07304	23/10/2003 15:31	Yes	4	3.72	-0.28
GSD-5	Stream Sediment, GBW07305	23/10/2003 15:57	Yes	4.6	3.68	-0.92
GSD-7	Stream Sediment, GBW07307	23/10/2003 16:50	Yes	5.4	4.79	-0.61
GSS-4	Soil, GBW07404	23/10/2003 22:06	Yes	5.7	5.21	-0.49
GSS-1	Soil, GBW07401	23/10/2003 21:12	Yes	6.1	6.63	0.53
GSR-7	Ijolite Syenite, GBW - 07109	23/10/2003 18:35	Yes	6.5	6.38	-0.13
WT-L	Sludge from city water treatment	24/10/2003 10:01	Yes	10.8	11.45	0.65
GSS-5	Soil, GBW07405	23/10/2003 22:32	Yes	18	18.48	0.48
WT-H	Sludge from city water treatment	24/10/2003 09:35	Yes	20.3	21.01	0.71
WT-M	Sludge from city water treatment	24/10/2003 10:28	No	20.3	21.83	1.53
PACS-1	Marine Sediment	24/10/2003 02:33	No	41.1	36.50	-4.60
GSD-12	Stream Sediment, GBW07312	23/10/2003 17:42	Yes	54	53.43	-0.57
GXR-1	Jasperoid	23/10/2003 14:18	Yes	54	54.97	0.97
GSS-6	Soil, GBW07406	23/10/2003 22:58	Yes	72	71.44	-0.56
NIST2709	San Joaquin Soil	24/10/2003 01:13	No		1.70	1.70
SL-1	Lake Sediment	24/10/2003 02:59	No		2.94	2.94
NIST2711	Montana Soil	24/10/2003 02:06	No		4.41	4.41
NIST2710	Montana Soil	24/10/2003 01:40	No		7.52	7.52

Compound: Sb

Standard	Description	Date/Time	Included	Cchem. ppm	Ccalc. ppm	Diff(C) ppm
TRMAC-002	SiO2 100%	04/11/2003 18:10	Yes	0	0.00	0.00
TRACE-000	SiO2 75%: Al2O3 20%: Fe2O3 5%	04/11/2003 18:37	Yes	0	0.00	0.00
GSR-10	Gabbro, GBW - 07112	23/10/2003 19:54	Yes	0.042	0.00	-0.04
GSR-12	Dolomite, GBW - 07114	23/10/2003 20:46	Yes	0.044	0.22	0.17
GSR-9	Granodiorite, GBW - 07111	23/10/2003 19:29	Yes	0.061	0.40	0.34
SO-2	Soil Sample	24/10/2003 03:52	Yes	0.106	0.00	-0.11
GSR-2	Andesite, GBW07104	23/10/2003 18:08	Yes	0.12	0.16	0.04
GSR-7	Ijolite Syenite, GBW - 07109	23/10/2003 18:35	Yes	0.15	0.00	-0.15
SO-1	Soil Sample	24/10/2003 03:26	Yes	0.297	0.27	-0.02
SO-3	Soil Sample	24/10/2003 04:18	Yes	0.323	0.00	-0.32
GSR-11	Rhyolite, GBW - 07113	23/10/2003 20:20	Yes	0.38	0.04	-0.34
GSS-7	Soil, GBW07407	23/10/2003 23:23	Yes	0.42	0.00	-0.42
SO-4	Soil Sample	24/10/2003 09:08	Yes	0.71	0.13	-0.58
GSS-1	Soil, GBW07401	23/10/2003 21:12	Yes	0.87	0.85	-0.02
GSS-8	Soil, GBW07408	23/10/2003 23:50	Yes	1	0.94	-0.06
GSD-6	Stream Sediment, GBW07306	23/10/2003 16:23	Yes	1.25	1.40	0.15
GSS-2	Soil, GBW07402	23/10/2003 21:40	Yes	1.3	0.90	-0.40
SL-1	Lake Sediment	24/10/2003 02:59	Yes	1.31	1.28	-0.03
GSR-8	Trachyte Andesite, GBW - 07110	23/10/2003 19:01	Yes	1.34	1.35	0.01
GSD-4	Stream Sediment, GBW07304	23/10/2003 15:31	Yes	1.84	2.29	0.45
GSD-7	Stream Sediment, GBW07307	23/10/2003 16:50	Yes	2.6	2.21	-0.39
GSD-5	Stream Sediment, GBW07305	23/10/2003 15:57	Yes	3.9	3.54	-0.36
GSD-10	Stream Sediment, GBW07310	23/10/2003 17:15	Yes	6.3	5.59	-0.71
GSS-4	Soil, GBW07404	23/10/2003 22:06	Yes	6.3	6.61	0.31
NIST2709	San Joaquin Soil	24/10/2003 01:13	Yes	7.9	7.50	-0.40
WT-M	Sludge from city water treatment	24/10/2003 10:28	Yes	12.7	10.51	-2.19
WT-L	Sludge from city water treatment	24/10/2003 10:01	Yes	17.8	17.03	-0.77
NIST2711	Montana Soil	24/10/2003 02:06	Yes	19.4	17.42	-1.98
GSD-12	Stream Sediment, GBW07312	23/10/2003 17:42	Yes	24	23.73	-0.27
GSS-5	Soil, GBW07405	23/10/2003 22:32	Yes	35	36.60	1.60
GXR-3	Deposit	24/10/2003 00:46	Yes	38	43.09	5.09
NIST2710	Montana Soil	24/10/2003 01:40	Yes	38.4	34.18	-4.22
WT-H	Sludge from city water treatment	24/10/2003 09:35	Yes	43	39.01	-3.99
GXR-2	Soil	24/10/2003 00:18	Yes	49	41.89	-7.11
GSS-6	Soil, GBW07406	23/10/2003 22:58	Yes	60	61.37	1.37
GXR-1	Jasperoid	23/10/2003 14:18	Yes	122	121.57	-0.43
PACS-1	Marine Sediment	24/10/2003 02:33	Yes	171	173.15	2.15

Compound: Te

Standard	Description	Date/Time	Included	Cchem. ppm	Ccalc. ppm	Diff(C) ppm
TRACE-000	SiO2 75%: Al2O3 20%: Fe2O3 5%	04/11/2003 18:37	Yes	0	0.02	0.02
TRMAC-002	SiO2 100%	04/11/2003 18:10	Yes	0	0.00	0.00
GSR-8	Trachyte Andesite, GBW - 07110	23/10/2003 19:01	Yes	0.007	0.20	0.20
GSR-11	Rhyolite, GBW - 07113	23/10/2003 20:20	Yes	0.009	0.00	-0.01
GXR-3	Deposit	24/10/2003 00:46	Yes	0.009	0.00	-0.01
GSR-10	Gabbro, GBW - 07112	23/10/2003 19:54	Yes	0.01	0.00	-0.01
GSR-9	Granodiorite, GBW - 07111	23/10/2003 19:29	Yes	0.011	0.00	-0.01
GSR-12	Dolomite, GBW - 07114	23/10/2003 20:46	Yes	0.012	0.00	-0.01
GSR-7	Ijolite Syenite, GBW - 07109	23/10/2003 18:35	Yes	0.012	0.07	0.06
GSR-2	Andesite, GBW07104	23/10/2003 18:08	Yes	0.017	0.00	-0.02
SO-4	Soil Sample	24/10/2003 09:08	Yes	0.03	0.00	-0.03
GSS-2	Soil, GBW07402	23/10/2003 21:40	Yes	0.035	0.00	-0.04
SO-1	Soil Sample	24/10/2003 03:26	Yes	0.04	0.00	-0.04
GSS-8	Soil, GBW07408	23/10/2003 23:50	Yes	0.046	0.00	-0.05
GSS-1	Soil, GBW07401	23/10/2003 21:12	Yes	0.047	0.00	-0.05
GSS-7	Soil, GBW07407	23/10/2003 23:23	Yes	0.047	0.21	0.17
GSD-7	Stream Sediment, GBW07307	23/10/2003 16:50	Yes	0.06	0.00	-0.06
GSD-4	Stream Sediment, GBW07304	23/10/2003 15:31	Yes	0.07	0.00	-0.07
GSD-10	Stream Sediment, GBW07310	23/10/2003 17:15	Yes	0.08	0.20	0.12
GSD-5	Stream Sediment, GBW07305	23/10/2003 15:57	Yes	0.12	0.00	-0.12
GSD-6	Stream Sediment, GBW07306	23/10/2003 16:23	Yes	0.13	0.04	-0.09
GSS-4	Soil, GBW07404	23/10/2003 22:06	Yes	0.15	0.31	0.16
GSD-12	Stream Sediment, GBW07312	23/10/2003 17:42	Yes	0.29	0.42	0.13
GSS-6	Soil, GBW07406	23/10/2003 22:58	Yes	0.4	0.34	-0.06
GXR-2	Soil	24/10/2003 00:18	No	0.69	0.12	-0.57
GSS-5	Soil, GBW07405	23/10/2003 22:32	No	4	4.69	0.69
GXR-1	Jasperoid	23/10/2003 14:18	Yes	13	12.99	-0.01
NIST2711	Montana Soil	24/10/2003 02:06	No		0.95	0.95
NIST2710	Montana Soil	24/10/2003 01:40	No		2.72	2.72
NIST2709	San Joaquin Soil	24/10/2003 01:13	No			
PACS-1	Marine Sediment	24/10/2003 02:33	No			
SL-1	Lake Sediment	24/10/2003 02:59	No			
SO-2	Soil Sample	24/10/2003 03:52	No			
SO-3	Soil Sample	24/10/2003 04:18	No			
WT-H	Sludge from city water treatment	24/10/2003 09:35	No			
WT-L	Sludge from city water treatment	24/10/2003 10:01	No			
WT-M	Sludge from city water treatment	24/10/2003 10:28	No			

Compound: I

Standard	Description	Date/Time	Included	Cchem. ppm	Ccalc. ppm	Diff(C) ppm
TRMAC-002	SiO2 100%	04/11/2003 18:10	Yes	0	0.00	0.00
TRACE-000	SiO2 75%: Al2O3 20%: Fe2O3 5%	04/11/2003 18:37	Yes	0	0.00	0.00
GSR-8	Trachyte Andesite, GBW - 07110	23/10/2003 19:01	Yes	0.067	0.45	0.39
GSR-9	Granodiorite, GBW - 07111	23/10/2003 19:29	No	0.078	2.55	2.47
GSR-10	Gabbro, GBW - 07112	23/10/2003 19:54	Yes	0.08	0.00	-0.08
GSR-11	Rhyolite, GBW - 07113	23/10/2003 20:20	Yes	0.093	0.09	0.00
GSR-7	Ijolite Syenite, GBW - 07109	23/10/2003 18:35	Yes	0.14	0.00	-0.14
GSR-12	Dolomite, GBW - 07114	23/10/2003 20:46	Yes	0.23	0.06	-0.17
SO-3	Soil Sample	24/10/2003 04:18	Yes	1	0.13	-0.87
GSD-10	Stream Sediment, GBW07310	23/10/2003 17:15	Yes	1.6	0.88	-0.72
GSS-8	Soil, GBW07408	23/10/2003 23:50	Yes	1.6	1.61	0.01
GSD-12	Stream Sediment, GBW07312	23/10/2003 17:42	Yes	1.8	1.08	-0.72
GSS-2	Soil, GBW07402	23/10/2003 21:40	Yes	1.8	1.84	0.04
GSS-1	Soil, GBW07401	23/10/2003 21:12	Yes	1.9	2.49	0.59
NIST2711	Montana Soil	24/10/2003 02:06	Yes	3	2.27	-0.73
SO-4	Soil Sample	24/10/2003 09:08	Yes	3	1.84	-1.16
GSS-5	Soil, GBW07405	23/10/2003 22:32	Yes	3.8	3.53	-0.27
NIST2709	San Joaquin Soil	24/10/2003 01:13	Yes	5	4.75	-0.25
GSS-4	Soil, GBW07404	23/10/2003 22:06	Yes	9.4	8.80	-0.60
SO-1	Soil Sample	24/10/2003 03:26	No	12	4.26	-7.74
SO-2	Soil Sample	24/10/2003 03:52	No	15	9.75	-5.25
GSS-7	Soil, GBW07407	23/10/2003 23:23	Yes	19	19.24	0.24
GSS-6	Soil, GBW07406	23/10/2003 22:58	Yes	19.4	19.73	0.33
SL-1	Lake Sediment	24/10/2003 02:59	No	28	8.21	-19.79
GSD-6	Stream Sediment, GBW07306	23/10/2003 16:23	No		0.02	0.02
GSD-7	Stream Sediment, GBW07307	23/10/2003 16:50	No		0.51	0.51
GSR-2	Andesite, GBW07104	23/10/2003 18:08	No		1.17	1.17
GXR-1	Jasperoid	23/10/2003 14:18	No		1.74	1.74
GSD-4	Stream Sediment, GBW07304	23/10/2003 15:31	No		1.75	1.75
GSD-5	Stream Sediment, GBW07305	23/10/2003 15:57	No		1.87	1.87
WT-L	Sludge from city water treatment	24/10/2003 10:01	No		1.90	1.90
NIST2710	Montana Soil	24/10/2003 01:40	No		3.15	3.15
GXR-2	Soil	24/10/2003 00:18	No		6.26	6.26
WT-M	Sludge from city water treatment	24/10/2003 10:28	No		9.06	9.06
WT-H	Sludge from city water treatment	24/10/2003 09:35	Yes		9.46	9.46
GXR-3	Deposit	24/10/2003 00:46	No		10.03	10.03
PACS-1	Marine Sediment	24/10/2003 02:33	No		64.82	64.82

Compound: Cs

Standard	Description	Date/Time	Included	Cchem. ppm	Ccalc. ppm	Diff(C) ppm
TRMAC-002	SiO2 100%	04/11/2003 18:10	No	0	3.21	3.21
TRACE-000	SiO2 75%: Al2O3 20%: Fe2O3 5%	04/11/2003 18:37	No	0	2.31	2.31
GSR-12	Dolomite, GBW - 07114	23/10/2003 20:46	No	0.071	1.52	1.45
GSR-10	Gabbro, GBW - 07112	23/10/2003 19:54	Yes	0.17	0.53	0.36
SO-2	Soil Sample	24/10/2003 03:52	Yes	0.41	1.18	0.77
GSR-9	Granodiorite, GBW - 07111	23/10/2003 19:29	Yes	0.97	2.97	2.00
SO-3	Soil Sample	24/10/2003 04:18	Yes	1.12	1.13	0.01
WT-H	Sludge from city water treatment	24/10/2003 09:35	Yes	2	2.19	0.19
WT-M	Sludge from city water treatment	24/10/2003 10:28	Yes	2	2.42	0.42
GSR-7	Ijolite Syenite, GBW - 07109	23/10/2003 18:35	Yes	2.05	1.33	-0.72
GSD-10	Stream Sediment, GBW07310	23/10/2003 17:15	No	2.3	2.59	0.29
GSR-2	Andesite, GBW07104	23/10/2003 18:08	Yes	2.3	2.45	0.15
GSS-7	Soil, GBW07407	23/10/2003 23:23	Yes	2.7	1.67	-1.03
SO-4	Soil Sample	24/10/2003 09:08	Yes	2.88	3.54	0.66
GXR-1	Jasperoid	23/10/2003 14:18	Yes	3	1.88	-1.12
WT-L	Sludge from city water treatment	24/10/2003 10:01	Yes	3	2.60	-0.40
GSR-11	Rhyolite, GBW - 07113	23/10/2003 20:20	Yes	3.34	2.52	-0.82
GSS-2	Soil, GBW07402	23/10/2003 21:40	Yes	4.9	3.96	-0.94
SO-1	Soil Sample	24/10/2003 03:26	Yes	5.07	4.01	-1.06
GXR-2	Soil	24/10/2003 00:18	No	5.2	5.46	0.26
NIST2709	San Joaquin Soil	24/10/2003 01:13	Yes	5.3	6.00	0.70
GSD-7	Stream Sediment, GBW07307	23/10/2003 16:50	Yes	5.9	4.83	-1.07
NIST2711	Montana Soil	24/10/2003 02:06	Yes	6.1	5.79	-0.31
SL-1	Lake Sediment	24/10/2003 02:59	Yes	7.01	6.93	-0.08
GSR-8	Trachyte Andesite, GBW - 07110	23/10/2003 19:01	Yes	7.16	6.94	-0.22
GSS-8	Soil, GBW07408	23/10/2003 23:50	Yes	7.5	7.53	0.03
GSD-12	Stream Sediment, GBW07312	23/10/2003 17:42	Yes	7.9	6.96	-0.94
GSS-1	Soil, GBW07401	23/10/2003 21:12	Yes	9	8.65	-0.35
GSD-6	Stream Sediment, GBW07306	23/10/2003 16:23	Yes	9.1	8.28	-0.82
GSD-5	Stream Sediment, GBW07305	23/10/2003 15:57	Yes	9.4	8.29	-1.11
GSD-4	Stream Sediment, GBW07304	23/10/2003 15:31	Yes	10	9.07	-0.93
GSS-6	Soil, GBW07406	23/10/2003 22:58	Yes	10.8	9.03	-1.77
GSS-5	Soil, GBW07405	23/10/2003 22:32	Yes	15	13.47	-1.53
GSS-4	Soil, GBW07404	23/10/2003 22:06	Yes	21.4	21.10	-0.30
NIST2710	Montana Soil	24/10/2003 01:40	Yes	107	107.89	0.89
GXR-3	Deposit	24/10/2003 00:46	No	175	213.27	38.27
PACS-1	Marine Sediment	24/10/2003 02:33	No		1.44	1.44

Compound: Ba

Standard	Description	Date/Time	Included	Cchem. ppm	Ccalc. ppm	Diff(C) ppm
TRMAC-002	SiO2 100%	04/11/2003 18:10	Yes	0	-0.20	-0.20
TRACE-000	SiO2 75%: Al2O3 20%: Fe2O3 5%	04/11/2003 18:37	Yes	0	0.60	0.60
GSD-10	Stream Sediment, GBW07310	23/10/2003 17:15	Yes	42	32.81	-9.19
GSR-12	Dolomite, GBW - 07114	23/10/2003 20:46	Yes	44.3	42.46	-1.84
GSR-10	Gabbro, GBW - 07112	23/10/2003 19:54	Yes	86.2	97.21	11.01
GSS-6	Soil, GBW07406	23/10/2003 22:58	Yes	118	107.32	-10.68
GSS-7	Soil, GBW07407	23/10/2003 23:23	Yes	180	198.73	18.73
GSD-12	Stream Sediment, GBW07312	23/10/2003 17:42	Yes	206	198.62	-7.38
GSS-4	Soil, GBW07404	23/10/2003 22:06	Yes	213	212.66	-0.34
GSR-7	Ijolite Syenite, GBW - 07109	23/10/2003 18:35	Yes	251	251.52	0.52
SO-3	Soil Sample	24/10/2003 04:18	Yes	290	292.60	2.60
GSS-5	Soil, GBW07405	23/10/2003 22:32	Yes	296	310.96	14.96
GSD-6	Stream Sediment, GBW07306	23/10/2003 16:23	Yes	330	323.52	-6.48
GSD-5	Stream Sediment, GBW07305	23/10/2003 15:57	Yes	440	440.58	0.58
GSD-4	Stream Sediment, GBW07304	23/10/2003 15:31	Yes	470	455.67	-14.33
GSS-8	Soil, GBW07408	23/10/2003 23:50	Yes	480	492.49	12.49
GSR-11	Rhyolite, GBW - 07113	23/10/2003 20:20	Yes	506	483.05	-22.95
GSS-1	Soil, GBW07401	23/10/2003 21:12	Yes	590	582.72	-7.28
SL-1	Lake Sediment	24/10/2003 02:59	Yes	639	659.21	20.21
SO-4	Soil Sample	24/10/2003 09:08	Yes	700	706.01	6.01
NIST2710	Montana Soil	24/10/2003 01:40	Yes	707	724.06	17.06
GSD-7	Stream Sediment, GBW07307	23/10/2003 16:50	Yes	720	730.63	10.63
NIST2711	Montana Soil	24/10/2003 02:06	Yes	726	717.14	-8.86
GXR-1	Jasperoid	23/10/2003 14:18	No	750	901.52	151.52
WT-H	Sludge from city water treatment	24/10/2003 09:35	No	772	677.23	-94.77
WT-L	Sludge from city water treatment	24/10/2003 10:01	No	781	698.59	-82.41
WT-M	Sludge from city water treatment	24/10/2003 10:28	No	787	658.76	-128.24
SO-1	Soil Sample	24/10/2003 03:26	Yes	870	915.30	45.30
GSS-2	Soil, GBW07402	23/10/2003 21:40	Yes	930	870.26	-59.74
NIST2709	San Joaquin Soil	24/10/2003 01:13	Yes	968	919.39	-48.61
SO-2	Soil Sample	24/10/2003 03:52	Yes	1000	1023.60	23.64
GSR-2	Andesite, GBW07104	23/10/2003 18:08	Yes	1020	1023.50	3.45
GSR-8	Trachyte Andesite, GBW - 07110	23/10/2003 19:01	Yes	1053	1053.10	0.07
GSR-9	Granodiorite, GBW - 07111	23/10/2003 19:29	Yes	1899	1979.90	80.91
GXR-2	Soil	24/10/2003 00:18	Yes	2240	2169.10	-70.92
GXR-3	Deposit	24/10/2003 00:46	No	5000	6691.70	1691.70
PACS-1	Marine Sediment	24/10/2003 02:33	No		695.45	695.45

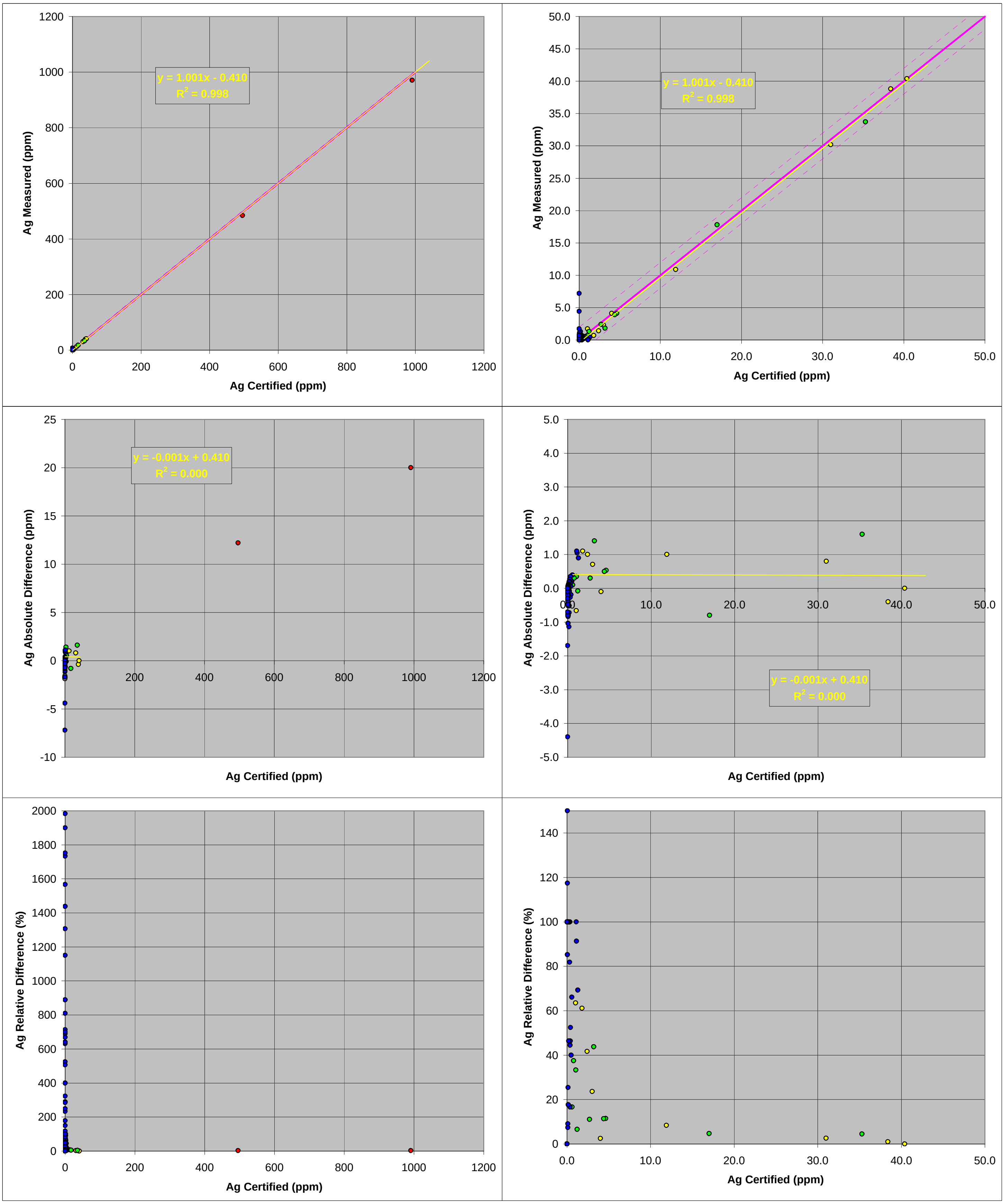
Compound: La

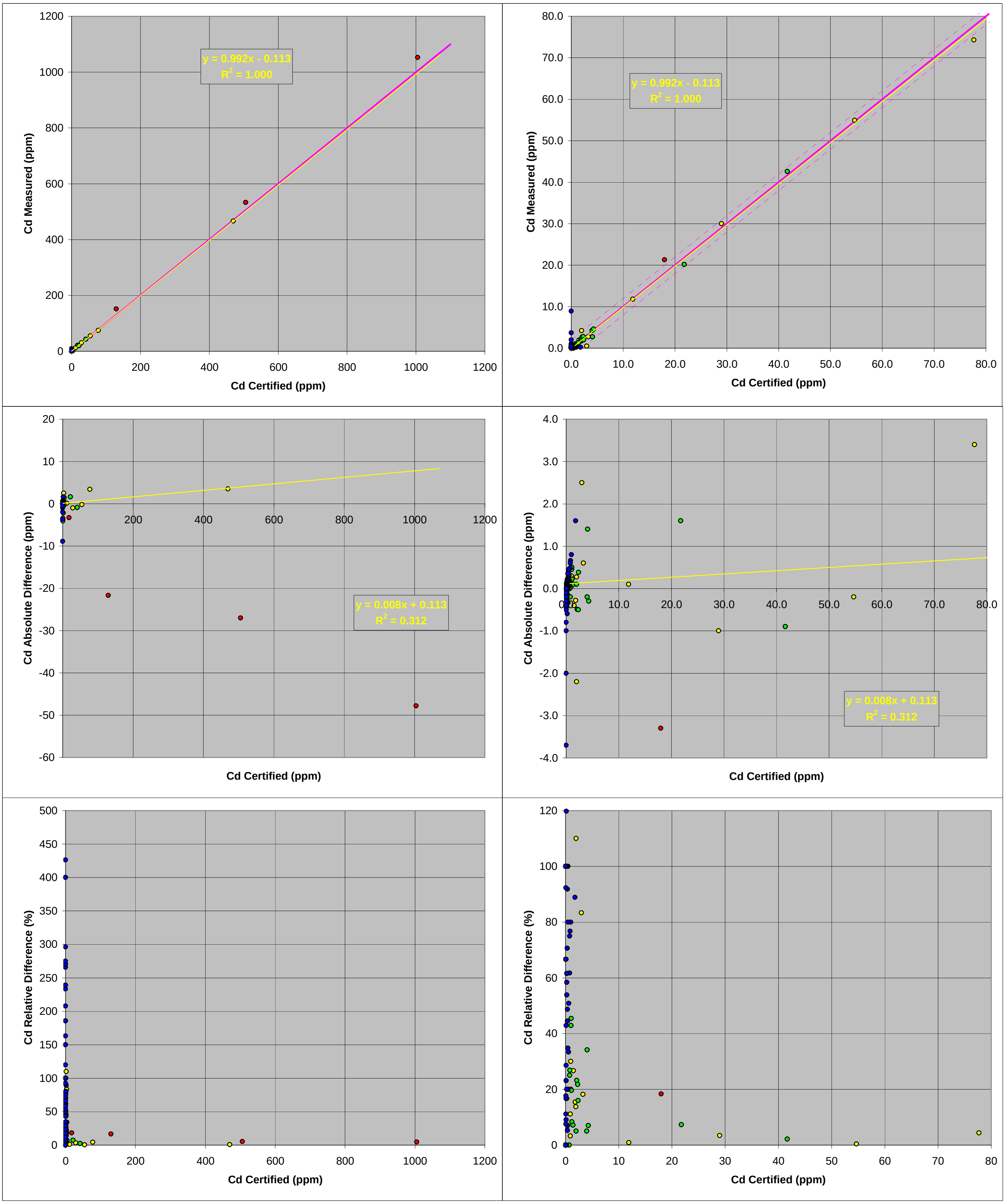
Standard	Description	Date/Time	Included	Cchem. ppm	Ccalc. ppm	Diff(C) ppm
TRMAC-002	SiO2 100%	04/11/2003 18:10	Yes	0	-0.61	-0.61
TRACE-000	SiO2 75%: Al2O3 20%: Fe2O3 5%	04/11/2003 18:37	Yes	0	0.66	0.66
GSR-12	Dolomite, GBW - 07114	23/10/2003 20:46	Yes	1.34	0.94	-0.40
GSR-10	Gabbro, GBW - 07112	23/10/2003 19:54	Yes	1.71	4.41	2.70
GXR-1	Jasperoid	23/10/2003 14:18	Yes	7.5	8.47	0.97
GXR-3	Deposit	24/10/2003 00:46	Yes	8.8	5.67	-3.13
GSD-10	Stream Sediment, GBW07310	23/10/2003 17:15	Yes	13	11.51	-1.49
WT-M	Sludge from city water treatment	24/10/2003 10:28	Yes	13	8.29	-4.71
WT-H	Sludge from city water treatment	24/10/2003 09:35	Yes	15	9.99	-5.01
WT-L	Sludge from city water treatment	24/10/2003 10:01	Yes	15	11.34	-3.66
SO-3	Soil Sample	24/10/2003 04:18	Yes	16.9	17.11	0.21
GSR-2	Andesite, GBW07104	23/10/2003 18:08	Yes	21.8	20.74	-1.06
NIST2709	San Joaquin Soil	24/10/2003 01:13	Yes	23	20.89	-2.11
GXR-2	Soil	24/10/2003 00:18	Yes	25.6	21.02	-4.58
SO-4	Soil Sample	24/10/2003 09:08	Yes	28.2	26.06	-2.14
GSS-6	Soil, GBW07406	23/10/2003 22:58	Yes	30	30.67	0.67
GSD-12	Stream Sediment, GBW07312	23/10/2003 17:42	Yes	32.7	32.03	-0.67
GSS-1	Soil, GBW07401	23/10/2003 21:12	Yes	34	33.88	-0.12
NIST2710	Montana Soil	24/10/2003 01:40	Yes	34	32.06	-1.94
GSS-5	Soil, GBW07405	23/10/2003 22:32	Yes	36	38.49	2.49
GSS-8	Soil, GBW07408	23/10/2003 23:50	Yes	36	36.53	0.53
GSD-6	Stream Sediment, GBW07306	23/10/2003 16:23	Yes	39	38.73	-0.27
GSD-4	Stream Sediment, GBW07304	23/10/2003 15:31	Yes	40	40.38	0.38
NIST2711	Montana Soil	24/10/2003 02:06	Yes	40	38.41	-1.59
GSD-7	Stream Sediment, GBW07307	23/10/2003 16:50	Yes	45	43.72	-1.28
GSD-5	Stream Sediment, GBW07305	23/10/2003 15:57	Yes	46	42.97	-3.03
GSS-7	Soil, GBW07407	23/10/2003 23:23	No	46	52.02	6.02
SO-2	Soil Sample	24/10/2003 03:52	Yes	46.5	46.49	-0.01
SL-1	Lake Sediment	24/10/2003 02:59	Yes	52.6	51.11	-1.49
GSS-4	Soil, GBW07404	23/10/2003 22:06	Yes	53	54.75	1.75
SO-1	Soil Sample	24/10/2003 03:26	Yes	54	57.94	3.94
GSR-9	Granodiorite, GBW - 07111	23/10/2003 19:29	Yes	60.5	63.00	2.50
GSR-8	Trachyte Andesite, GBW - 07110	23/10/2003 19:01	Yes	62.5	63.18	0.68
GSR-11	Rhyolite, GBW - 07113	23/10/2003 20:20	Yes	82.7	85.96	3.26
GSR-7	Ijolite Syenite, GBW - 07109	23/10/2003 18:35	No	149	168.49	19.49
GSS-2	Soil, GBW07402	23/10/2003 21:40	No	164	159.66	-4.34
PACS-1	Marine Sediment	24/10/2003 02:33	No		16.87	16.87

Compound: Ce

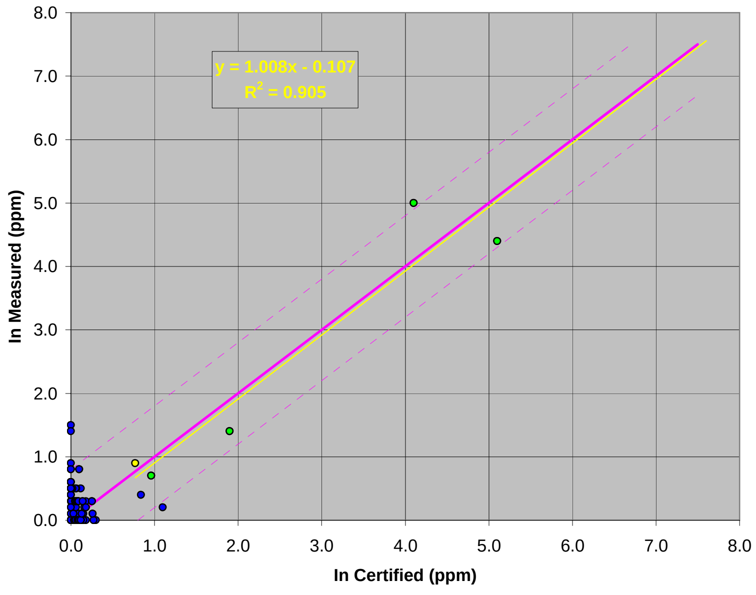
Standard	Description	Date/Time	Included	Cchem. ppm	Ccalc. ppm	Diff(C) ppm
TRMAC-002	SiO2 100%	04/11/2003 18:10	No	0	5.98	5.98
TRACE-000	SiO2 75%: Al2O3 20%: Fe2O3 5%	04/11/2003 18:37	No	0	3.64	3.64
GSR-12	Dolomite, GBW - 07114	23/10/2003 20:46	Yes	3.58	4.18	0.60
GSR-10	Gabbro, GBW - 07112	23/10/2003 19:54	Yes	4.18	3.91	-0.27
GXR-1	Jasperoid	23/10/2003 14:18	Yes	17	16.77	-0.23
GXR-3	Deposit	24/10/2003 00:46	Yes	18	14.77	-3.23
WT-H	Sludge from city water treatment	24/10/2003 09:35	No	30	23.55	-6.45
WT-L	Sludge from city water treatment	24/10/2003 10:01	No	30	22.86	-7.14
WT-M	Sludge from city water treatment	24/10/2003 10:28	No	30	21.21	-8.79
SO-3	Soil Sample	24/10/2003 04:18	Yes	34	33.76	-0.24
GSD-10	Stream Sediment, GBW07310	23/10/2003 17:15	Yes	38	36.07	-1.93
GSR-2	Andesite, GBW07104	23/10/2003 18:08	Yes	40	39.31	-0.69
NIST2709	San Joaquin Soil	24/10/2003 01:13	Yes	42	39.36	-2.64
GXR-2	Soil	24/10/2003 00:18	Yes	51.4	43.10	-8.30
SO-4	Soil Sample	24/10/2003 09:08	Yes	54	47.99	-6.01
NIST2710	Montana Soil	24/10/2003 01:40	Yes	57	53.80	-3.20
GSD-12	Stream Sediment, GBW07312	23/10/2003 17:42	Yes	61	58.69	-2.31
GSS-6	Soil, GBW07406	23/10/2003 22:58	Yes	66	66.70	0.70
GSS-8	Soil, GBW07408	23/10/2003 23:50	Yes	66	66.90	0.90
GSD-6	Stream Sediment, GBW07306	23/10/2003 16:23	Yes	68	71.75	3.75
NIST2711	Montana Soil	24/10/2003 02:06	Yes	69	69.02	0.02
GSS-1	Soil, GBW07401	23/10/2003 21:12	Yes	70	67.85	-2.15
GSD-4	Stream Sediment, GBW07304	23/10/2003 15:31	Yes	78	82.36	4.36
GSD-7	Stream Sediment, GBW07307	23/10/2003 16:50	Yes	78	79.88	1.88
GSD-5	Stream Sediment, GBW07305	23/10/2003 15:57	Yes	89	90.46	1.46
GSS-5	Soil, GBW07405	23/10/2003 22:32	Yes	91	97.40	6.40
GSS-7	Soil, GBW07407	23/10/2003 23:23	No	98	115.81	17.81
SO-1	Soil Sample	24/10/2003 03:26	Yes	102	110.92	8.92
GSR-9	Granodiorite, GBW - 07111	23/10/2003 19:29	Yes	112	119.06	7.06
SO-2	Soil Sample	24/10/2003 03:52	Yes	112	112.62	0.62
GSR-8	Trachyte Andesite, GBW - 07110	23/10/2003 19:01	Yes	117	116.36	-0.64
SL-1	Lake Sediment	24/10/2003 02:59	No	117	98.36	-18.64
GSS-4	Soil, GBW07404	23/10/2003 22:06	Yes	136	139.15	3.15
GSR-11	Rhyolite, GBW - 07113	23/10/2003 20:20	Yes	163	160.42	-2.58
GSR-7	Ijolite Syenite, GBW - 07109	23/10/2003 18:35	No	242	269.42	27.42
GSS-2	Soil, GBW07402	23/10/2003 21:40	Yes	402	396.63	-5.37
PACS-1	Marine Sediment	24/10/2003 02:33	No		32.52	32.52

APPENDIX 9 – Accuracy and Bias (UKAS)

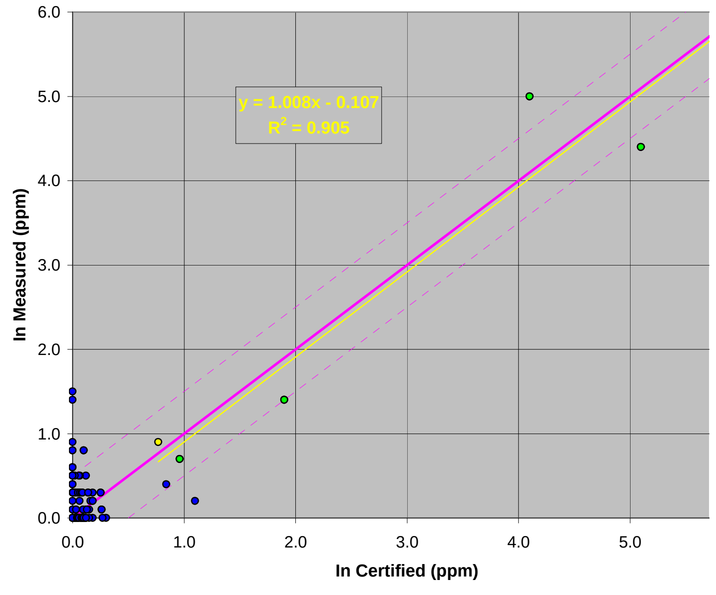

y = 1.001x - 0.410
R² = 0.998
Ag Measured (ppm)
Ag Certified (ppm)
y = 1.001x - 0.410
R² = 0.998
Ag Measured (ppm)
Ag Certified (ppm)
y = -0.001x + 0.410
R² = 0.000
Ag Absolute Difference (ppm)
Ag Certified (ppm)
y = -0.001x + 0.410
R² = 0.000
Ag Absolute Difference (ppm)
Ag Certified (ppm)
Ag Relative Difference (%)
Ag Certified (ppm)
Ag Relative Difference (%)
Ag Certified (ppm)



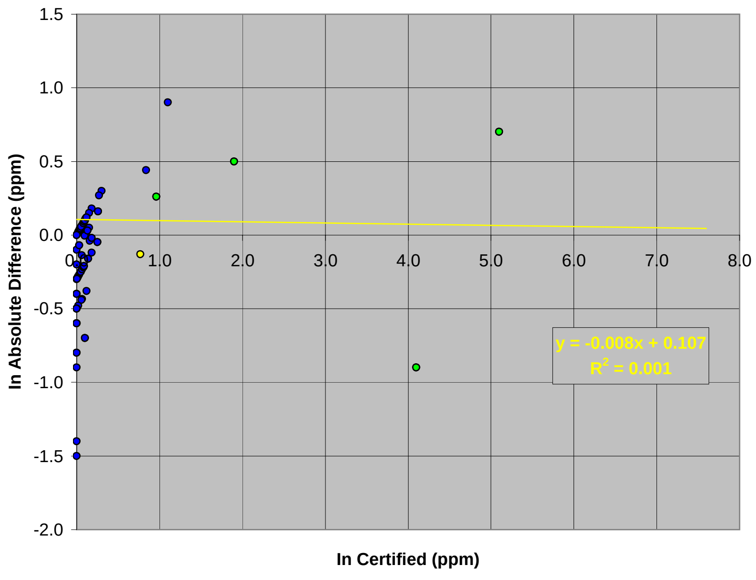
Cd Measured (ppm)
Cd Certified (ppm)
y = 0.992x - 0.113
R^2 = 1.000
Cd Absolute Difference (ppm)
y = 0.008x + 0.113
R^2 = 0.312
Cd Relative Difference (%)



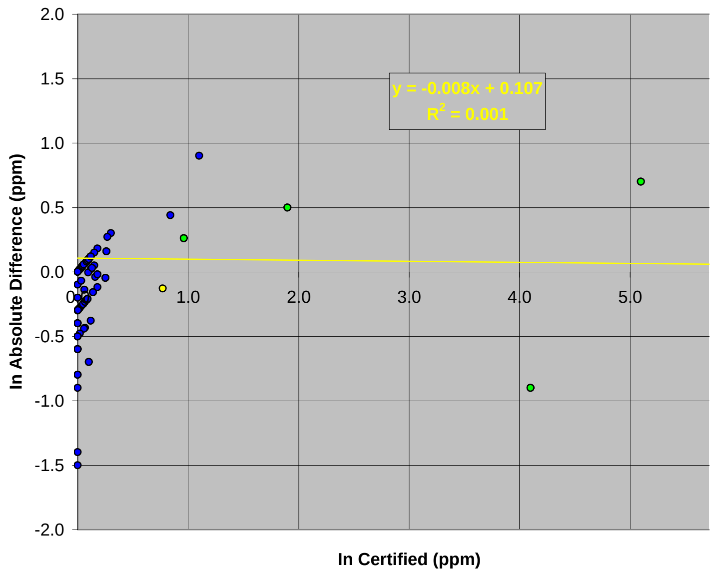
y = 1.008x - 0.107
R^2 = 0.905
In Measured (ppm)
In Certified (ppm)



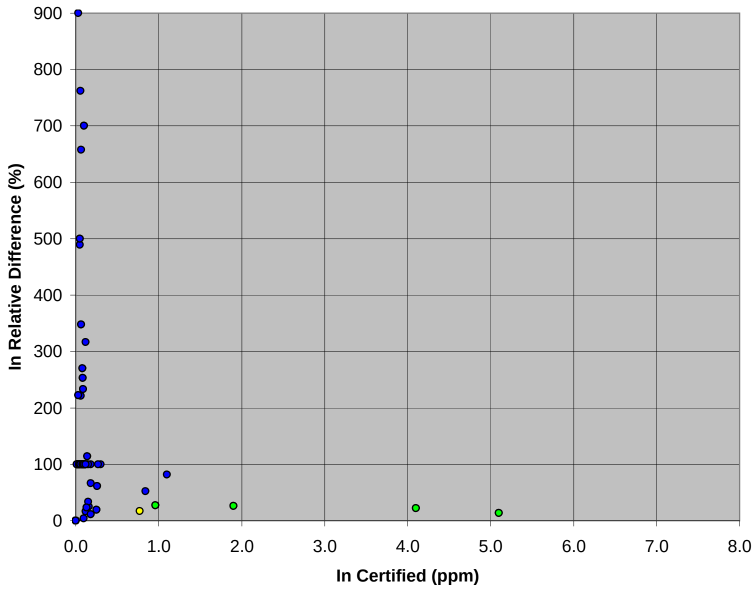
y = 1.008x - 0.107
R^2 = 0.905
In Measured (ppm)
In Certified (ppm)



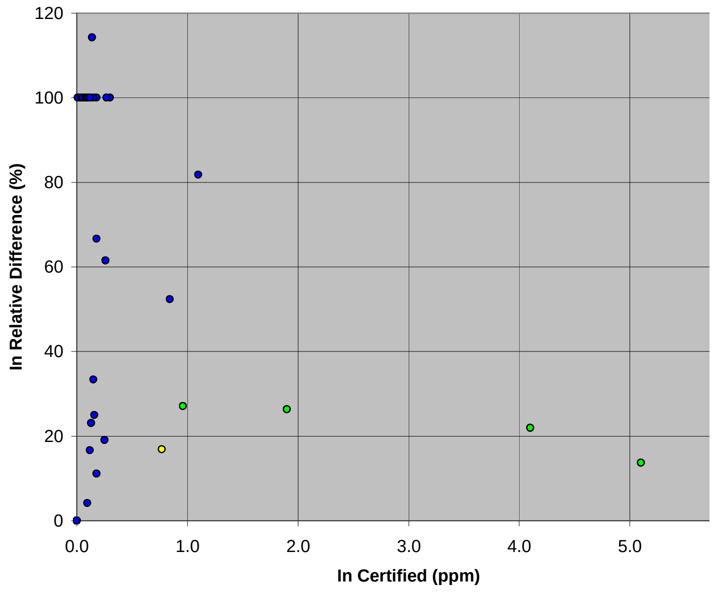
y = -0.008x + 0.107
R^2 = 0.001
In Absolute Difference (ppm)
In Certified (ppm)



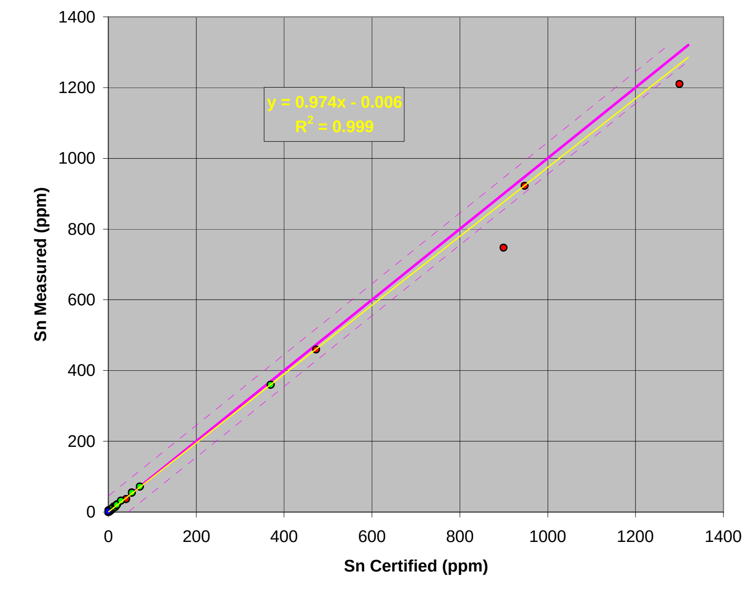
y = -0.008x + 0.107
R^2 = 0.001
In Absolute Difference (ppm)
In Certified (ppm)

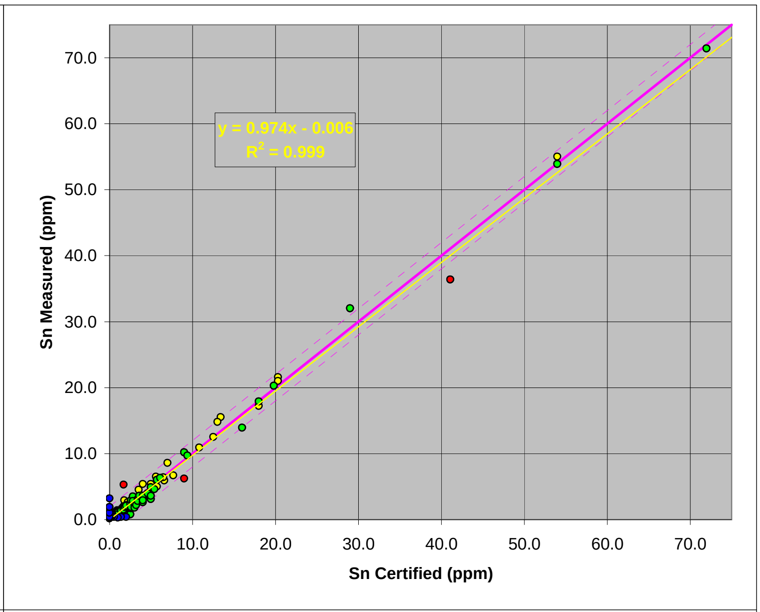


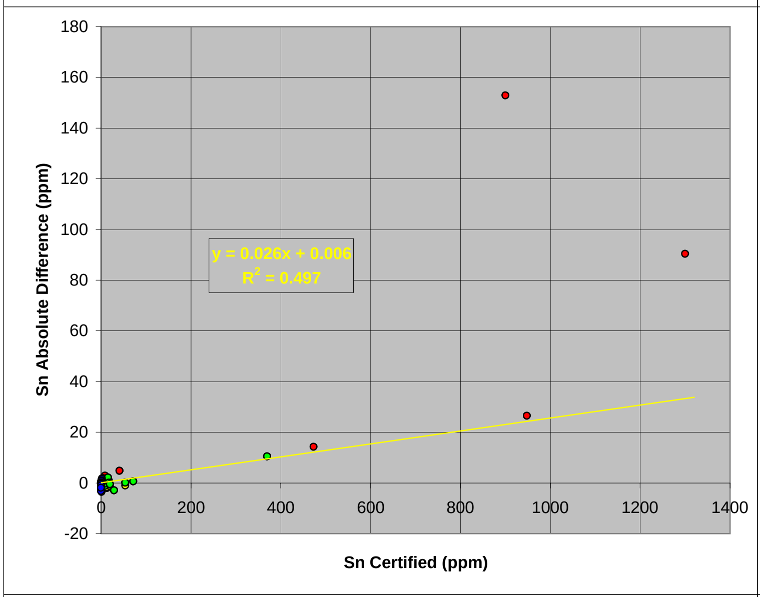
In Relative Difference (%)
In Certified (ppm)

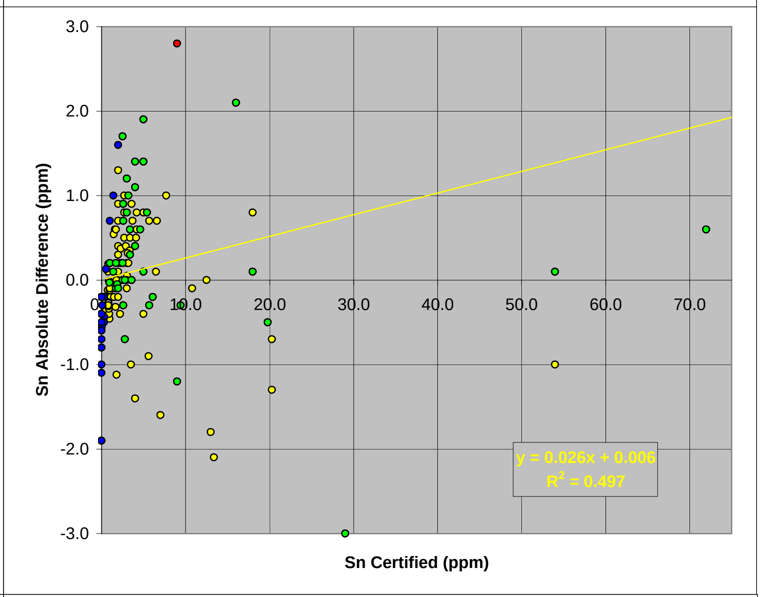


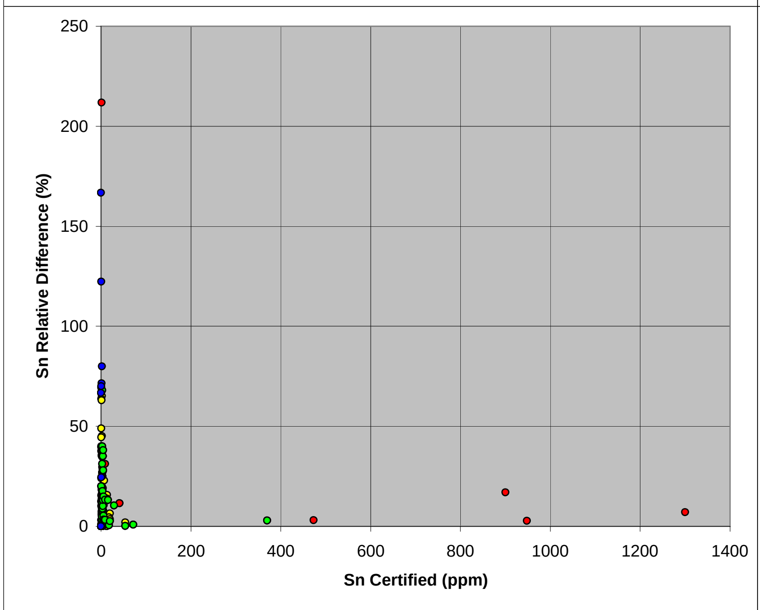
In Relative Difference (%)
In Certified (ppm)

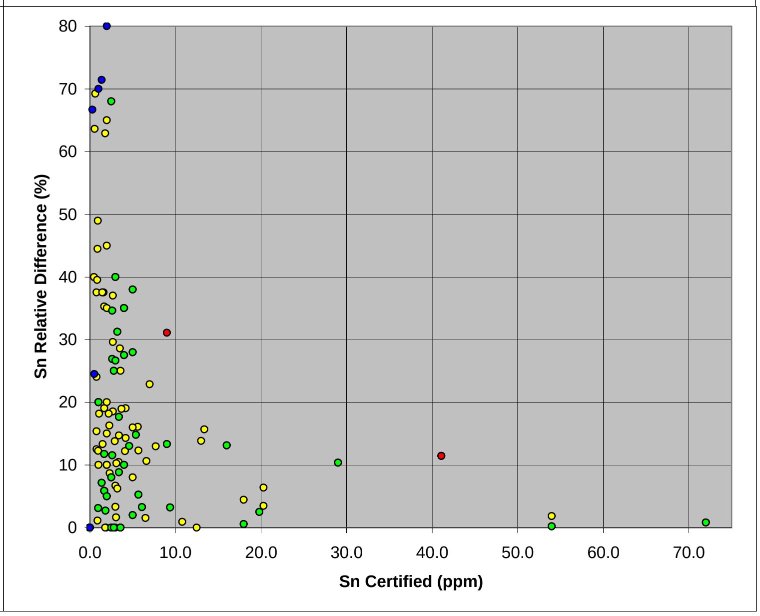

y = 0.974x - 0.006
R^2 = 0.999
Sn Measured (ppm)
Sn Certified (ppm)

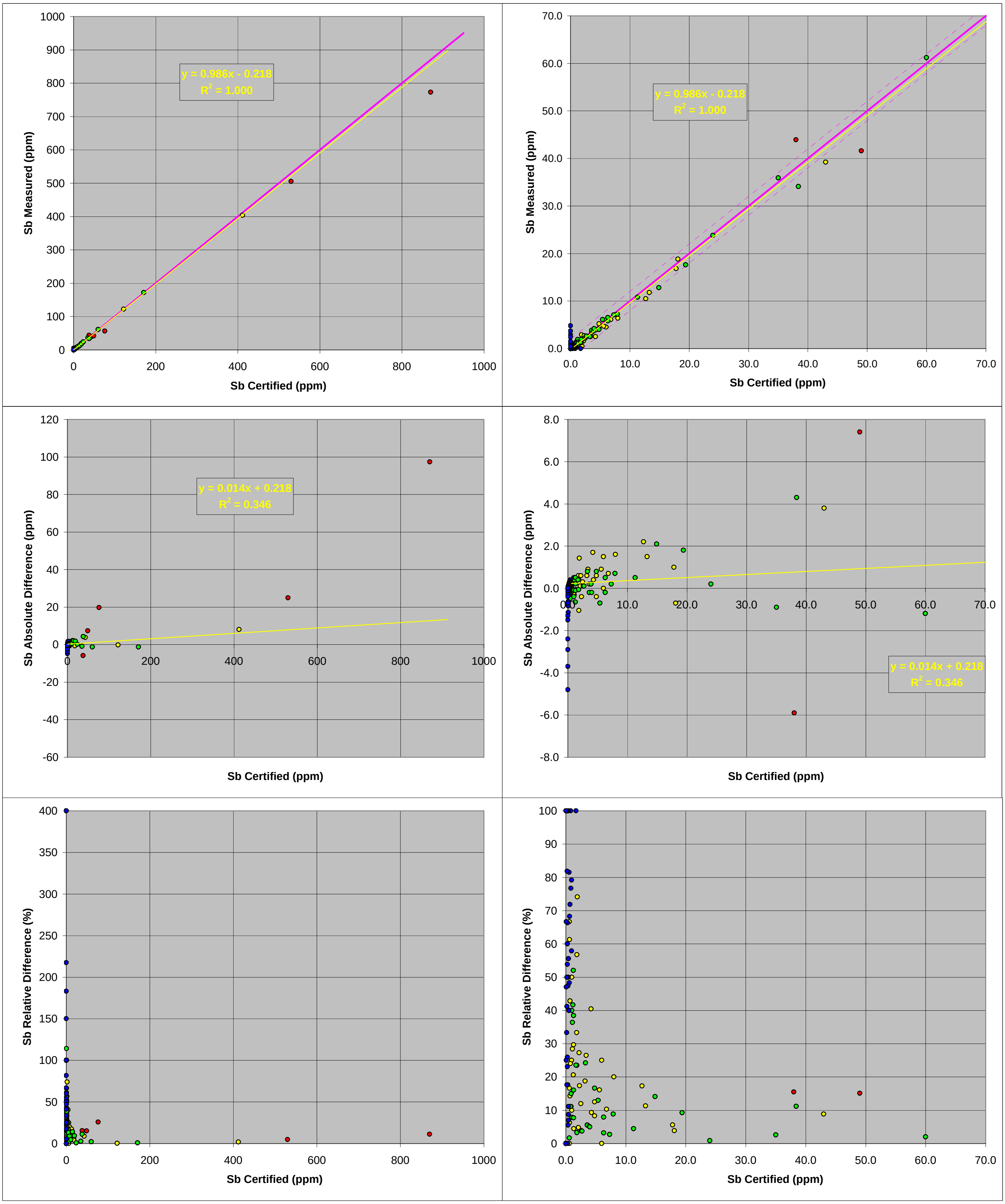

y = 0.974x - 0.006
R^2 = 0.999
Sn Measured (ppm)
Sn Certified (ppm)

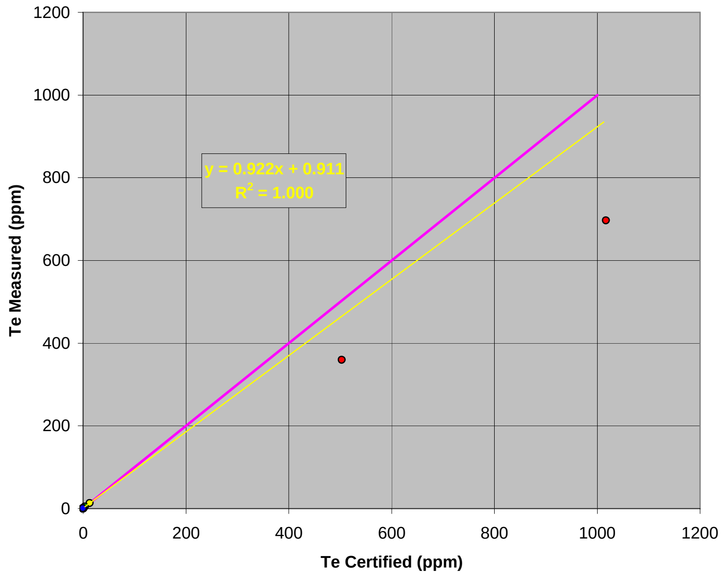

y = 0.026x + 0.006
R^2 = 0.497
Sn Absolute Difference (ppm)
Sn Certified (ppm)

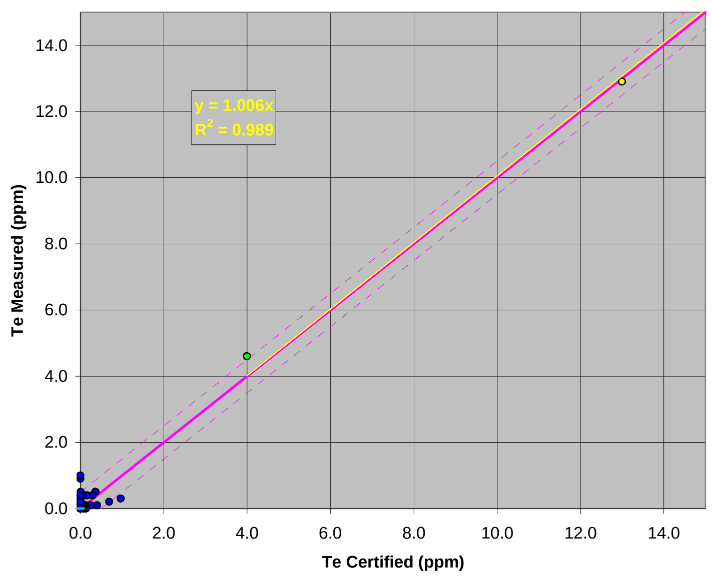

y = 0.026x + 0.006
R^2 = 0.497
Sn Absolute Difference (ppm)
Sn Certified (ppm)

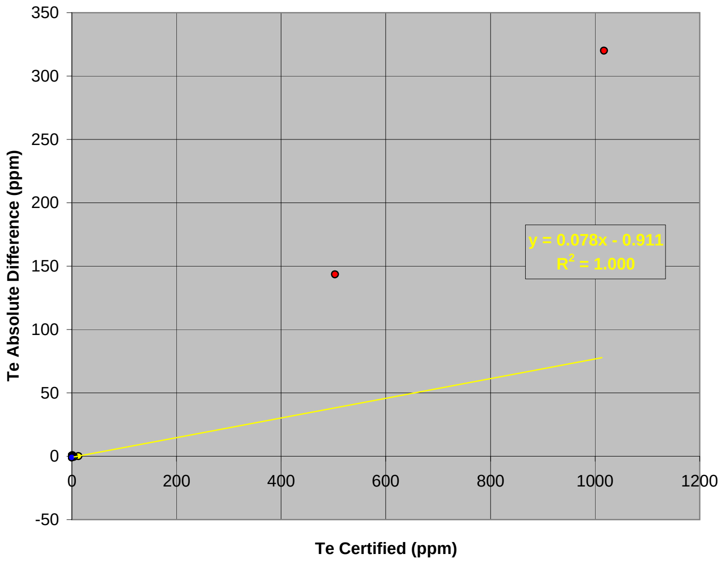

Sn Relative Difference (%)
Sn Certified (ppm)

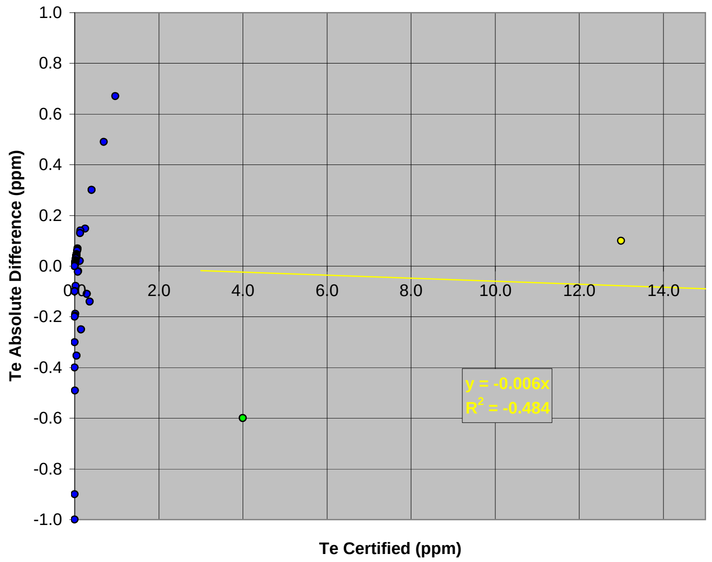

Sn Relative Difference (%)
Sn Certified (ppm)

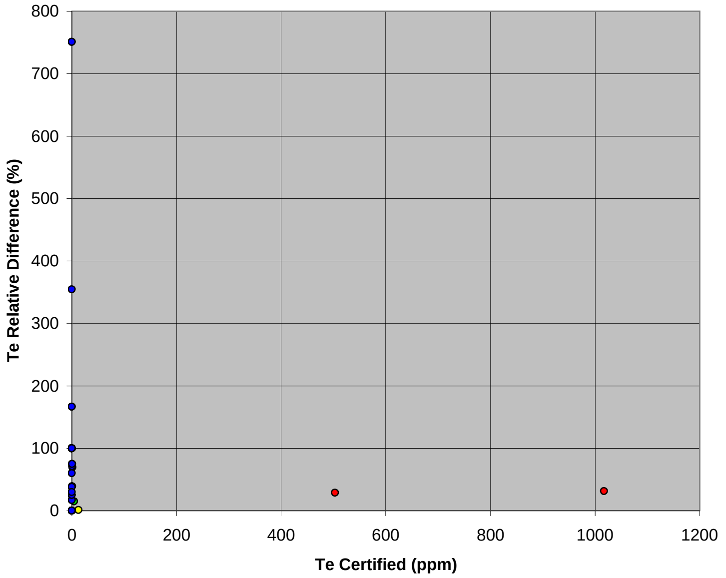

y = 0.986x - 0.218
R² = 1.000
Sb Measured (ppm)
Sb Certified (ppm)
y = 0.014x + 0.218
R² = 0.346
Sb Absolute Difference (ppm)
Sb Relative Difference (%)

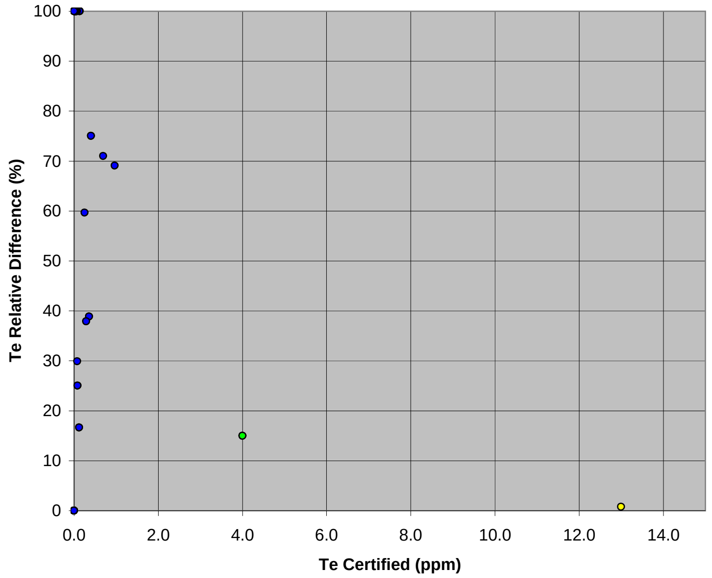

Te Measured (ppm)
Te Certified (ppm)
y = 0.922x + 0.911
R^2 = 1.000

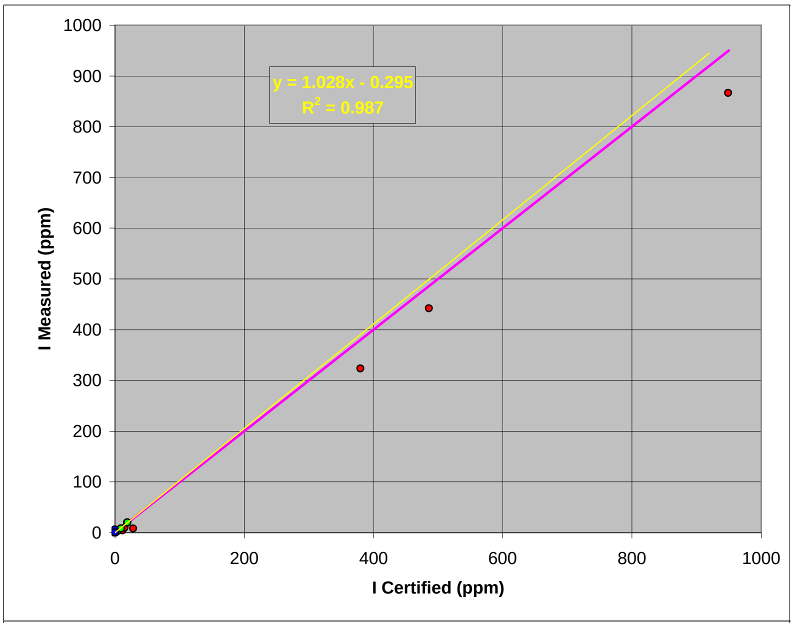

Te Measured (ppm)
Te Certified (ppm)
y = 1.006x
R^2 = 0.989

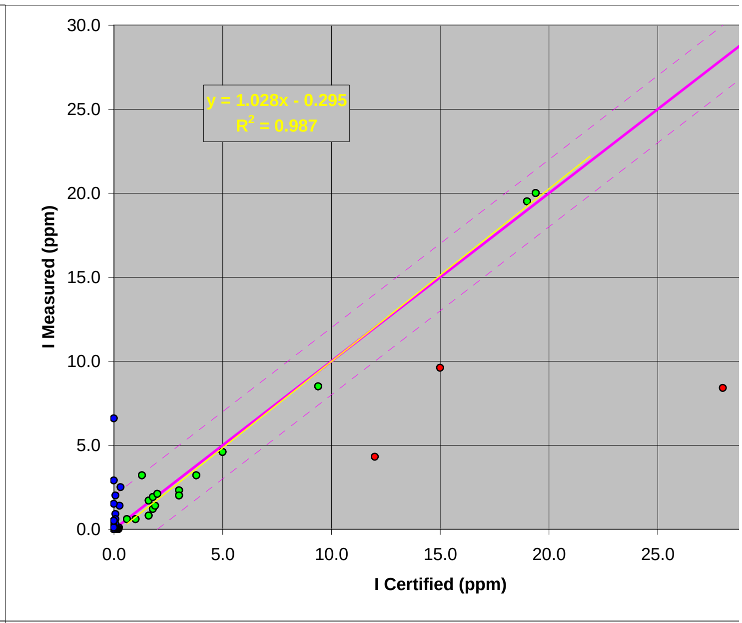

Te Absolute Difference (ppm)
Te Certified (ppm)
y = 0.078x - 0.911
R^2 = 1.000

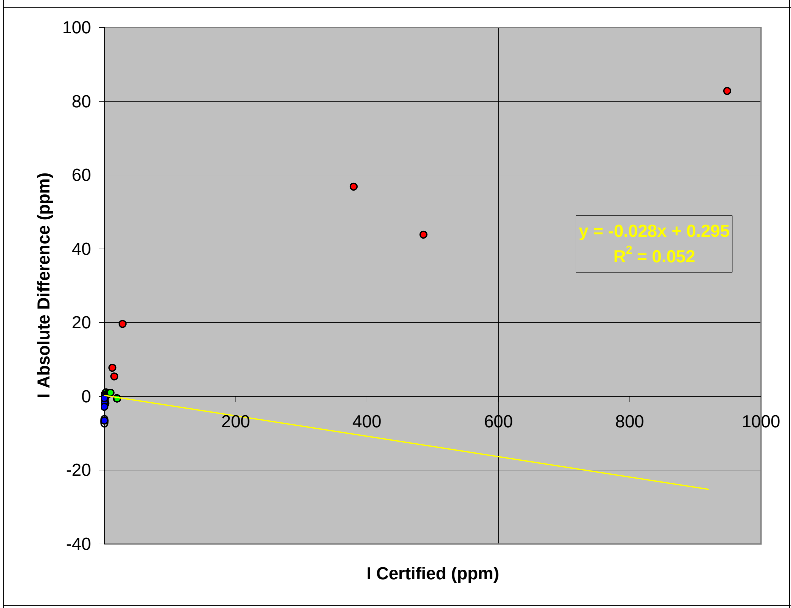

Te Absolute Difference (ppm)
Te Certified (ppm)
y = -0.006x
R^2 = -0.484

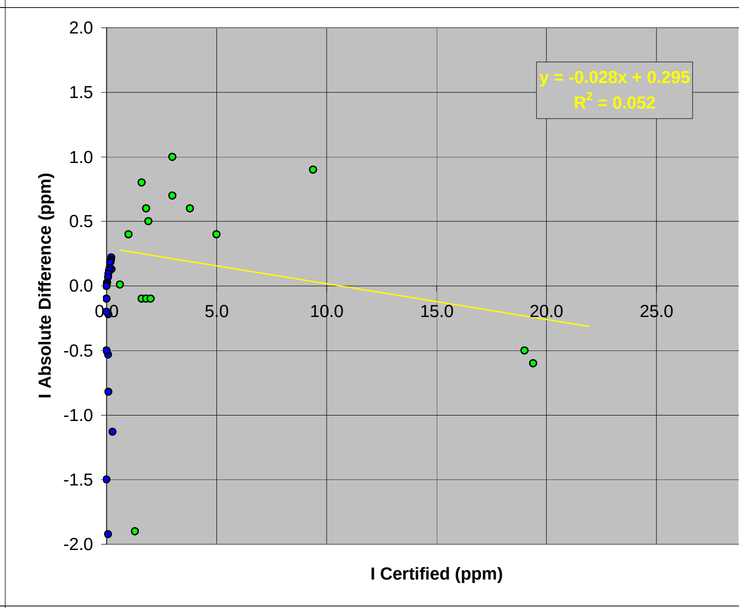

Te Relative Difference (%)
Te Certified (ppm)

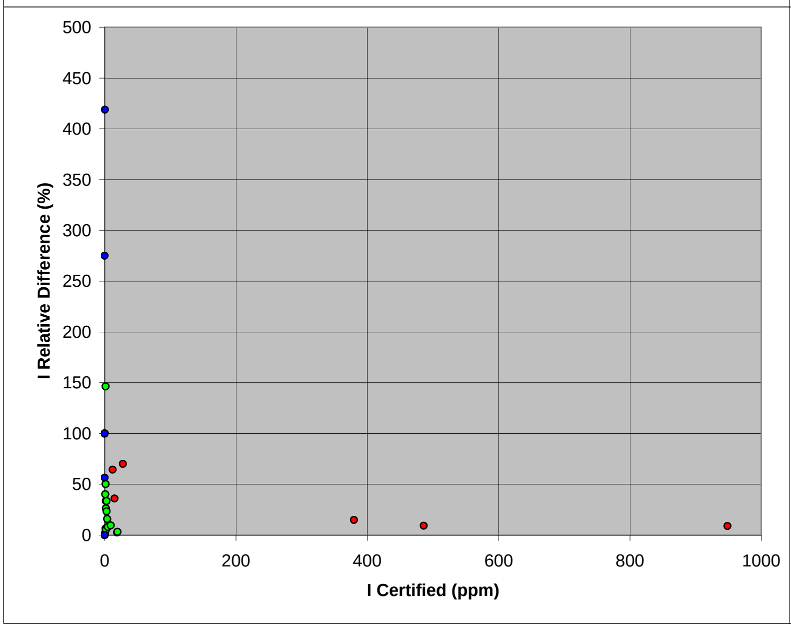

Te Relative Difference (%)
Te Certified (ppm)

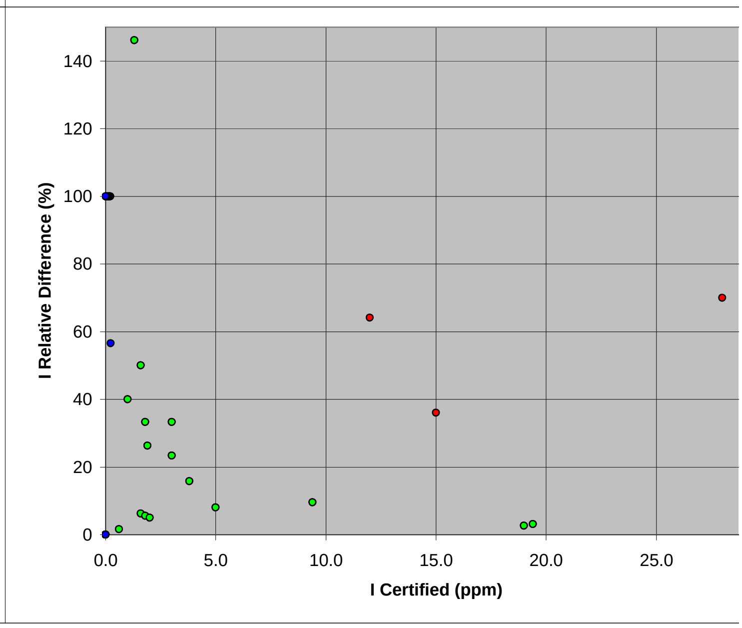

y = 1.028x - 0.295
R^2 = 0.987
I Measured (ppm)
I Certified (ppm)
0
100
200
300
400
500
600
700
800
900
1000

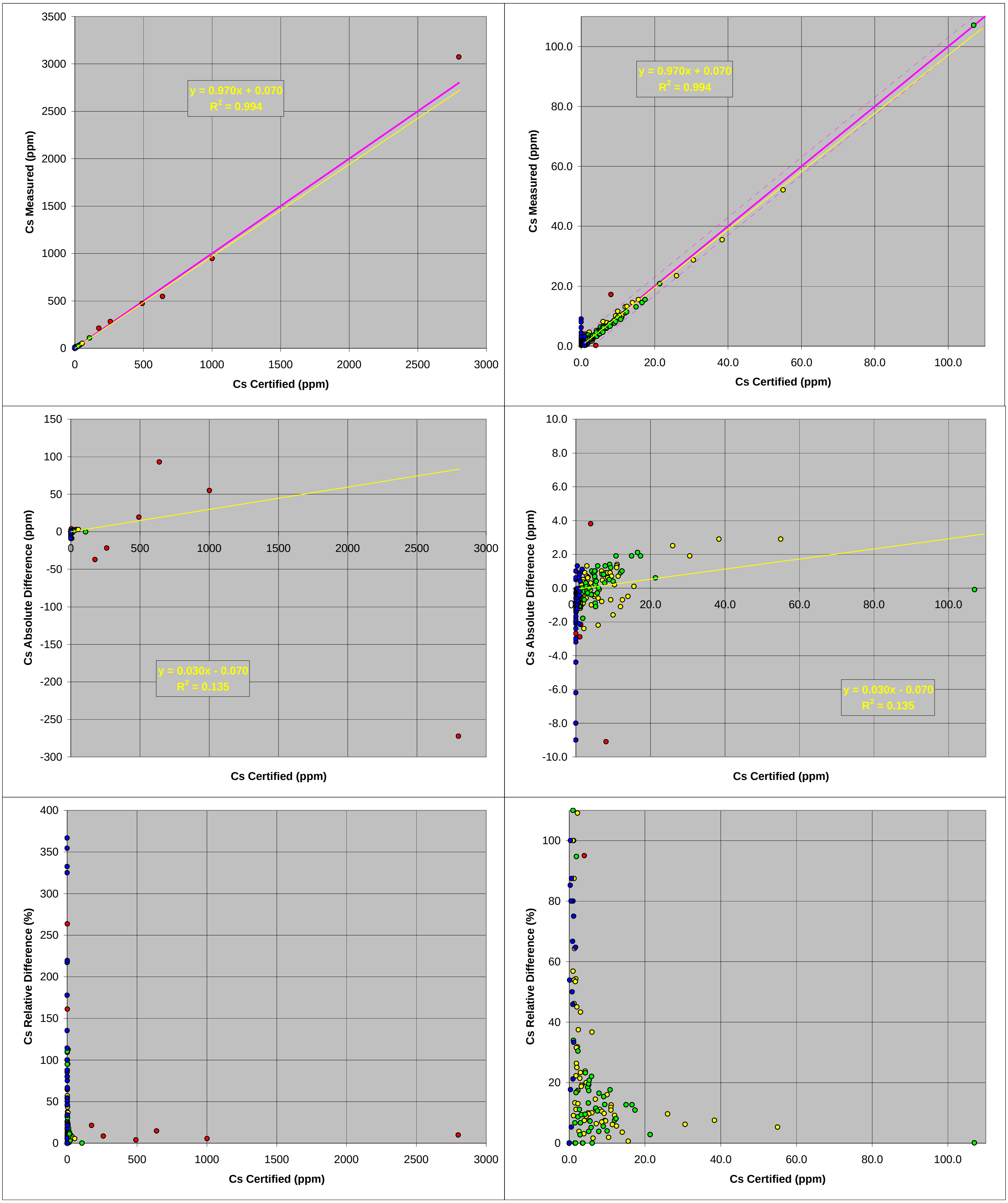

y = 1.028x - 0.295
R^2 = 0.987
I Measured (ppm)
I Certified (ppm)
0.0
5.0
10.0
15.0
20.0
25.0
30.0

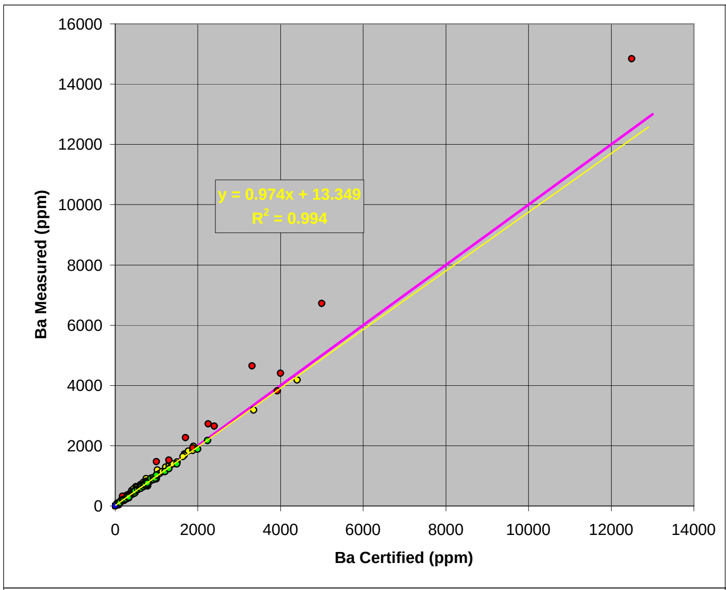

y = -0.028x + 0.295
R^2 = 0.052
I Absolute Difference (ppm)
I Certified (ppm)
-40
-20
0
20
40
60
80
100
200
400
600
800
1000

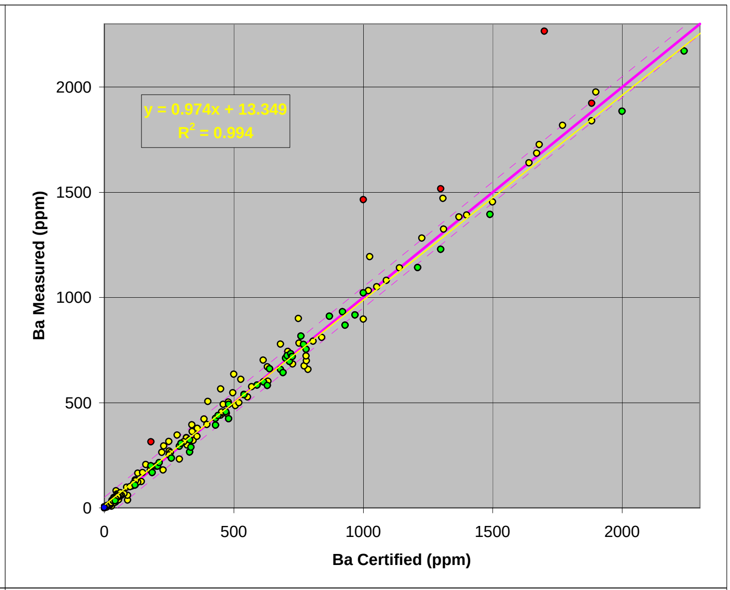

y = -0.028x + 0.295
R^2 = 0.052
I Absolute Difference (ppm)
I Certified (ppm)
-2.0
-1.5
-1.0
-0.5
0.0
0.5
1.0
1.5
2.0
5.0
10.0
15.0
20.0
25.0

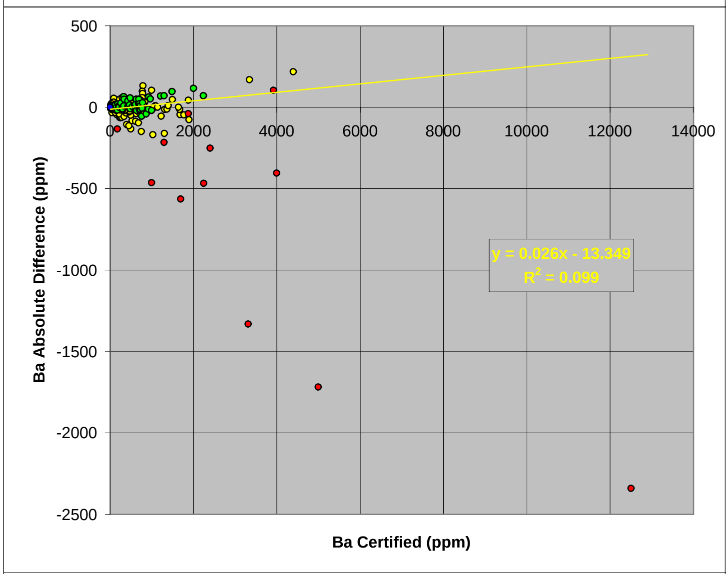

I Relative Difference (%)
I Certified (ppm)
0
50
100
150
200
250
300
350
400
450
500
200
400
600
800
1000

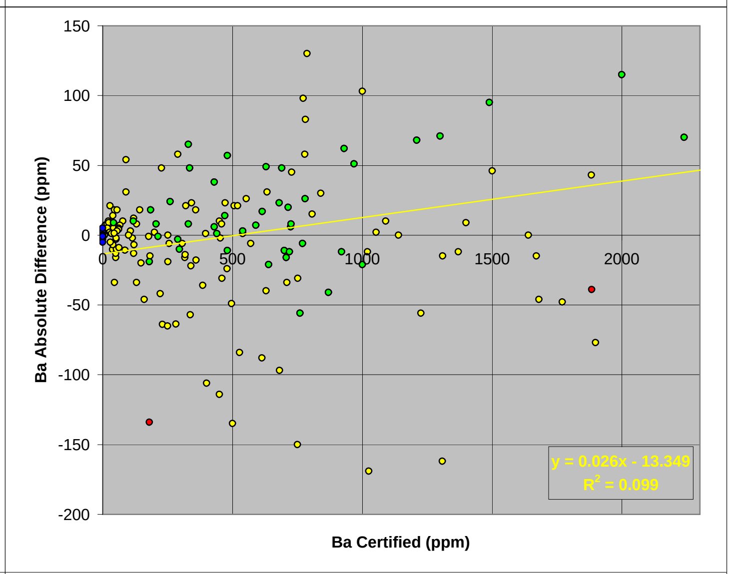

I Relative Difference (%)
I Certified (ppm)
0
20
40
60
80
100
120
140
0.0
5.0
10.0
15.0
20.0
25.0

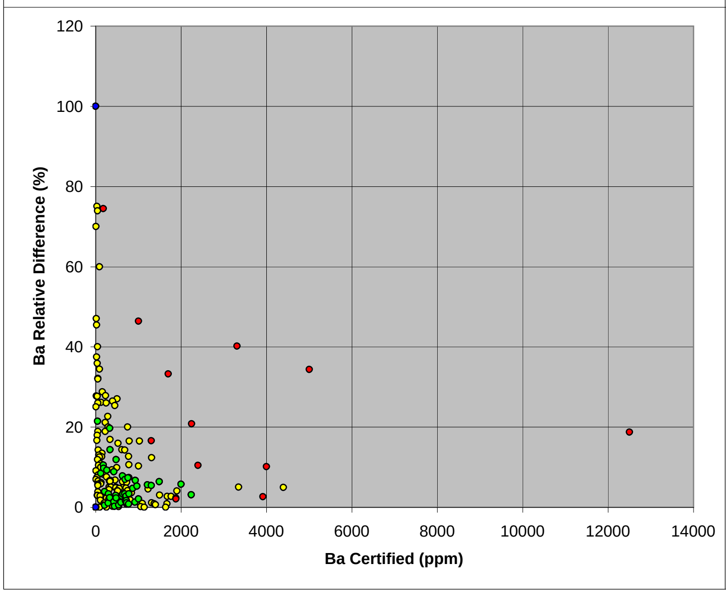

Cs Measured (ppm)
Cs Certified (ppm)
y = 0.970x + 0.070
R^2 = 0.994
Cs Absolute Difference (ppm)
y = 0.030x - 0.070
R^2 = 0.135
Cs Relative Difference (%)

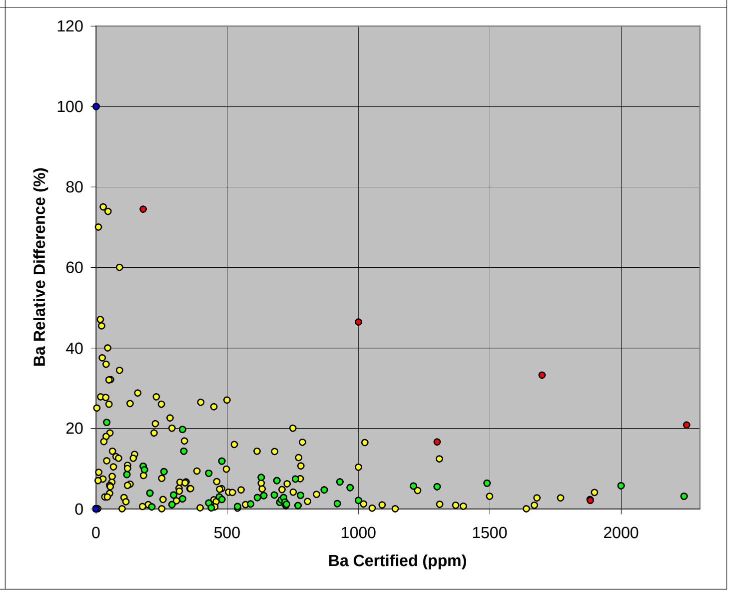

y = 0.974x + 13.349
R2 = 0.994
Ba Measured (ppm)
Ba Certified (ppm)
0
2000
4000
6000
8000
10000
12000
14000
16000

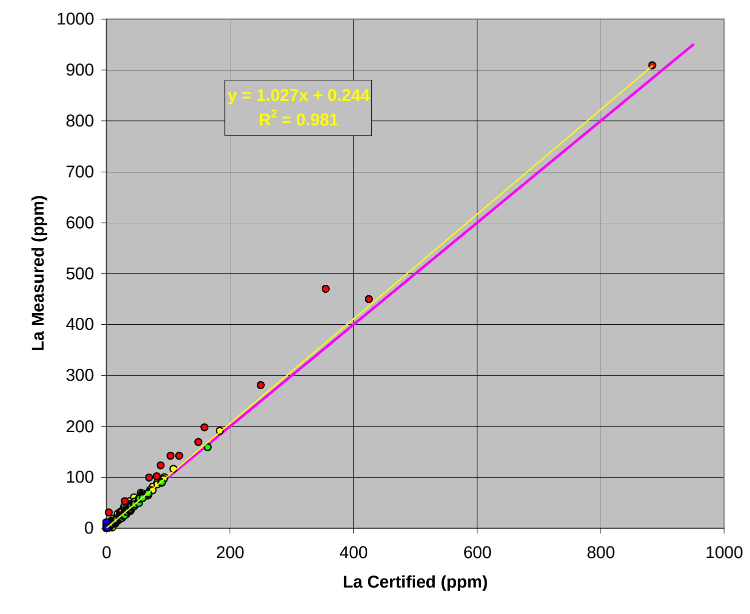

y = 0.974x + 13.349
R2 = 0.994
Ba Measured (ppm)
Ba Certified (ppm)
0
500
1000
1500
2000

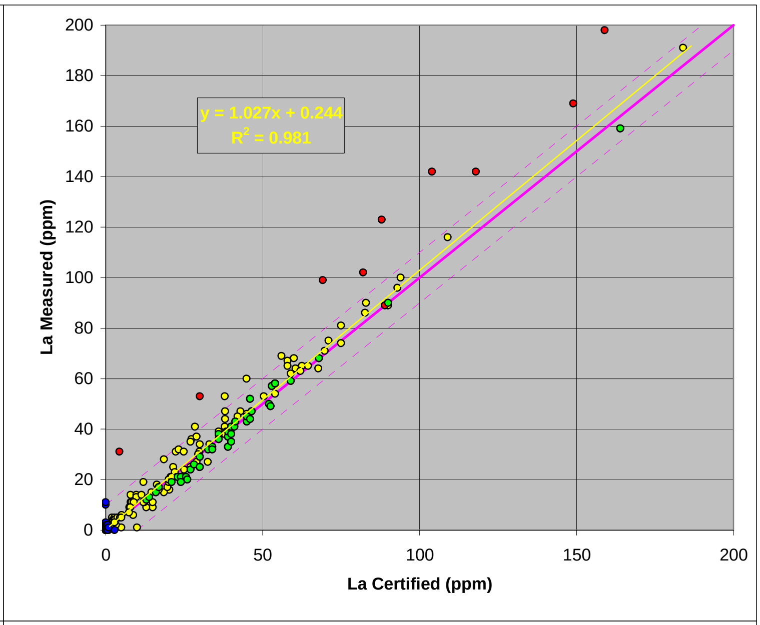

y = 0.026x - 13.349
R2 = 0.099
Ba Absolute Difference (ppm)
Ba Certified (ppm)
500
0
-500
-1000
-1500
-2000
-2500
2000
4000
6000
8000
10000
12000
14000

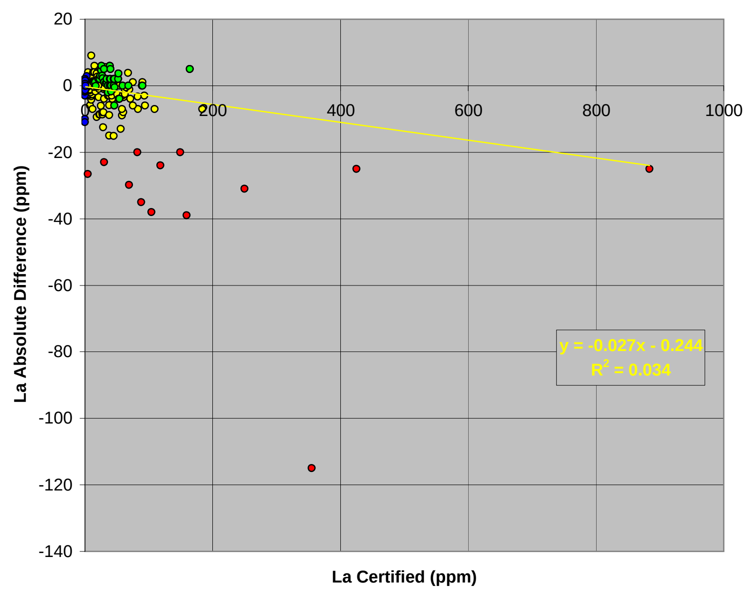

y = 0.026x - 13.349
R2 = 0.099
Ba Absolute Difference (ppm)
Ba Certified (ppm)
150
100
50
0
-50
-100
-150
-200
500
1000
1500
2000

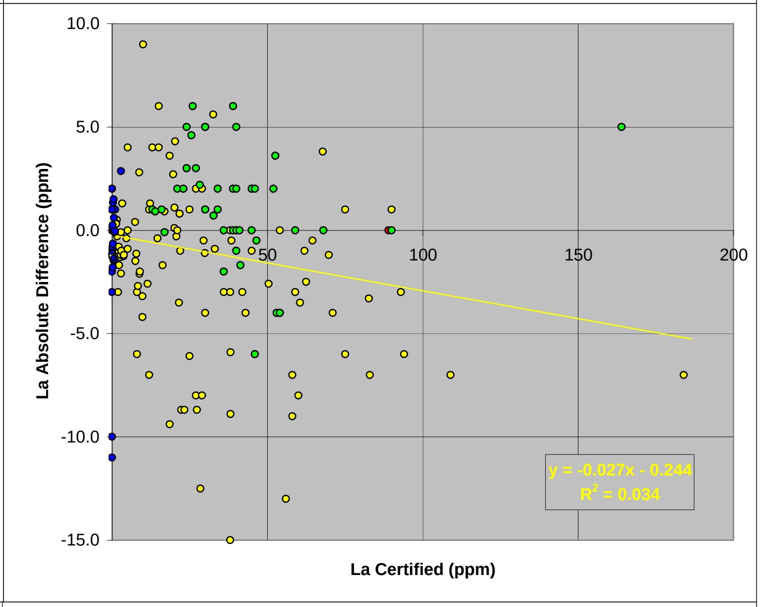

Ba Relative Difference (%)
Ba Certified (ppm)
0
20
40
60
80
100
120
2000
4000
6000
8000
10000
12000
14000

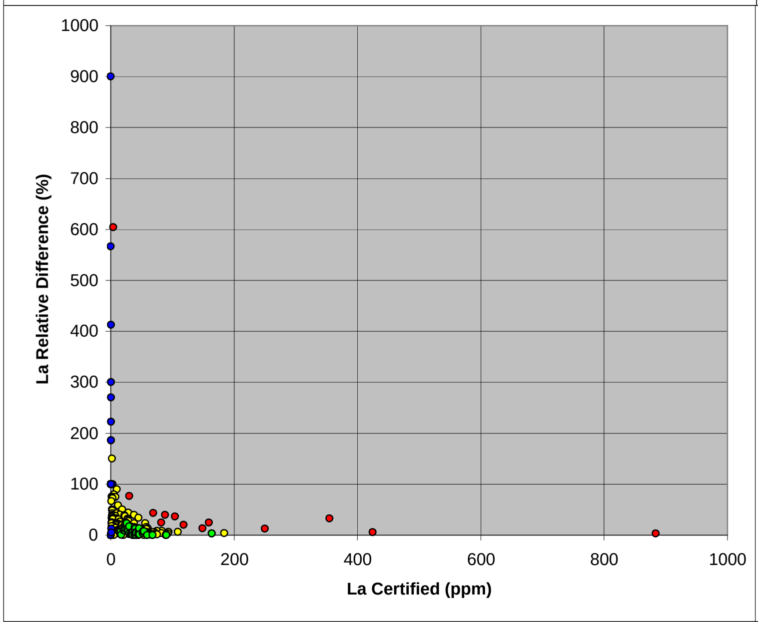

Ba Relative Difference (%)
Ba Certified (ppm)
0
20
40
60
80
100
120
500
1000
1500
2000

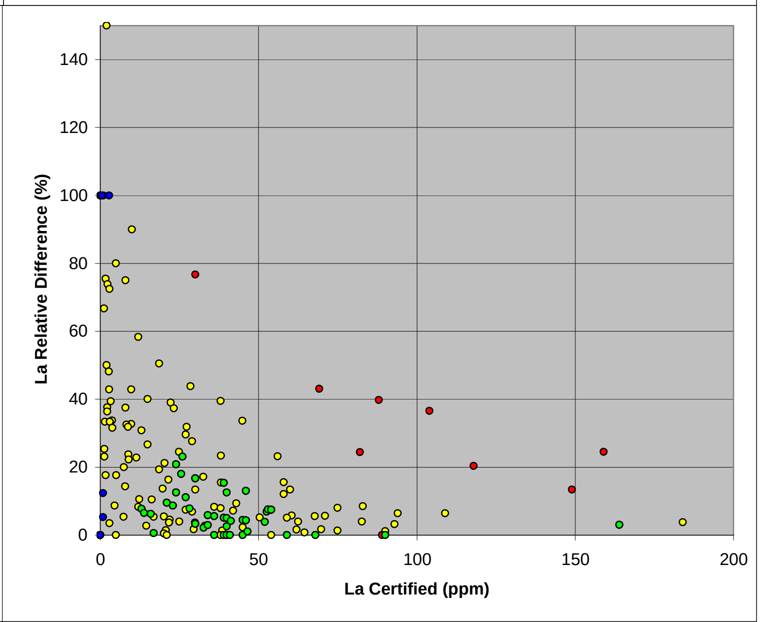

y = 1.027x + 0.244
R2 = 0.981
La Measured (ppm)
La Certified (ppm)

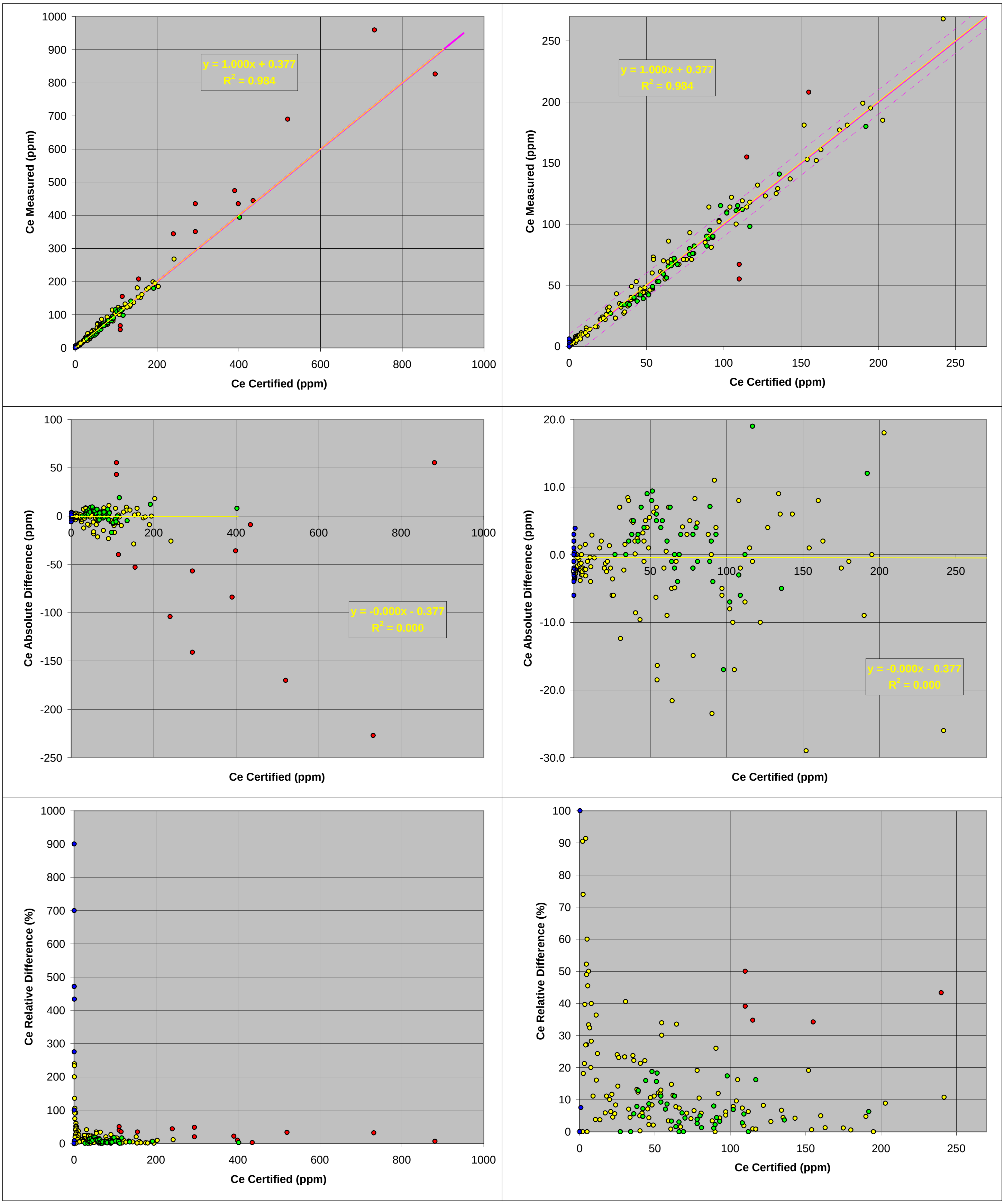

y = 1.027x + 0.244
R2 = 0.981
La Measured (ppm)
La Certified (ppm)


y = -0.027x - 0.244
R2 = 0.034
La Absolute Difference (ppm)
La Certified (ppm)


y = -0.027x - 0.244
R2 = 0.034
La Absolute Difference (ppm)
La Certified (ppm)


La Relative Difference (%)
La Certified (ppm)


La Relative Difference (%)
La Certified (ppm)


y = 1.000x + 0.377
R^2 = 0.984
Ce Measured (ppm)
Ce Certified (ppm)
y = -0.000x - 0.377
R^2 = 0.000
Ce Absolute Difference (ppm)
Ce Relative Difference (%)

APPENDIX 10 – Precision and Bias (MCERTS)

CLI = 8

CRM CMI 7004	PC Ag-Ce
Sample name	Cd
	ppm
Certified Value	1.52
Uncertainty	±0.15
Pellet 1A	2.1
Pellet 1B	1.5
Pellet 2A	1.6
Pellet 2B	1.6
Pellet 3A	1.5
Pellet 3B	1.5
Pellet 4A	2.0
Pellet 4B	1.8
Pellet 5A	1.3
Pellet 5B	1.7
Pellet 6A	1.6
Pellet 6B	2.2
Pellet 7A	1.5
Pellet 7B	1.9
Pellet 8A	1.6
Pellet 8B	2.0
Pellet 9A	1.6
Pellet 9B	2.0
Pellet 10A	1.7
Pellet 10B	1.7
Pellet 11A	2.0
Pellet 11B	1.8

Mean		1.74
Within batch sd		0.256
Between batch sd		0.212
total sd		0.236
Relative sd		13.60%
Target sd (5% of mean or 1/40 CLI)		0.200
F 0.05 from Tables		1.56
F-value calculated		1.39
Estimate degrees of freedom		21
Assessment		**PASS**
Reference concentration		1.52
Mean measured value	Bias = 0.22	1.74
Estimated mean recovery		114.2%
sd of mean recovery		0.150
Standard error of mean recovery		0.045
95% confidence limits on mean recovery		±0.082
Upper confidence level		2.14
Lower confidence level		1.34
Recovery range	87.9%	140.6%
Assessment		**TRUE**

Anova: Single Factor

SUMMARY

Groups	*Count*	*Sum*	*Average*	*Variance*
Row 1	2	3.6	1.8	0.18
Row 2	2	3.2	1.6	0
Row 3	2	3	1.5	0
Row 4	2	3.8	1.9	0.02
Row 5	2	3	1.5	0.08
Row 6	2	3.8	1.9	0.18
Row 7	2	3.4	1.7	0.08
Row 8	2	3.6	1.8	0.08
Row 9	2	3.6	1.8	0.08
Row 10	2	3.4	1.7	0
Row 11	2	3.8	1.9	0.02

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	0.4509	10	0.0451	0.6889	0.7176	2.8536
Within Groups	0.7200	11	0.0655			
Total	1.1709	21				

CLI = 8

CRM CMI 7002	PC Ag-Ce
Sample name	Cd
	ppm
Certified Value	0.31
Uncertainty	±0.04
Pellet 1/1	0.0
Pellet 1/2	0.3
Pellet 2/1	0.3
Pellet 2/2	0.4
Pellet 3/1	0.2
Pellet 3/2	0.0
Pellet 4/1	0.5
Pellet 4/2	0.5
Pellet 5/1	0.1
Pellet 5/2	0.4
Pellet 6/1	0.2
Pellet 6/2	0.6
Pellet 7/1	0.3
Pellet 7/2	0.2
Pellet 8/1	0.4
Pellet 8/2	0.4
Pellet 9/1	0.7
Pellet 9/2	0.4
Pellet 10/1	0.4
Pellet 10/2	0.2
Pellet 11/1	0.2
Pellet 11/2	0.3

Mean		0.32
Within batch sd		0.157
Between batch sd		0.196
total sd		0.176
Relative sd		55.41%
Target sd (5% of mean or 1/40 CLI)		0.200
F 0.05 from Tables		1.57
F-value calculated		0.78
Estimate degrees of freedom		20
Assessment		**PASS**
Reference concentration		0.31
Mean measured value	Bias = 0.01	0.32
Estimated mean recovery		102.6%
sd of mean recovery		0.138
Standard error of mean recovery		0.042
95% confidence limits on mean recovery		±0.076
Upper confidence level		0.72
Lower confidence level		-0.08
Recovery range	-26.4%	231.7%
Assessment		**TRUE**

Anova: Single Factor

SUMMARY

Groups	*Count*	*Sum*	*Average*	*Variance*
Row 1	2	0.3	0.15	0.045
Row 2	2	0.7	0.35	0.005
Row 3	2	0.2	0.1	0.02
Row 4	2	1	0.5	0
Row 5	2	0.5	0.25	0.045
Row 6	2	0.8	0.4	0.08
Row 7	2	0.5	0.25	0.005
Row 8	2	0.8	0.4	0
Row 9	2	1.1	0.55	0.045
Row 10	2	0.6	0.3	0.02
Row 11	2	0.5	0.25	0.005

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	0.3827	10	0.0383	1.5593	0.2384	2.8536
Within Groups	0.2700	11	0.0245			
Total	0.6527	21				

CLI = 8

CRM GSS-6		PC Ag-Ce
Sample name		Cd
		ppm
Certified Value		0.13
Uncertainty		±0.03
Pellet 1A		0.0
Pellet 1B		0.1
Pellet 2A		0.0
Pellet 2B		0.4
Pellet 3A		0.1
Pellet 3B		0.2
Pellet 4A		0.4
Pellet 4B		0.1
Pellet 5A		0.0
Pellet 5B		0.2
Pellet 6A		0.1
Pellet 6B		0.1
Pellet 7A		0.3
Pellet 7B		0.3
Pellet 8A		0.1
Pellet 8B		0.1
Pellet 9A		0.3
Pellet 9B		0.2
Pellet 10A		0.0
Pellet 10B		0.3
Pellet 11A		0.1
Pellet 11B		0.0
Mean		0.15
Within batch sd		0.138
Between batch sd		0.120
total sd		0.130
Relative sd		84.08%
Target sd (5% of mean or 1/40 CLI)		0.200
F 0.05 from Tables		1.56
F-value calculated		0.42
Estimate degrees of freedom		21
Assessment		**PASS**
Reference concentration		0.13
Mean measured value	Bias = 0.02	0.15
Estimated mean recovery		118.9%
sd of mean recovery		0.085
Standard error of mean recovery		0.026
95% confidence limits on mean recovery		±0.046
Upper confidence level		0.55
Lower confidence level		-0.25
Recovery range	-188.8%	426.6%
Assessment		**TRUE**

Anova: Single Factor

SUMMARY

Groups	*Count*	*Sum*	*Average*	*Variance*
Row 1	2	0.1	0.05	0.005
Row 2	2	0.4	0.2	0.08
Row 3	2	0.3	0.15	0.005
Row 4	2	0.5	0.25	0.045
Row 5	2	0.2	0.1	0.02
Row 6	2	0.2	0.1	0
Row 7	2	0.6	0.3	0
Row 8	2	0.2	0.1	0
Row 9	2	0.5	0.25	0.005
Row 10	2	0.3	0.15	0.045
Row 11	2	0.1	0.05	0.005

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	0.1445	10	0.0145	0.7571	0.6657	2.8536
Within Groups	0.2100	11	0.0191			
Total	0.3545	21				

CLI = 8

CRM NIST 2710	PC Ag-Ce
Sample name	Cd
	ppm
Certified Value	21.8
Uncertainty	±0.2
Pellet 1A	20.3
Pellet 1B	20.4
Pellet 2A	20.0
Pellet 2B	20.1
Pellet 3A	20.6
Pellet 3B	20.5
Pellet 4A	19.6
Pellet 4B	19.8
Pellet 5A	20.2
Pellet 5B	19.9
Pellet 6A	20.6
Pellet 6B	20.1
Pellet 7A	20.3
Pellet 7B	20.1
Pellet 8A	20.4
Pellet 8B	20.0
Pellet 9A	19.5
Pellet 9B	20.1
Pellet 10A	20.3
Pellet 10B	20.3
Pellet 11A	20.0
Pellet 11B	20.2

Mean		20.15
Within batch sd		0.214
Between batch sd		0.351
total sd		0.287
Relative sd		1.43%
Target sd (5% of mean or 1/40 CLI)		1.008
F 0.05 from Tables		1.62
F-value calculated		0.08
Estimate degrees of freedom		17
Assessment		**PASS**
Reference concentration		21.8
Mean measured value	Bias = 1.65	20.15
Estimated mean recovery		92.4%
sd of mean recovery		0.248
Standard error of mean recovery		0.075
95% confidence limits on mean recovery		±0.135
Upper confidence level		20.285
Lower confidence level		20.015
Recovery range	91.8%	93.1%
Assessment		**TRUE**

Anova: Single Factor

SUMMARY

Groups	*Count*	*Sum*	*Average*	*Variance*
Row 1	2	40.7	20.35	0.005
Row 2	2	40.1	20.05	0.005
Row 3	2	41.1	20.55	0.005
Row 4	2	39.4	19.7	0.02
Row 5	2	40.1	20.05	0.045
Row 6	2	40.7	20.35	0.125
Row 7	2	40.4	20.2	0.02
Row 8	2	40.4	20.2	0.08
Row 9	2	39.6	19.8	0.18
Row 10	2	40.6	20.3	0
Row 11	2	40.2	20.1	0.02

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	1.2300	10	0.1230	2.6792	0.0606	2.8536
Within Groups	0.5050	11	0.0459			
Total	1.7350	21				

CLI = 10

CRM CMI 7004	PC Ag-Ce
Sample name	Sb
	ppm
Certified Value	
Uncertainty	
Pellet 1A	2.8
Pellet 1B	3.1
Pellet 2A	2.8
Pellet 2B	2.9
Pellet 3A	3.3
Pellet 3B	3.2
Pellet 4A	3.0
Pellet 4B	2.6
Pellet 5A	2.8
Pellet 5B	2.3
Pellet 6A	2.5
Pellet 6B	2.6
Pellet 7A	2.6
Pellet 7B	2.7
Pellet 8A	2.3
Pellet 8B	2.7
Pellet 9A	3.2
Pellet 9B	2.4
Pellet 10A	3.1
Pellet 10B	3.0
Pellet 11A	2.9
Pellet 11B	3.1
Mean	2.81
Within batch sd	0.251
Between batch sd	0.336
total sd	0.295
Relative sd	10.48%
Target sd (7.5% of mean or 1/40 CLI)	0.250
F 0.05 from Tables	1.59
F-value calculated	1.39
Estimate degrees of freedom	19
Assessment	**PASS**
Reference concentration	
Mean measured value	
Estimated mean recovery	
sd of mean recovery	
Standard error of mean recovery	
95% confidence limits on mean recovery	
Upper confidence level	
Lower confidence level	
Recovery range	
Assessment	

Anova: Single Factor

SUMMARY

Groups	*Count*	*Sum*	*Average*	*Variance*
Row 1	2	5.9	2.95	0.045
Row 2	2	5.7	2.85	0.005
Row 3	2	6.5	3.25	0.005
Row 4	2	5.6	2.8	0.08
Row 5	2	5.1	2.55	0.125
Row 6	2	5.1	2.55	0.005
Row 7	2	5.3	2.65	0.005
Row 8	2	5	2.5	0.08
Row 9	2	5.6	2.8	0.32
Row 10	2	6.1	3.05	0.005
Row 11	2	6	3	0.02

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	1.1309	10	0.1131	1.7899	0.1767	2.8536
Within Groups	0.6950	11	0.0632			
Total	1.8259	21				

CLI = 10

CRM CMI 7002	PC Ag-Ce
Sample name	Sb
	ppm
Certified Value	
Uncertainty	
Pellet 1/1	1.4
Pellet 1/2	1.9
Pellet 2/1	1.4
Pellet 2/2	1.8
Pellet 3/1	1.8
Pellet 3/2	1.5
Pellet 4/1	1.3
Pellet 4/2	1.4
Pellet 5/1	1.6
Pellet 5/2	1.3
Pellet 6/1	1.7
Pellet 6/2	0.8
Pellet 7/1	1.6
Pellet 7/2	1.2
Pellet 8/1	1.2
Pellet 8/2	1.8
Pellet 9/1	1.7
Pellet 9/2	1.4
Pellet 10/1	1.2
Pellet 10/2	1.5
Pellet 11/1	1.4
Pellet 11/2	1.5
Mean	1.47
Within batch sd	0.310
Between batch sd	0.185
total sd	0.259
Relative sd	17.55%
Target sd (7.5% of mean or 1/40 CLI)	0.250
F 0.05 from Tables	1.60
F-value calculated	1.07
Estimate degrees of freedom	18
Assessment	**PASS**
Reference concentration	
Mean measured value	
Estimated mean recovery	
sd of mean recovery	
Standard error of mean recovery	
95% confidence limits on mean recovery	
Upper confidence level	
Lower confidence level	
Recovery range	
Assessment	

Anova: Single Factor

SUMMARY

Groups	*Count*	*Sum*	*Average*	*Variance*
Row 1	2	3.3	1.65	0.125
Row 2	2	3.2	1.6	0.08
Row 3	2	3.3	1.65	0.045
Row 4	2	2.7	1.35	0.005
Row 5	2	2.9	1.45	0.045
Row 6	2	2.5	1.25	0.405
Row 7	2	2.8	1.4	0.08
Row 8	2	3	1.5	0.18
Row 9	2	3.1	1.55	0.045
Row 10	2	2.7	1.35	0.045
Row 11	2	2.9	1.45	0.005

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	0.3436	10	0.0344	0.3566	0.9423	2.8536
Within Groups	1.0600	11	0.0964			
Total	1.4036	21				

CLI = 10

CRM GSS-6	PC Ag-Ce
Sample name	Sb
	ppm
Certified Value	60
Uncertainty	±7
Pellet 1A	60.2
Pellet 1B	60.1
Pellet 2A	60.7
Pellet 2B	60.7
Pellet 3A	59.8
Pellet 3B	60.5
Pellet 4A	60.1
Pellet 4B	60.8
Pellet 5A	60.8
Pellet 5B	60.7
Pellet 6A	60.5
Pellet 6B	61.0
Pellet 7A	60.2
Pellet 7B	60.7
Pellet 8A	60.6
Pellet 8B	61.4
Pellet 9A	60.5
Pellet 9B	60.6
Pellet 10A	59.9
Pellet 10B	61.1
Pellet 11A	60.6
Pellet 11B	60.6

Mean		60.55
Within batch sd		0.404
Between batch sd		0.361
total sd		0.384
Relative sd		0.63%
Target sd (7.5% of mean or 1/40 CLI)		4.541
F 0.05 from Tables		1.56
F-value calculated		0.01
Estimate degrees of freedom		21
Assessment		**PASS**
Reference concentration		60
Mean measured value	Bias = 0.5	60.55
Estimated mean recovery		100.9%
sd of mean recovery		0.255
Standard error of mean recovery		0.077
95% confidence limits on mean recovery		±0.139
Upper confidence level		60.689
Lower confidence level		60.411
Recovery range	100.7%	101.1%
Assessment		**TRUE**

Anova: Single Factor

SUMMARY

Groups	*Count*	*Sum*	*Average*	*Variance*
Row 1	2	120.3	60.15	0.005
Row 2	2	121.4	60.7	0
Row 3	2	120.3	60.15	0.245
Row 4	2	120.9	60.45	0.245
Row 5	2	121.5	60.75	0.005
Row 6	2	121.5	60.75	0.125
Row 7	2	120.9	60.45	0.125
Row 8	2	122	61	0.32
Row 9	2	121.1	60.55	0.005
Row 10	2	121	60.5	0.72
Row 11	2	121.2	60.6	0

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	1.3000	10	0.1300	0.7967	0.6362	2.8536
Within Groups	1.7950	11	0.1632			
Total	3.0950	21				

CLI = 10

CRM NIST 2710	PC Ag-Ce
Sample name	Sb
	ppm
Certified Value	38.4
Uncertainty	±3
Pellet 1A	32.9
Pellet 1B	33.3
Pellet 2A	33.0
Pellet 2B	33.2
Pellet 3A	33.0
Pellet 3B	33.0
Pellet 4A	33.2
Pellet 4B	32.9
Pellet 5A	32.6
Pellet 5B	32.7
Pellet 6A	32.8
Pellet 6B	33.1
Pellet 7A	33.0
Pellet 7B	32.5
Pellet 8A	32.7
Pellet 8B	32.5
Pellet 9A	32.8
Pellet 9B	33.3
Pellet 10A	32.8
Pellet 10B	32.8
Pellet 11A	32.6
Pellet 11B	33.0

Mean		32.90
Within batch sd		0.223
Between batch sd		0.258
total sd		0.240
Relative sd		0.73%
Target sd (7.5% of mean or 1/40 CLI)		2.467
F 0.05 from Tables		1.57
F-value calculated		0.01
Estimate degrees of freedom		20
Assessment		**PASS**
Reference concentration		38.4
Mean measured value	Bias = 5.5	32.90
Estimated mean recovery		85.7%
sd of mean recovery		0.182
Standard error of mean recovery		0.055
95% confidence limits on mean recovery		±0.100
Upper confidence level		32.995
Lower confidence level		32.796
Recovery range	85.4%	85.9%
Assessment		**TRUE**

Anova: Single Factor

SUMMARY

Groups	*Count*	*Sum*	*Average*	*Variance*
Row 1	2	66.2	33.1	0.08
Row 2	2	66.2	33.1	0.02
Row 3	2	66	33	0
Row 4	2	66.1	33.05	0.045
Row 5	2	65.3	32.65	0.005
Row 6	2	65.9	32.95	0.045
Row 7	2	65.5	32.75	0.125
Row 8	2	65.2	32.6	0.02
Row 9	2	66.1	33.05	0.125
Row 10	2	65.6	32.8	0
Row 11	2	65.6	32.8	0.08

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	0.6645	10	0.0665	1.3413	0.3177	2.8536
Within Groups	0.5450	11	0.0495			
Total	1.2095	21				

CRM CMI 7004	PC Ag-Ce
Sample name	Ba
	ppm
Certified Value	(568)
Uncertainty	±27
Pellet 1A	536.0
Pellet 1B	537.1
Pellet 2A	535.3
Pellet 2B	537.8
Pellet 3A	535.6
Pellet 3B	536.8
Pellet 4A	538.5
Pellet 4B	536.7
Pellet 5A	539.0
Pellet 5B	540.0
Pellet 6A	537.0
Pellet 6B	540.4
Pellet 7A	535.2
Pellet 7B	537.1
Pellet 8A	532.7
Pellet 8B	530.4
Pellet 9A	536.1
Pellet 9B	538.1
Pellet 10A	536.4
Pellet 10B	534.3
Pellet 11A	537.9
Pellet 11B	537.5

Mean		536.63
Within batch sd		1.384
Between batch sd		2.922
total sd		2.252
Relative sd		0.42%
Target sd (5% of mean or 1/40 CLI)		26.832
F 0.05 from Tables		1.69
F-value calculated		0.01
Estimate degrees of freedom		14
Assessment		**PASS**
Reference concentration		*568*
Mean measured value	Bias = 31.4	536.63
Estimated mean recovery		94.5%
sd of mean recovery		2.066
Standard error of mean recovery		0.623
95% confidence limits on mean recovery		±1.129
Upper confidence level		537.761
Lower confidence level		535.503
Recovery range	94.3%	94.7%
Assessment		**TRUE**

Anova: Single Factor

SUMMARY

Groups	*Count*	*Sum*	*Average*	*Variance*
Row 1	2	1073	536.55	0.605
Row 2	2	1073	536.55	3.125
Row 3	2	1072	536.2	0.72
Row 4	2	1075	537.6	1.62
Row 5	2	1079	539.5	0.5
Row 6	2	1077	538.7	5.78
Row 7	2	1072	536.15	1.805
Row 8	2	1063	531.55	2.645
Row 9	2	1074	537.1	2
Row 10	2	1071	535.35	2.205
Row 11	2	1075	537.7	0.08

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	85.4027	10	8.5403	4.4554	0.0107	2.8536
Within Groups	21.0850	11	1.9168			
Total	106.4877	21				

CRM CMI 7002	PC Ag-Ce
Sample name	Ba
	ppm
Certified Value	(987)
Uncertainty	±86
Pellet 1/1	903.0
Pellet 1/2	903.1
Pellet 2/1	907.6
Pellet 2/2	903.6
Pellet 3/1	906.8
Pellet 3/2	907.2
Pellet 4/1	900.9
Pellet 4/2	902.4
Pellet 5/1	908.4
Pellet 5/2	907.3
Pellet 6/1	906.7
Pellet 6/2	905.8
Pellet 7/1	906.1
Pellet 7/2	904.6
Pellet 8/1	907.8
Pellet 8/2	911.4
Pellet 9/1	905.2
Pellet 9/2	905.2
Pellet 10/1	902.1
Pellet 10/2	900.6
Pellet 11/1	901.8
Pellet 11/2	903.2

Mean		905.04
Within batch sd		1.346
Between batch sd		3.740
total sd		2.759
Relative sd		0.30%
Target sd (5% of mean or 1/40 CLI)		45.252
F 0.05 from Tables		1.72
F-value calculated		0.00
Estimate degrees of freedom		13
Assessment		**PASS**
Reference concentration		*987*
Mean measured value	Bias = 82.0	905.04
Estimated mean recovery		91.7%
sd of mean recovery		2.645
Standard error of mean recovery		0.797
95% confidence limits on mean recovery		±1.445
Upper confidence level		906.481
Lower confidence level		903.591
Recovery range	91.5%	91.8%
Assessment		**TRUE**

Anova: Single Factor

SUMMARY

Groups	*Count*	*Sum*	*Average*	*Variance*
Row 1	2	1806	903.05	0.005
Row 2	2	1811	905.6	8
Row 3	2	1814	907	0.08
Row 4	2	1803	901.65	1.125
Row 5	2	1816	907.85	0.605
Row 6	2	1813	906.25	0.405
Row 7	2	1811	905.35	1.125
Row 8	2	1819	909.6	6.48
Row 9	2	1810	905.2	0
Row 10	2	1803	901.35	1.125
Row 11	2	1805	902.5	0.98

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	139.9009	10	13.9901	7.7216	0.0011	2.8536
Within Groups	19.9300	11	1.8118			
Total	159.8309	21				

CRM GSS-6		PC Ag-Ce
Sample name		Ba
		ppm
Certified Value		118.0
Uncertainty		±14
Pellet 1A		105.9
Pellet 1B		105.1
Pellet 2A		104.3
Pellet 2B		105.3
Pellet 3A		106.1
Pellet 3B		106.0
Pellet 4A		105.0
Pellet 4B		106.3
Pellet 5A		105.2
Pellet 5B		105.8
Pellet 6A		104.9
Pellet 6B		105.9
Pellet 7A		106.1
Pellet 7B		104.3
Pellet 8A		106.3
Pellet 8B		106.7
Pellet 9A		107.1
Pellet 9B		106.3
Pellet 10A		105.6
Pellet 10B		105.3
Pellet 11A		105.8
Pellet 11B		106.8
Mean		105.73
Within batch sd		0.668
Between batch sd		0.825
total sd		0.747
Relative sd		0.71%
Target sd (5% of mean or 1/40 CLI)		5.287
F 0.05 from Tables		1.57
F-value calculated		0.02
Estimate degrees of freedom		20
Assessment		**PASS**
Reference concentration		118
Mean measured value	Bias = 12.3	105.73
Estimated mean recovery		89.6%
sd of mean recovery		0.584
Standard error of mean recovery		0.176
95% confidence limits on mean recovery		±0.319
Upper confidence level		106.051
Lower confidence level		105.413
Recovery range	89.3%	89.9%
Assessment		**FALSE**

Anova: Single Factor

SUMMARY

Groups	*Count*	*Sum*	*Average*	*Variance*
Row 1	2	211	105.5	0.32
Row 2	2	210	104.8	0.5
Row 3	2	212	106.05	0.005
Row 4	2	211	105.65	0.845
Row 5	2	211	105.5	0.18
Row 6	2	211	105.4	0.5
Row 7	2	210	105.2	1.62
Row 8	2	213	106.5	0.08
Row 9	2	213	106.7	0.32
Row 10	2	211	105.45	0.045
Row 11	2	213	106.3	0.5

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	6.8127	10	0.6813	1.5247	0.2494	2.8536
Within Groups	4.9150	11	0.4468			
Total	11.7277	21				

CRM NIST 2710		PC Ag-Ce
Sample name		Ba
		ppm
Certified Value		707
Uncertainty		±51
Pellet 1A		710
Pellet 1B		710
Pellet 2A		710
Pellet 2B		711
Pellet 3A		709
Pellet 3B		713
Pellet 4A		709
Pellet 4B		716
Pellet 5A		712
Pellet 5B		715
Pellet 6A		713
Pellet 6B		715
Pellet 7A		708
Pellet 7B		712
Pellet 8A		712
Pellet 8B		715
Pellet 9A		710
Pellet 9B		713
Pellet 10A		712
Pellet 10B		713
Pellet 11A		710
Pellet 11B		716
Mean		712.03
Within batch sd		2.641
Between batch sd		2.076
total sd		2.389
Relative sd	target	0.34%
Target sd (5% of mean or 1/40 CLI)	5%	35.601
F 0.05 from Tables		1.57
F-value calculated	diff = 1.57	0.00
Estimate degrees of freedom		20
Assessment		**PASS**
Reference concentration		707
Mean measured value	Bias = 5.0	712.03
Estimated mean recovery		100.7%
sd of mean recovery		1.468
Standard error of mean recovery		0.443
95% confidence limits on mean recovery		±0.802
Upper confidence level		712.829
Lower confidence level		711.225
Recovery range	100.6%	100.8%
Assessment		**TRUE**

Anova: Single Factor

SUMMARY

Groups	*Count*	*Sum*	*Average*	*Variance*
Row 1	2	1419.4	709.7	0.02
Row 2	2	1420.8	710.4	0.98
Row 3	2	1422.2	711.1	9.68
Row 4	2	1425.6	712.8	23.12
Row 5	2	1427.6	713.8	4.5
Row 6	2	1427.7	713.85	2.645
Row 7	2	1420.8	710.4	8
Row 8	2	1427.2	713.6	3.38
Row 9	2	1423.5	711.75	5.445
Row 10	2	1424.8	712.4	0.98
Row 11	2	1425	712.5	18

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	43.0936	10	4.3094	0.6176	0.7719	2.8536
Within Groups	76.7500	11	6.9773			
Total	119.8436	21				

Summary Table CRM's

Analyte	Required targets		CRM 1 CMI 7004				CRM 2 CMI 7002				CRM-3 GSS-6 (NCS DC73324, GBW07406)			
	Prec	Bias	Certified value	Mean	Prec	Bias	Certified value	Mean	Prec	Bias	Certified value	Mean	Prec	Bias
Cd	* 0.20	* 0.40	1.52	1.74	0.24	0.22	0.31	0.32	0.18	0.01	0.13	0.15	0.13	0.02
Cd	1.01	2.18												
Sb	* 0.25	* 0.50	N/A	2.81	0.29	N/A	N/A	1.47	0.26	N/A				
Sb	4.54	9.00									60	60.55	0.38	0.55
Sb	2.47	5.76												
Ba	26.8	56.8	568	536.6	2.3	31.4								
Ba	45.3	98.7					987	905.0	2.8	82				
Ba	5.3	11.8									118.0	105.7	0.7	12.3
Ba	35.6	70.7												

All results in mg/kg **Date validation commenced: 14/03/2005.** **Date validation completed: 24/05/2005.**

Summary Table CRM's

Analyte	Required targets		CRM-4 NIST 2710			
	Prec	Bias	Certified value	Mean	Prec	Bias
Cd	* 0.20	* 0.40				
Cd	1.01	2.18	21.8	20.15	0.29	1.65
Sb	* 0.25	* 0.50				
Sb	4.54	9.00				
Sb	2.47	5.76	38.4	32.90	0.24	5.50
Ba	26.8	56.8				
Ba	45.3	98.7				
Ba	5.3	11.8				
Ba	35.6	70.7	707	712	2.4	5.0

All results in mg/kg **Date validation commenced: 14/03/2005.** **Date validation completed: 24/05/2005.**

APPENDIX 11 – Repeatability (QC Charts)

Quality Control Charts QC BGS High

Process Statistics

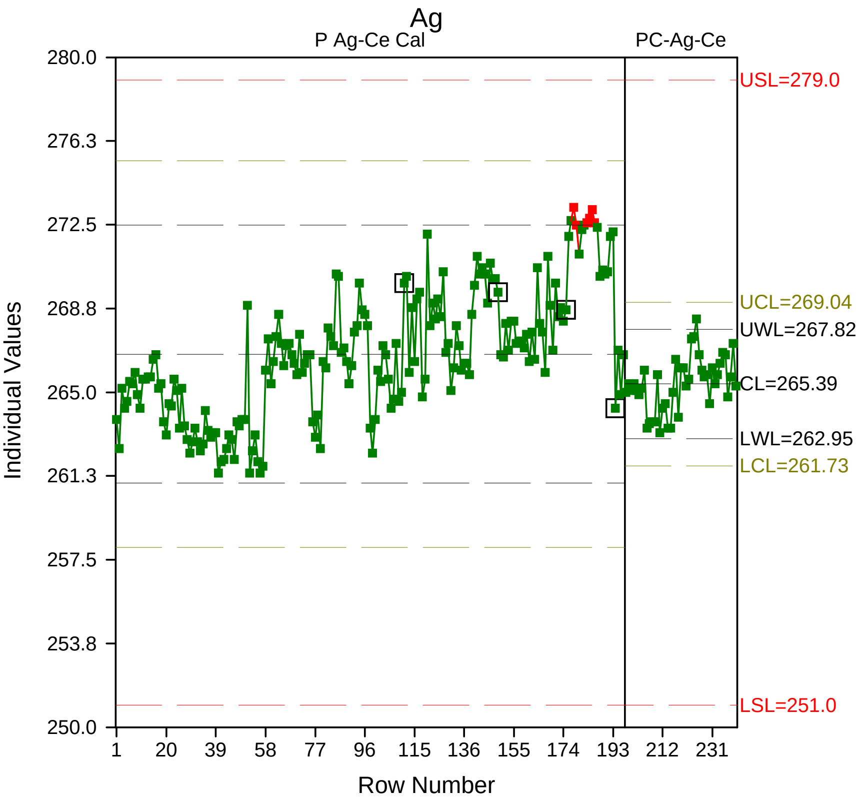
Total:	238
Rows:	All
Std Dev:	2.71
CpM:	N/A
CpK:	3.880
Est % out SL (Cap):	0.00
Act % out of SL:	0.00
Dist:	Normal
X-Bar:	266.48
Est Sigma:	2.71
Sigma Type:	N/A
MR-Bar:	1.22

Chart Point

Label:

X:
X UCL:
X CL:
X LCL:

MR:



Process Statistics

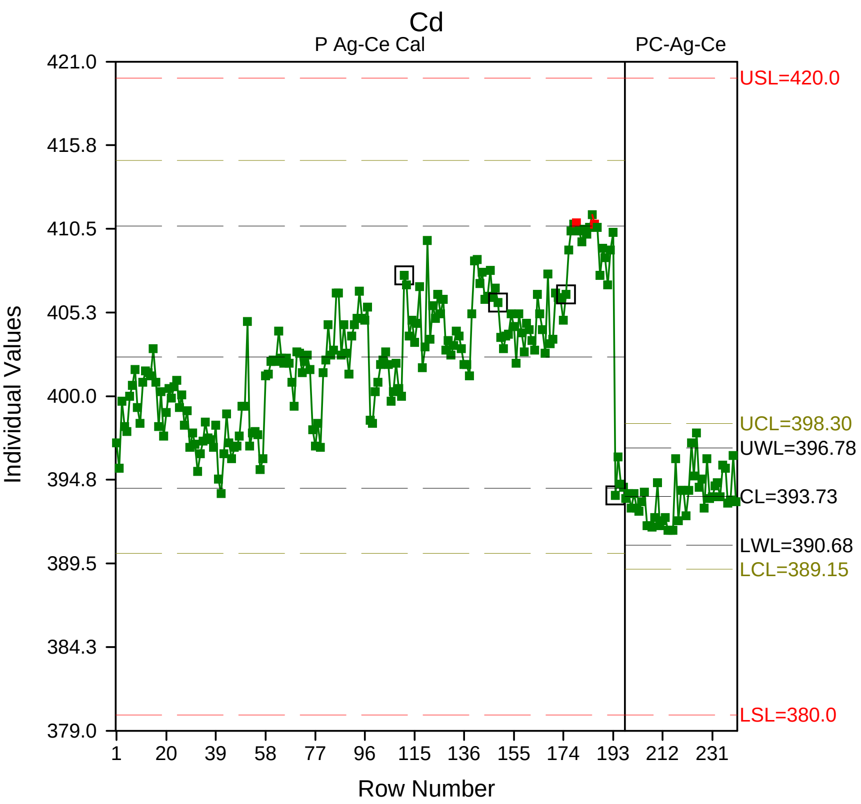
Total:	238
Rows:	All
Std Dev:	5.06
CpM:	N/A
CpK:	4.599
Est % out SL (Cap):	0.00
Act % out of SL:	0.00
Dist:	Normal
X-Bar:	400.90
Est Sigma:	5.06
Sigma Type:	N/A
MR-Bar:	1.56

Chart Point

Label:

X:
X UCL:
X CL:
X LCL:

MR:



Process Statistics

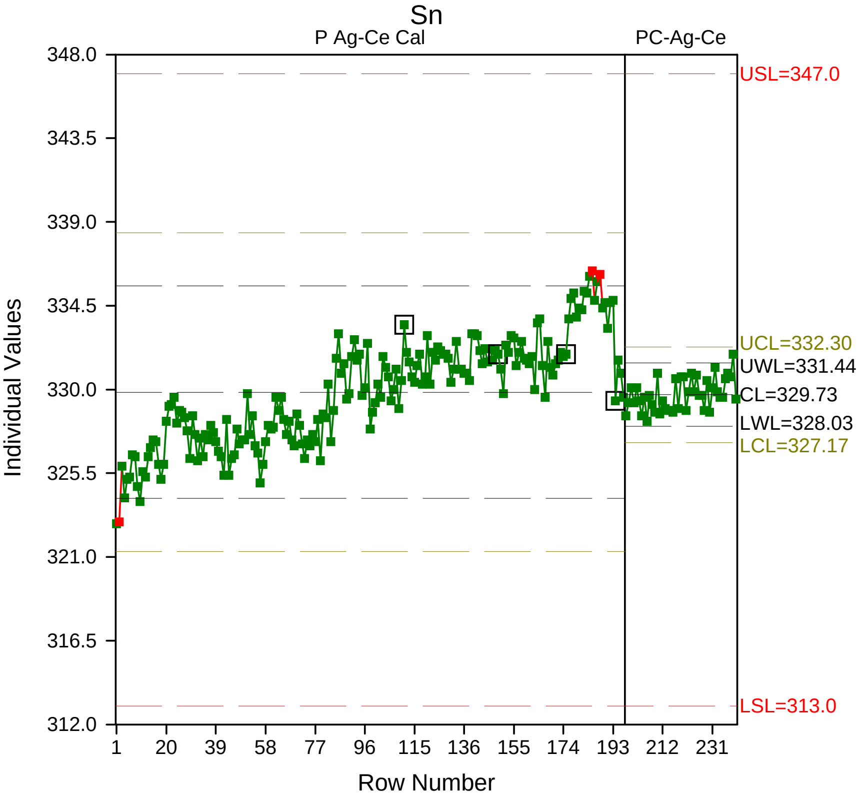
Total:	238
Rows:	All
Std Dev:	2.61
CpM:	N/A
CpK:	6.148
Est % out SL (Cap):	0.00
Act % out of SL:	0.00
Dist:	Normal
X-Bar:	329.85
Est Sigma:	2.61
Sigma Type:	N/A
MR-Bar:	1.03

Chart Point

Label:

X:
X UCL:
X CL:
X LCL:

MR:



Process Statistics

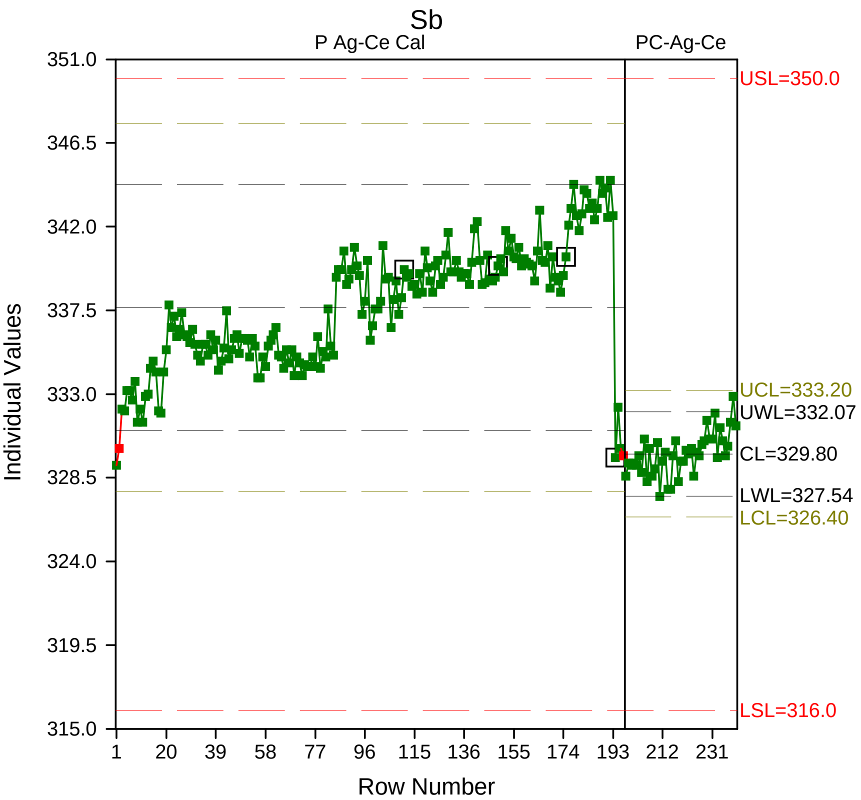
Total:	238
Rows:	All
Std Dev:	4.28
CpM:	N/A
CpK:	5.030
Est % out SL (Cap):	0.00
Act % out SL:	0.00
Dist:	Normal
X-Bar:	336.25
Est Sigma:	4.28
Sigma Type:	N/A
MR-Bar:	1.03

Chart Point

Label:

X:
X UCL:
X CL:
X LCL:

MR:

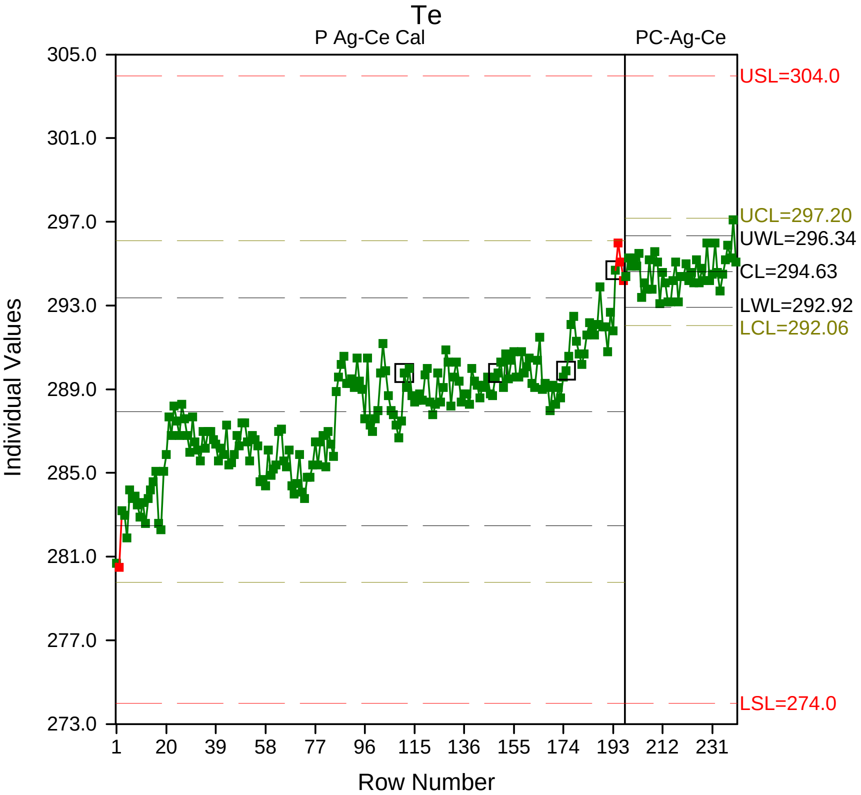


Process Statistics

Total:	238
Rows:	All
Std Dev:	3.58
CpM:	N/A
CpK:	6.164
Est % out SL (Cap):	0.00
Act % out of SL:	0.00
Dist:	Normal
X-Bar:	289.15
Est Sigma:	3.58
Sigma Type:	N/A
MR-Bar:	0.90

Chart Point

Label:
X:
X UCL:
X CL:
X LCL:
MR:

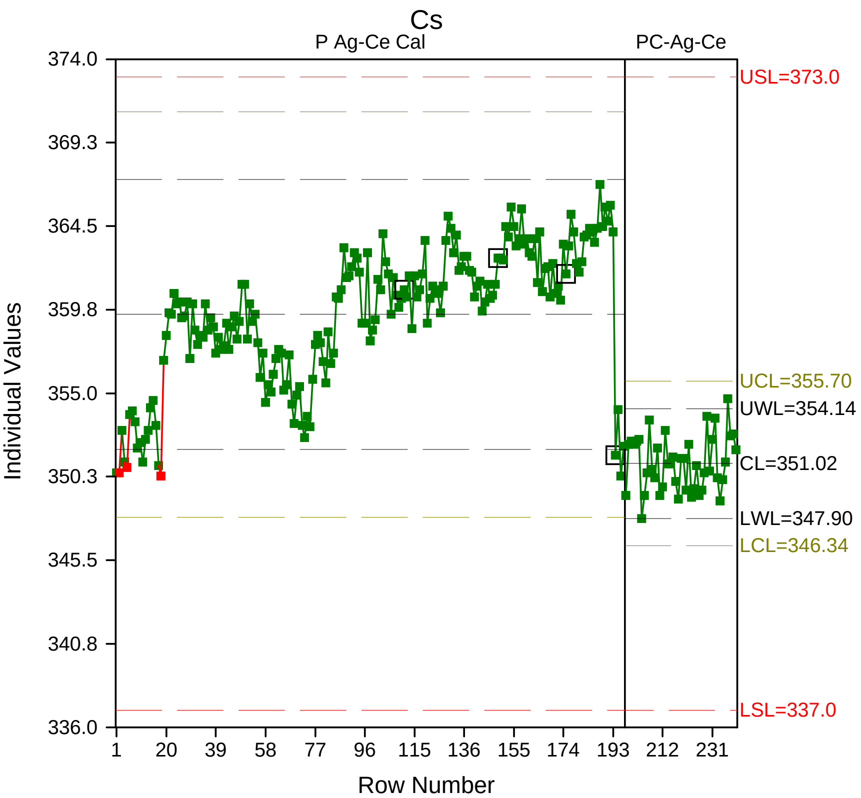


Process Statistics

Total:	238
Rows:	All
Std Dev:	4.82
CpM:	N/A
CpK:	4.077
Est % out SL (Cap):	0.00
Act % out of SL:	0.00
Dist:	Normal
X-Bar:	357.97
Est Sigma:	4.82
Sigma Type:	N/A
MR-Bar:	1.39

Chart Point

Label:
X:
X UCL:
X CL:
X LCL:
MR:



Process Statistics

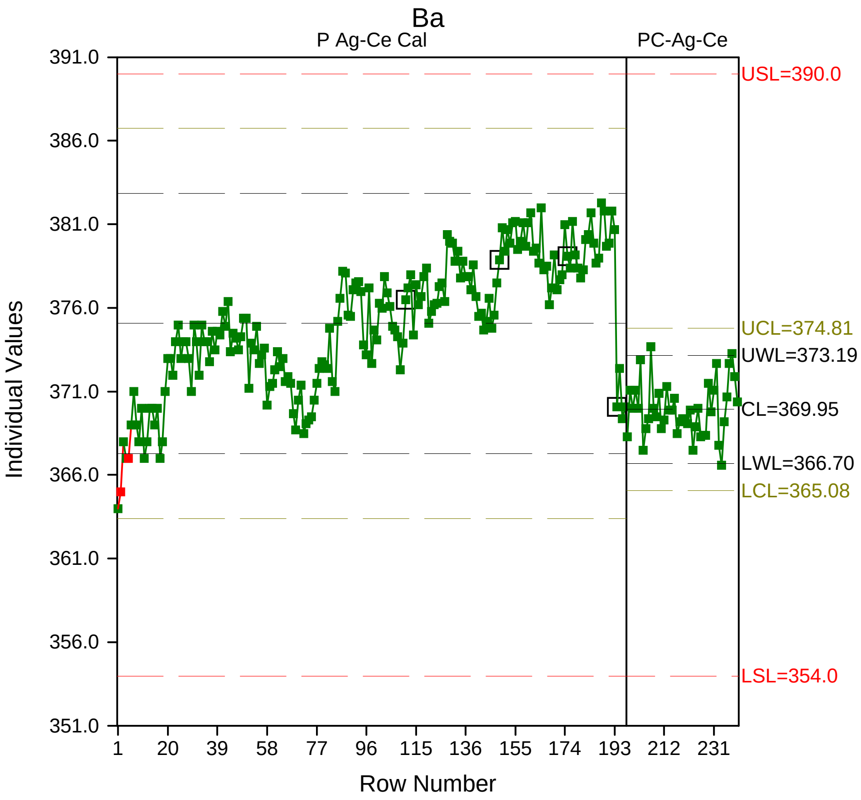
Total:	238
Rows:	All
Std Dev:	4.10
CpM:	N/A
CpK:	4.165
Est % out SL (Cap):	0.00
Act % out of SL:	0.00
Dist:	Normal
X-Bar:	374.16
Est Sigma:	4.10
Sigma Type:	N/A
MR-Bar:	1.43

Chart Point

Label:

X:
X UCL:
X CL:
X LCL:

MR:



Process Statistics

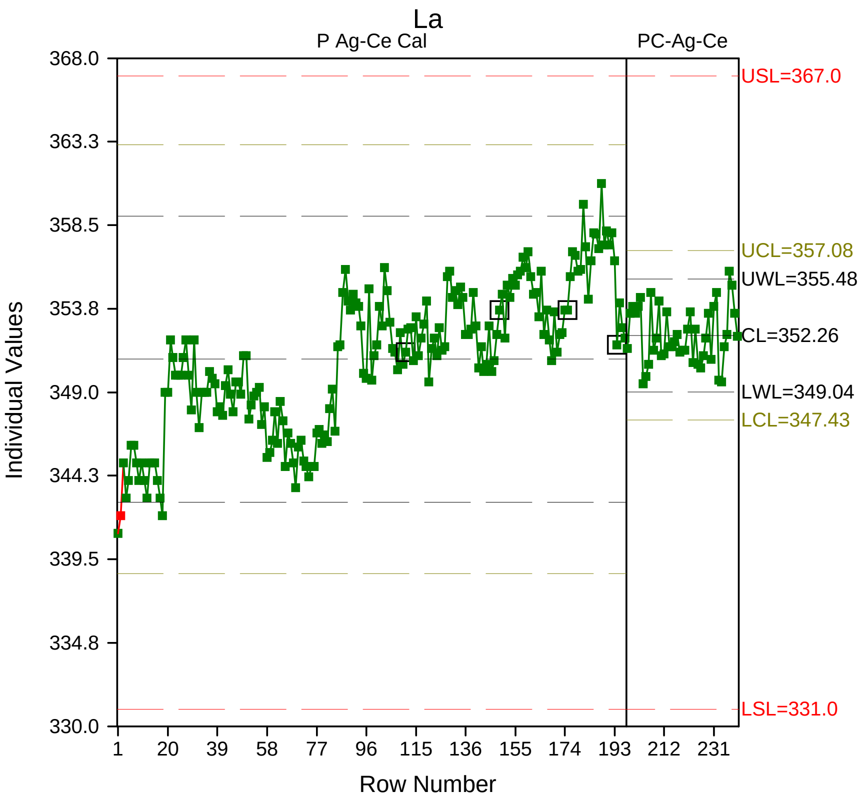
Total:	238
Rows:	All
Std Dev:	3.78
CpM:	N/A
CpK:	4.185
Est % out SL (Cap):	0.00
Act % out of SL:	0.00
Dist:	Normal
X-Bar:	351.15
Est Sigma:	3.78
Sigma Type:	N/A
MR-Bar:	1.42

Chart Point

Label:

X:
X UCL:
X CL:
X LCL:

MR:



Process Statistics

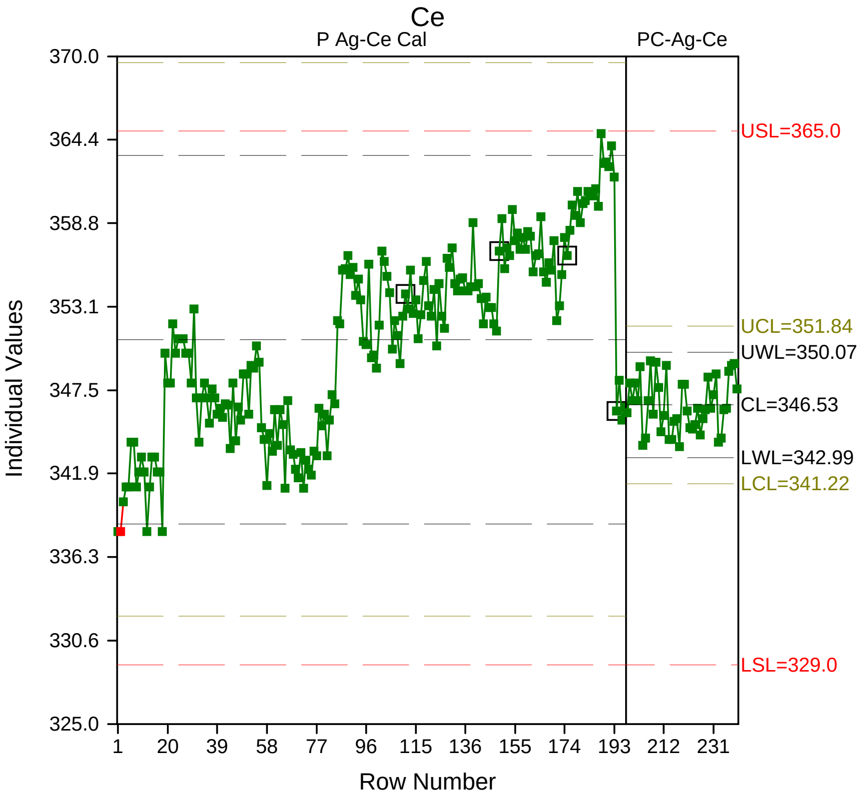
Total:	238
Rows:	All
Std Dev:	5.92
CpM:	N/A
CpK:	2.971
Est % out SL (Cap):	0.00
Act % out of SL:	0.00
Dist:	Normal
X-Bar:	350.13
Est Sigma:	5.92
Sigma Type:	N/A
MR-Bar:	1.88

Chart Point

Label:

X:
X UCL:
X CL:
X LCL:

MR:



Quality Control Charts QC BGS Low

Process Statistics

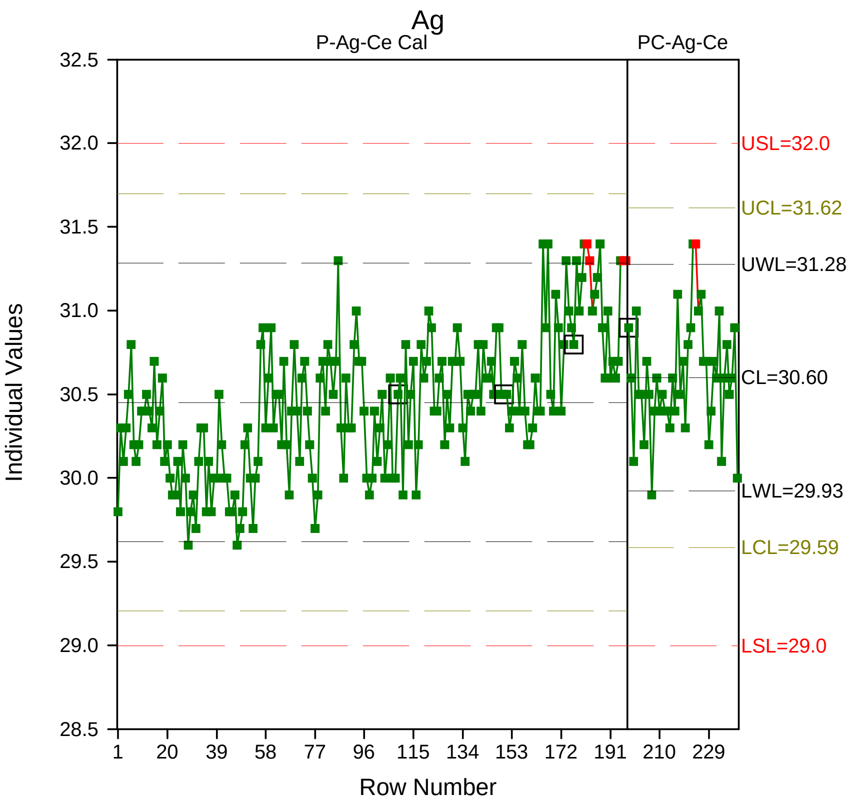
Total:	240
Rows:	All
Std Dev:	0.41
CpM:	N/A
CpK:	1.943
Est % out SL (Cap):	0.00
Act % out of SL:	0.00
Dist:	Normal
X-Bar:	30.48
Est Sigma:	0.41
Sigma Type:	N/A
MR-Bar:	0.29

Chart Point

Label:

X:
X UCL:
X CL:
X LCL:

MR:

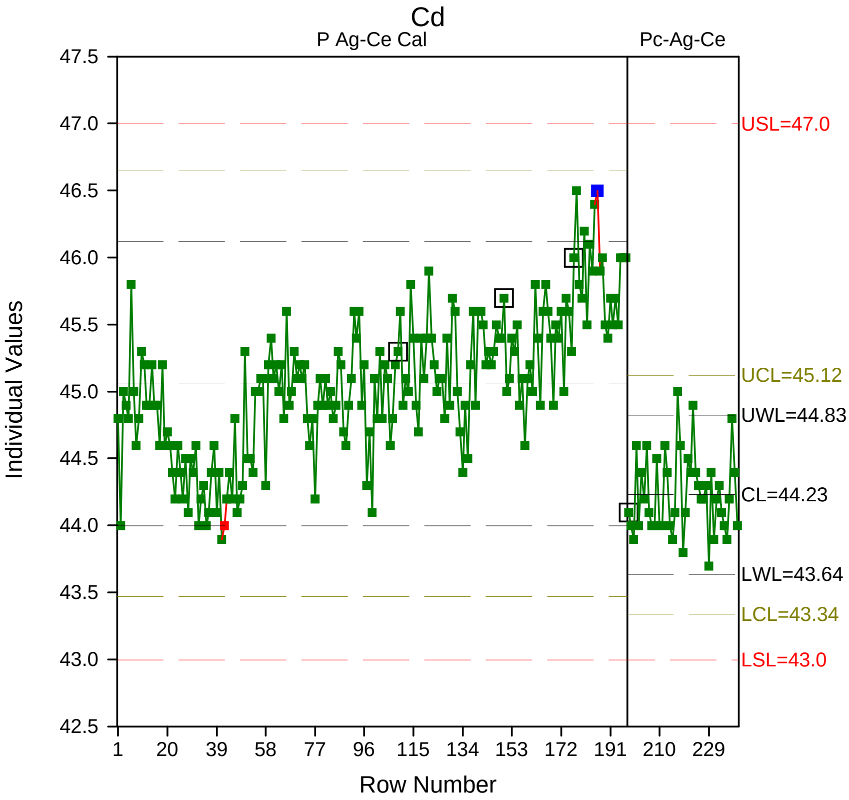


Process Statistics

Total:	240
Rows:	All
Std Dev:	0.59
CpM:	N/A
CpK:	2.100
Est % out SL (Cap):	0.00
Act % out SL:	0.00
Dist:	Normal
X-Bar:	44.91
Est Sigma:	0.59
Sigma Type:	N/A
MR-Bar:	0.35

Chart Point

Label:	
X:	
X UCL:	
X CL:	
X LCL:	
MR:	

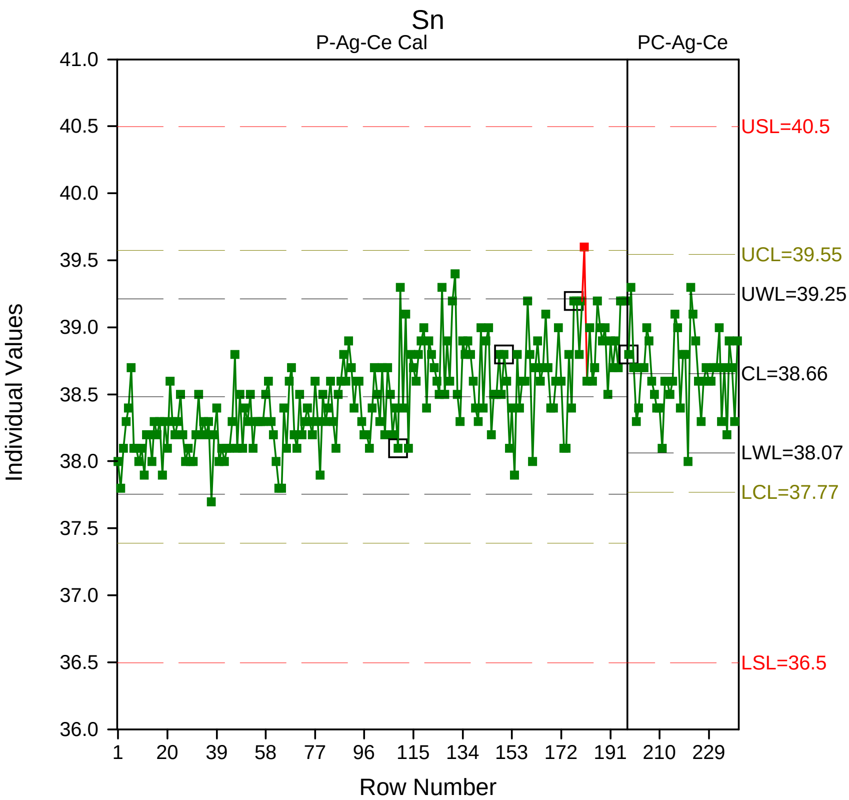


Process Statistics

Total:	240
Rows:	All
Std Dev:	0.36
CpM:	N/A
CpK:	2.505
Est % out SL (Cap):	0.00
Act % out of SL:	0.00
Dist:	Normal
X-Bar:	38.52
Est Sigma:	0.36
Sigma Type:	N/A
MR-Bar:	0.30

Chart Point

Label:	
X:	
X UCL:	
X CL:	
X LCL:	
MR:	



Process Statistics

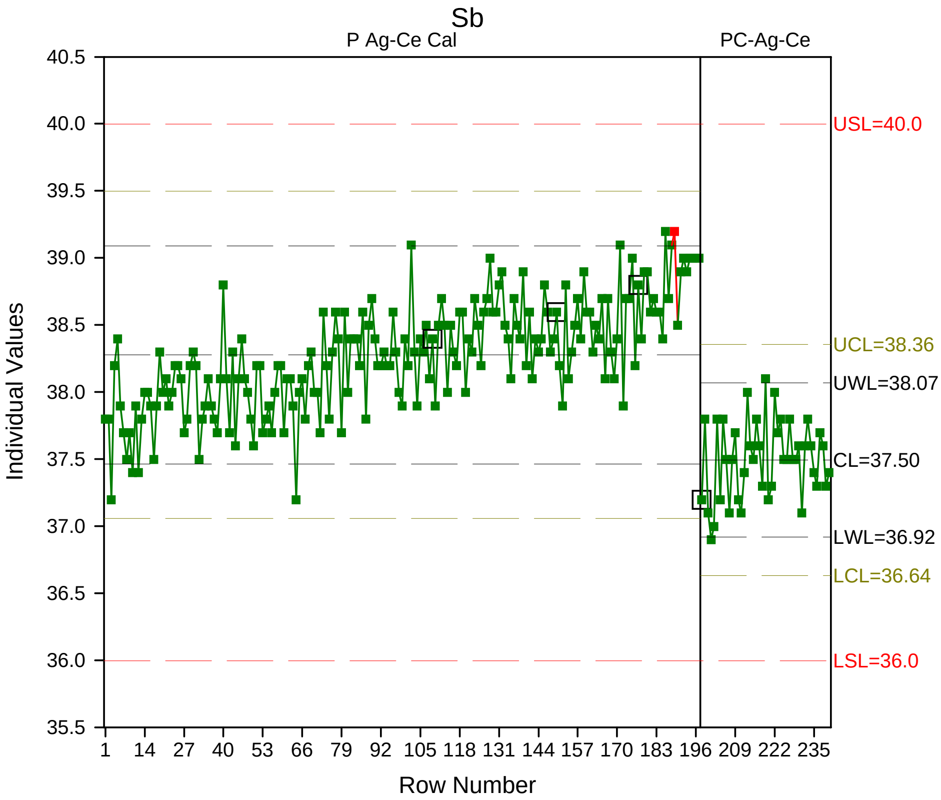
Total:	240
Rows:	All
Std Dev:	0.49
CpM:	N/A
CpK:	2.151
Est % out SL (Cap):	0.00
Act % out SL:	0.00
Dist:	Normal
X-Bar:	38.14
Est Sigma:	0.49
Sigma Type:	N/A
MR-Bar:	0.33

Chart Point

Label:

X:
X UCL:
X CL:
X LCL:

MR:



Process Statistics

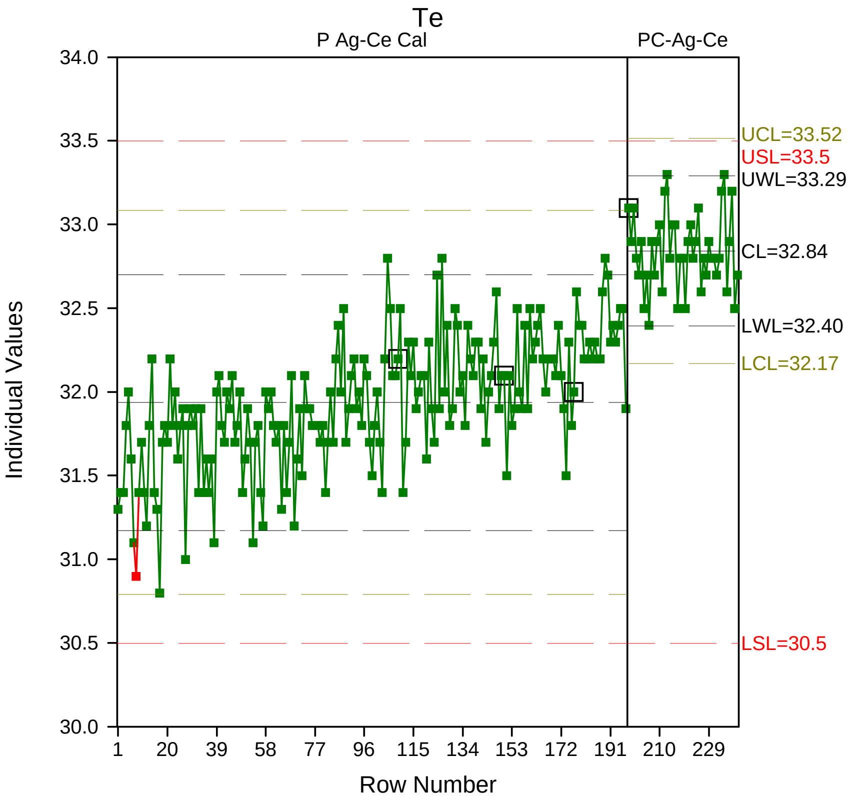
Total:	240
Rows:	All
Std Dev:	0.50
CpM:	N/A
CpK:	1.721
Est % out SL (Cap):	0.00
Act % out SL:	0.00
Dist:	Normal
X-Bar:	32.10
Est Sigma:	0.50
Sigma Type:	N/A
MR-Bar:	0.31

Chart Point

Label:

X:
X UCL:
X CL:
X LCL:

MR:



Process Statistics

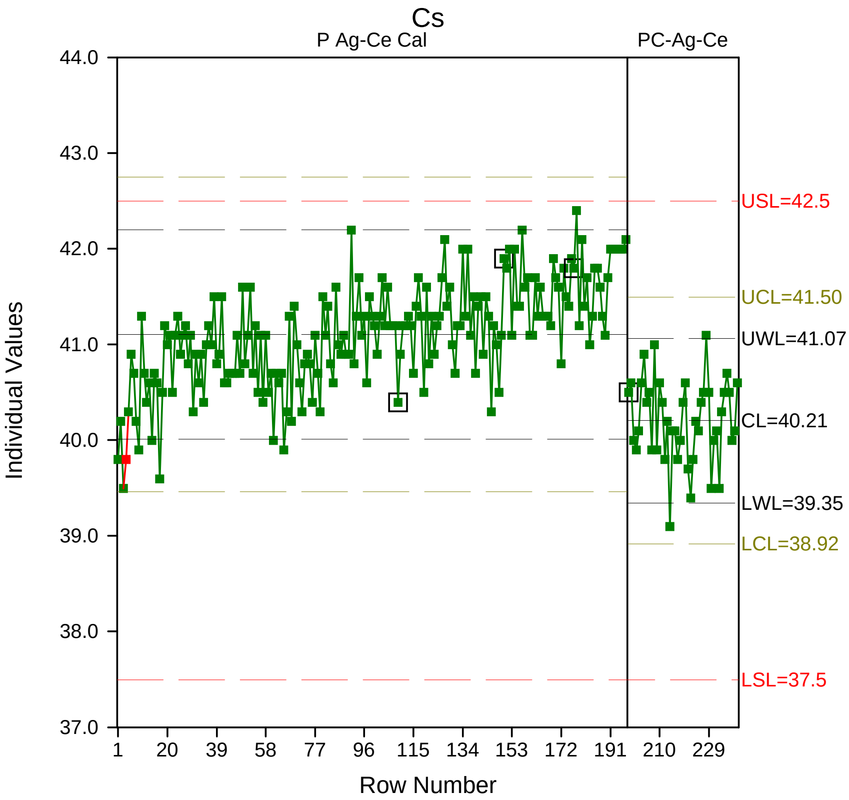
Total:	240
Rows:	All
Std Dev:	0.63
CpM:	N/A
CpK:	1.284
Est % out SL (Cap):	0.01
Act % out of SL:	0.00
Dist:	Normal
X-Bar:	40.95
Est Sigma:	0.63
Sigma Type:	N/A
MR-Bar:	0.46

Chart Point

Label:

X:
X UCL:
X CL:
X LCL:

MR:



Process Statistics

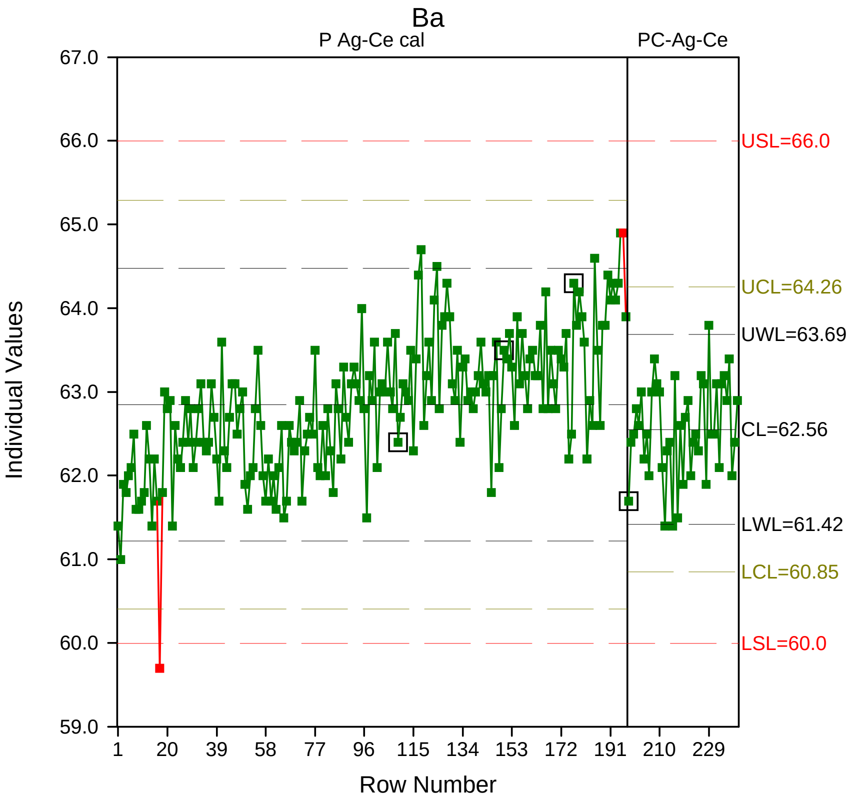
Total:	240
Rows:	All
Std Dev:	0.78
CpM:	N/A
CpK:	1.703
Est % out SL (Cap):	0.00
Act % out of SL:	0.42
Dist:	Normal
X-Bar:	62.80
Est Sigma:	0.78
Sigma Type:	N/A
MR-Bar:	0.62

Chart Point

Label:

X:
X UCL:
X CL:
X LCL:

MR:



Process Statistics

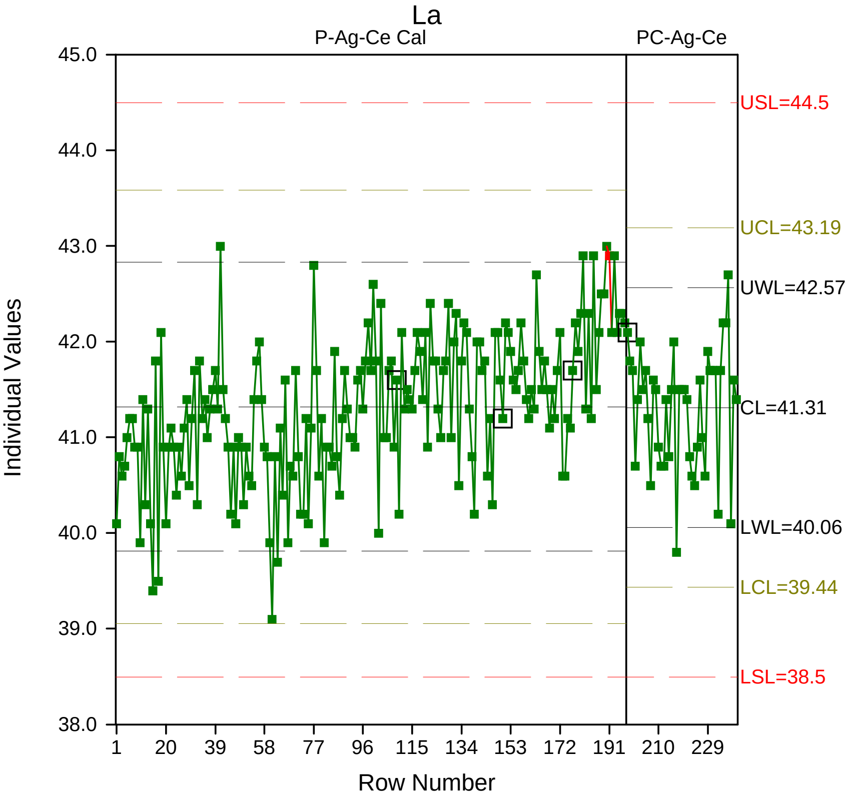
Total:	240
Rows:	All
Std Dev:	0.73
CpM:	N/A
CpK:	1.595
Est % out SL (Cap):	0.00
Act % out of SL:	0.00
Dist:	Normal
X-Bar:	41.32
Est Sigma:	0.73
Sigma Type:	N/A
MR-Bar:	0.66

Chart Point

Label:

X:
X UCL:
X CL:
X LCL:

MR:



Process Statistics

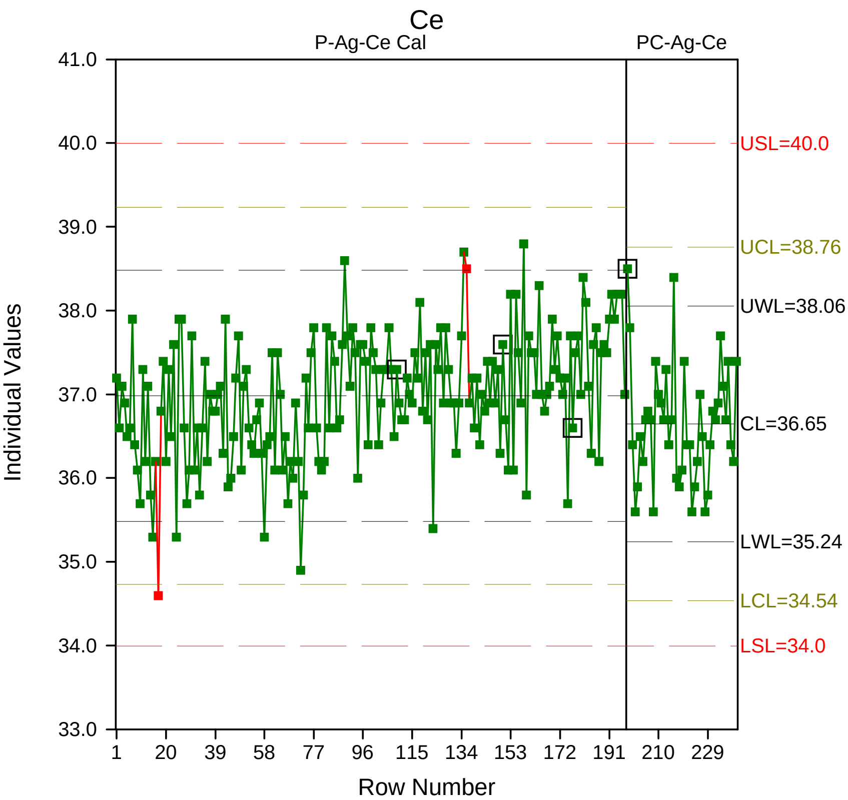
Total:	240
Rows:	All
Std Dev:	0.75
CpM:	N/A
CpK:	1.460
Est % out SL (Cap):	0.00
Act % out SL:	0.00
Dist:	Normal
X-Bar:	36.93
Est Sigma:	0.75
Sigma Type:	N/A
MR-Bar:	0.76

Chart Point

Label:

X:
X UCL:
X CL:
X LCL:

MR:



Quality Control Charts QC BGSMON

Process Statistics

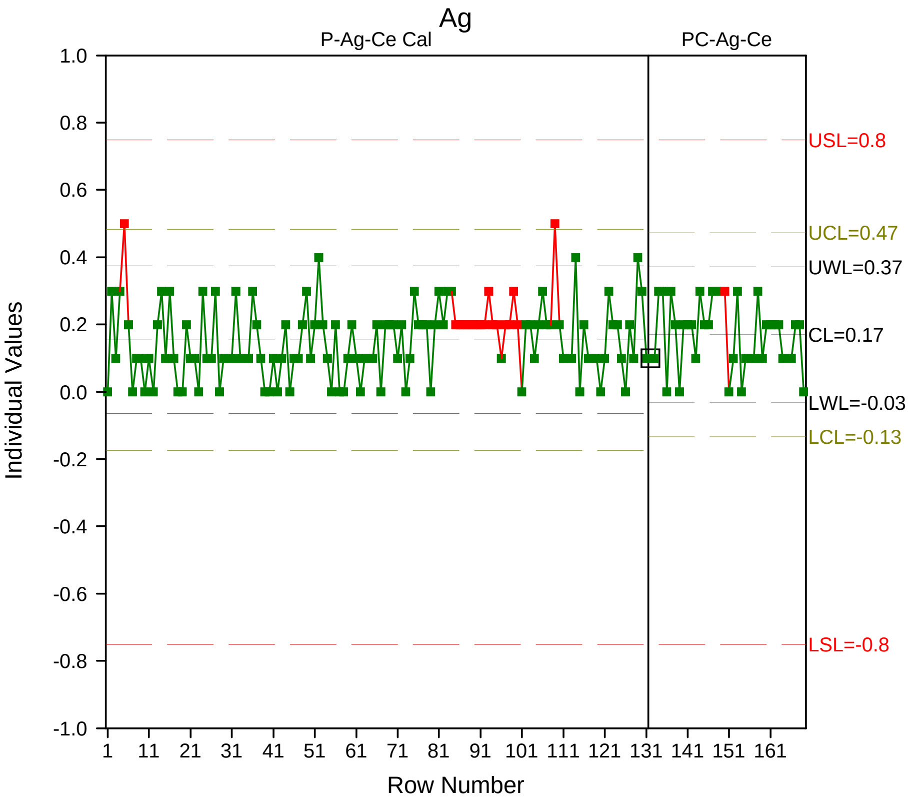
Total:	169
Rows:	All
Std Dev:	0.11
CpM:	N/A
CpK:	2.017
Est % out SL (Cap):	0.00
Act % out of SL:	0.00
Dist:	Normal
X-Bar:	0.16
Est Sigma:	0.11
Sigma Type:	N/A
MR-Bar:	0.11

Chart Point

Label:

X:
X UCL:
X CL:
X LCL:

MR:



Process Statistics

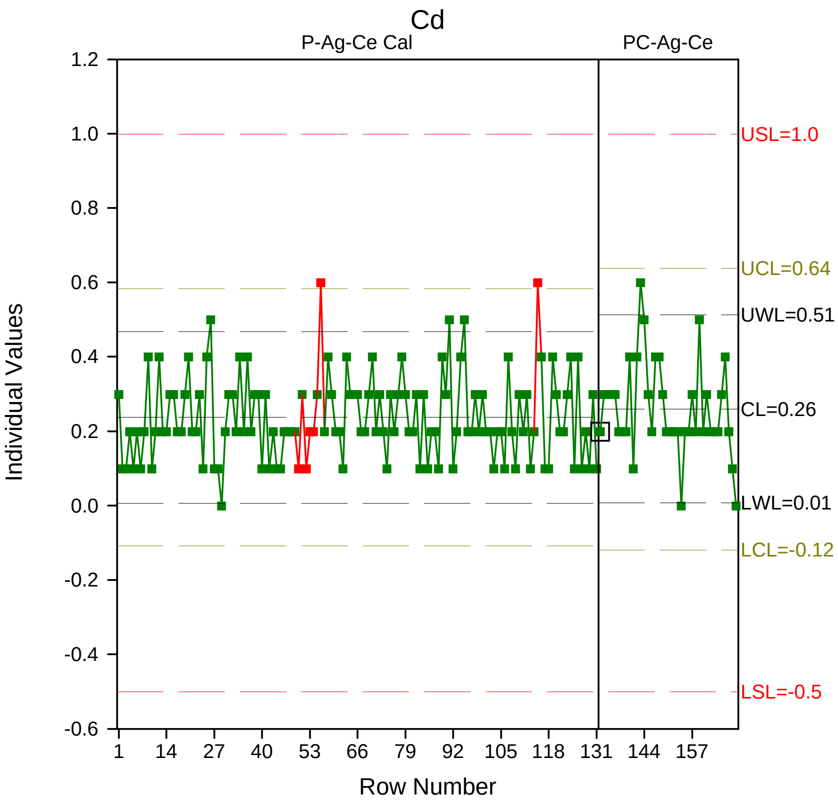
Total:	169
Rows:	All
Std Dev:	0.12
CpM:	N/A
CpK:	2.202
Est % out SL (Cap):	0.00
Act % out of SL:	0.00
Dist:	Normal
X-Bar:	0.24
Est Sigma:	0.12
Sigma Type:	N/A
MR-Bar:	0.13

Chart Point

Label:

X:
X UCL:
X CL:
X LCL:

MR:



Process Statistics

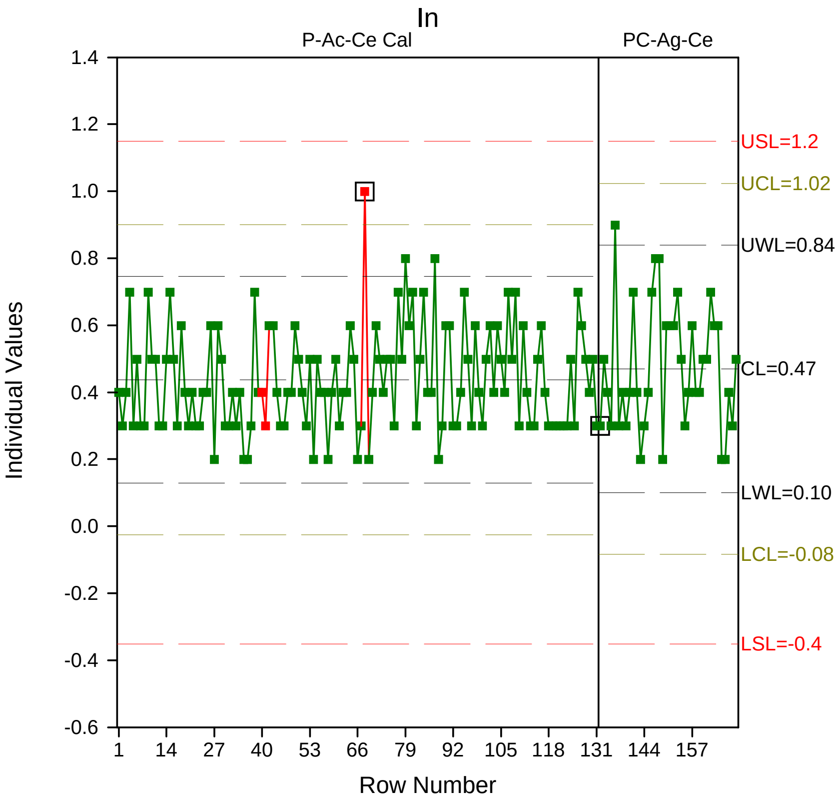
Total:	169
Rows:	All
Std Dev:	0.16
CpM:	N/A
CpK:	1.519
Est % out SL (Cap):	0.00
Act % out of SL:	0.00
Dist:	Normal
X-Bar:	0.45
Est Sigma:	0.16
Sigma Type:	N/A
MR-Bar:	0.17

Chart Point

Label:

X:
X UCL:
X CL:
X LCL:

MR:



Process Statistics

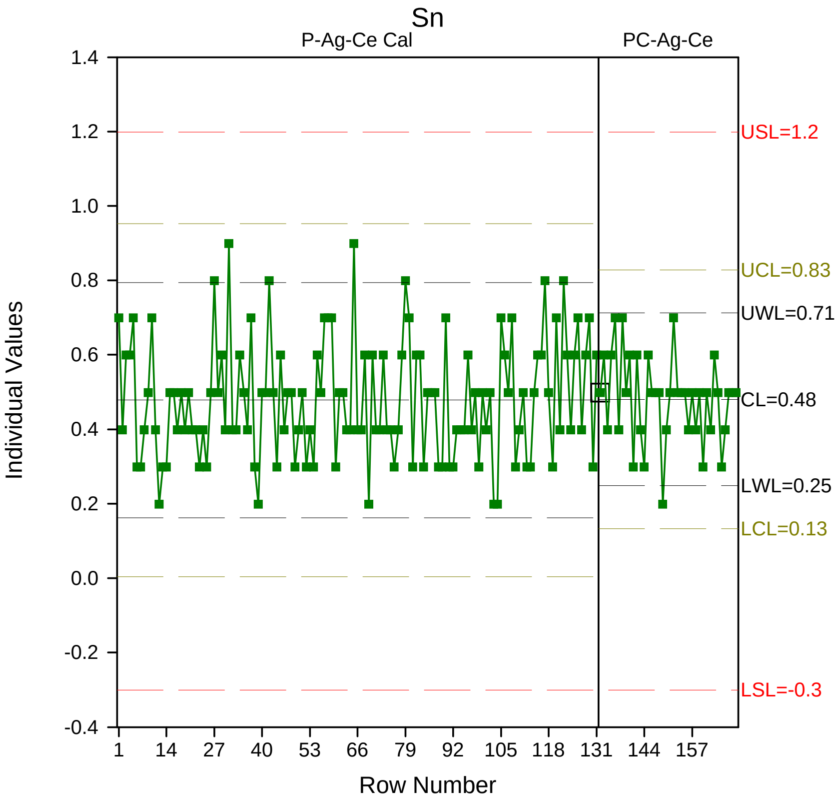
Total:	169
Rows:	All
Std Dev:	0.15
CpM:	N/A
CpK:	1.598
Est % out SL (Cap):	0.00
Act % out of SL:	0.00
Dist:	Normal
X-Bar:	0.48
Est Sigma:	0.15
Sigma Type:	N/A
MR-Bar:	0.17

Chart Point

Label:

X:
X UCL:
X CL:
X LCL:

MR:

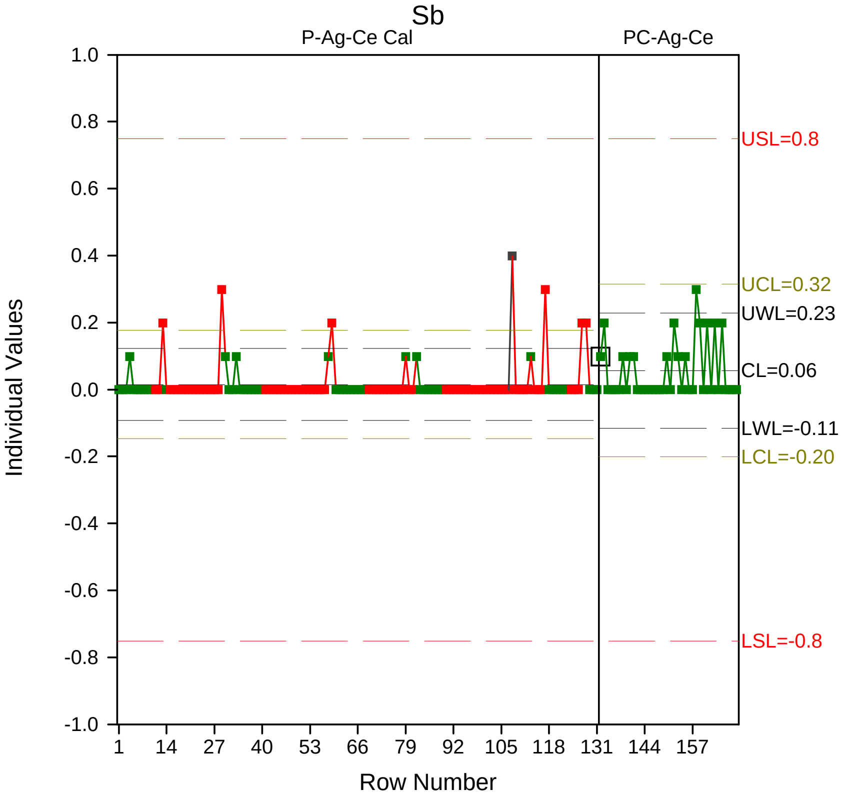


Process Statistics

Total:	168
Rows:	All
Std Dev:	0.06
CpM:	N/A
CpK:	6.751
Est % out SL (Cap):	0.00
Act % out SL:	0.00
Dist:	Normal
X-Bar:	0.03
Est Sigma:	0.06
Sigma Type:	N/A
MR-Bar:	0.04

Chart Point

Label:	
X:	
X UCL:	
X CL:	
X LCL:	
MR:	

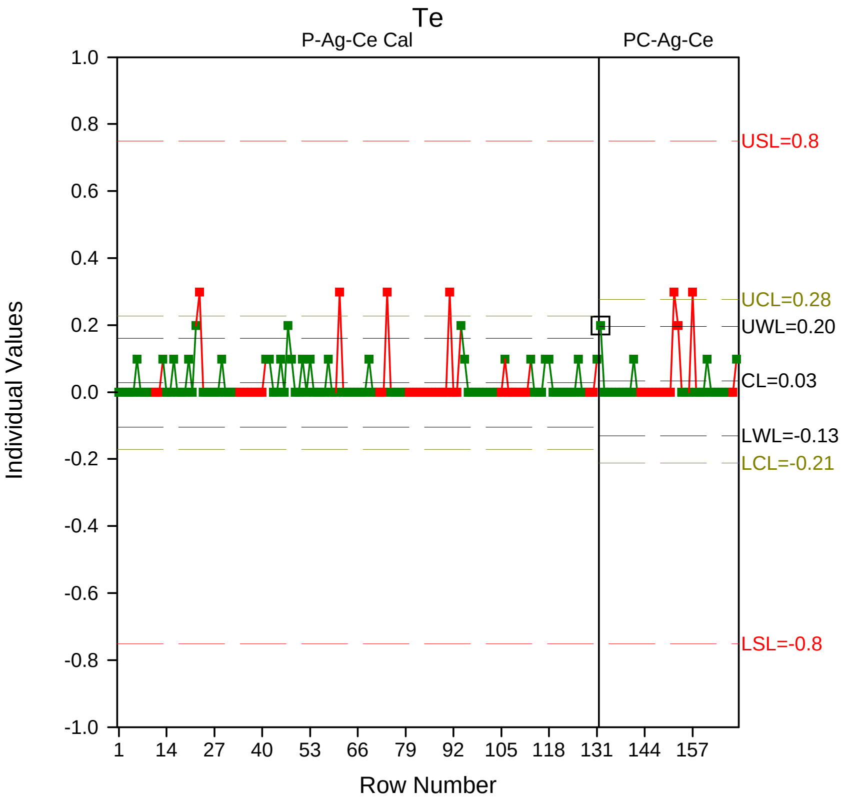


Process Statistics

Total:	169
Rows:	All
Std Dev:	0.07
CpM:	N/A
CpK:	5.514
Est % out SL (Cap):	0.00
Act % out SL:	0.00
Dist:	Normal
X-Bar:	0.03
Est Sigma:	0.07
Sigma Type:	N/A
MR-Bar:	0.05

Chart Point

Label:	
X:	
X UCL:	
X CL:	
X LCL:	
MR:	

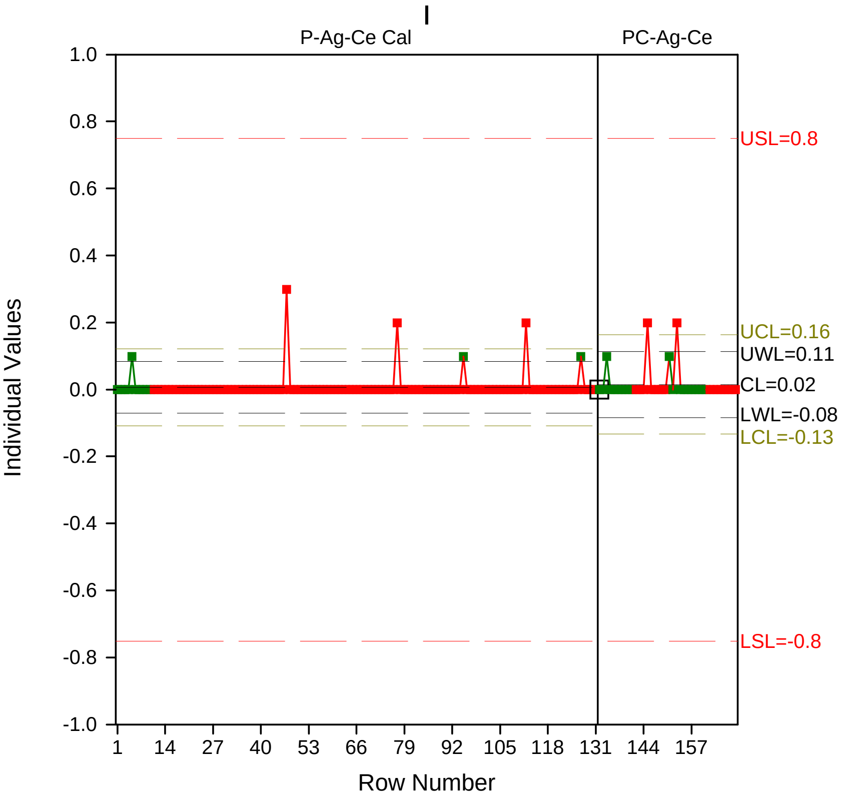


Process Statistics

Total:	169
Rows:	All
Std Dev:	0.04
CpM:	N/A
CpK:	14.536
Est % out SL (Cap):	0.00
Act % out SL:	0.00
Dist:	Normal
X-Bar:	0.01
Est Sigma:	0.04
Sigma Type:	N/A
MR-Bar:	0.02

Chart Point

Label:	
X:	
X UCL:	
X CL:	
X LCL:	
MR:	

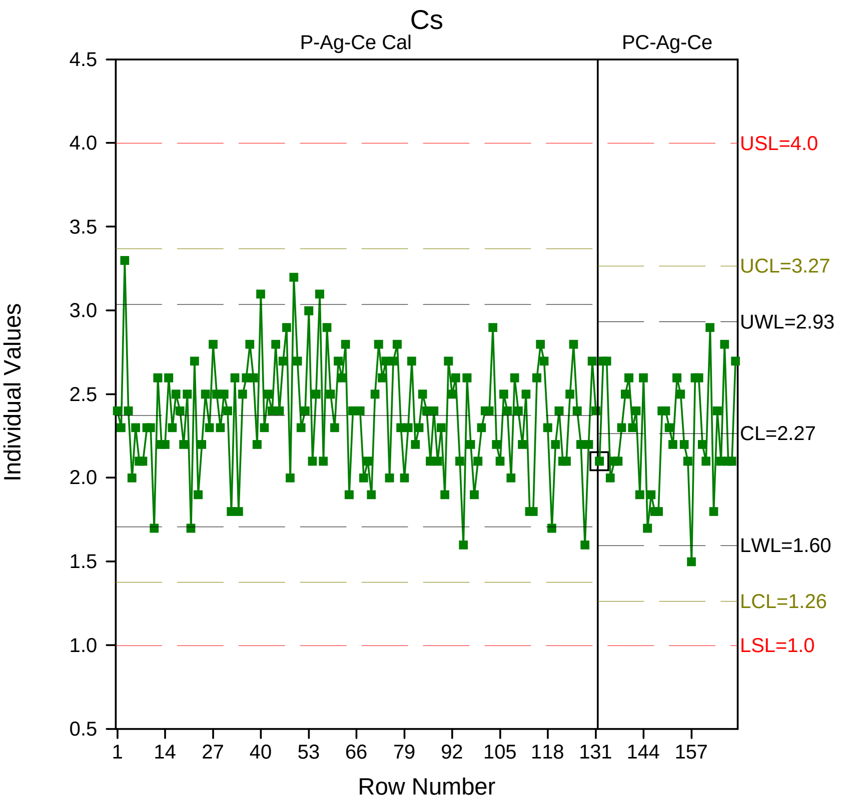


Process Statistics

Total:	169
Rows:	All
Std Dev:	0.33
CpM:	N/A
CpK:	1.324
Est % out SL (Cap):	0.00
Act % out of SL:	0.00
Dist:	Normal
X-Bar:	2.35
Est Sigma:	0.33
Sigma Type:	N/A
MR-Bar:	0.38

Chart Point

Label:	
X:	
X UCL:	
X CL:	
X LCL:	
MR:	



Process Statistics

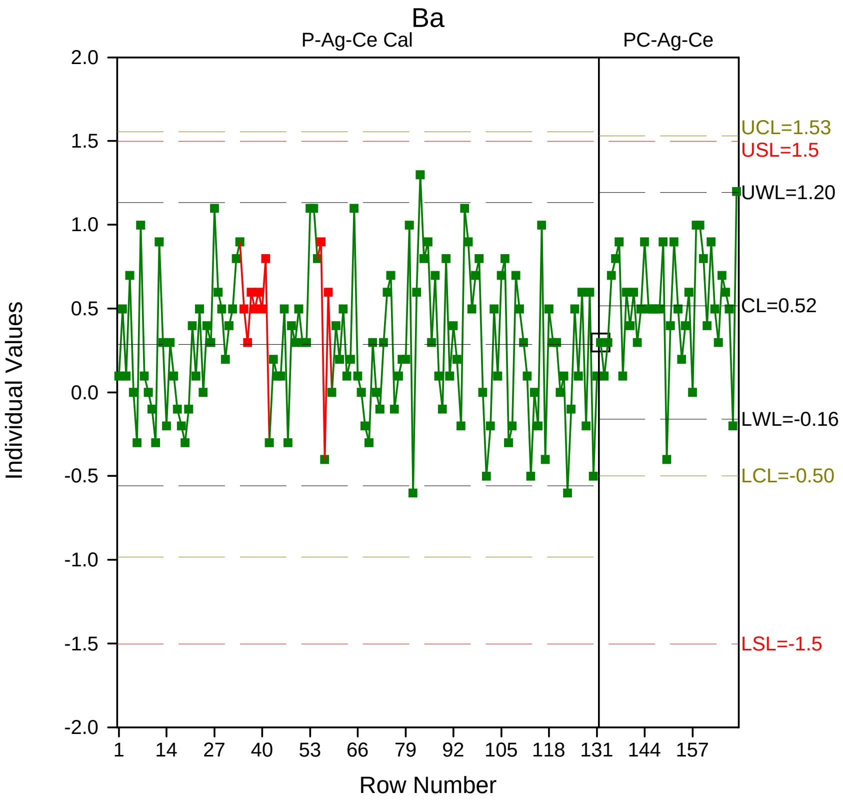
Total:	169
Rows:	All
Std Dev:	0.42
CpM:	N/A
CpK:	1.004
Est % out SL (Cap):	0.13
Act % out of SL:	0.00
Dist:	Normal
X-Bar:	0.34
Est Sigma:	0.42
Sigma Type:	N/A
MR-Bar:	0.43

Chart Point

Label:

X:
X UCL:
X CL:
X LCL:

MR:



Process Statistics

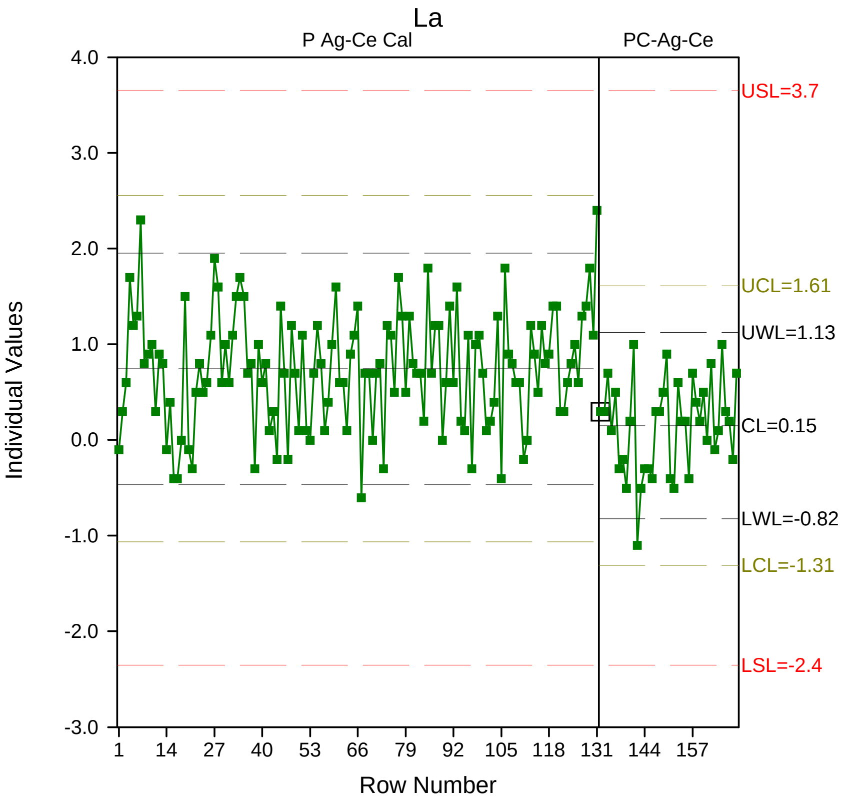
Total:	169
Rows:	All
Std Dev:	0.63
CpM:	N/A
CpK:	1.860
Est % out SL (Cap):	0.00
Act % out of SL:	0.00
Dist:	Normal
X-Bar:	0.61
Est Sigma:	0.63
Sigma Type:	N/A
MR-Bar:	0.61

Chart Point

Label:

X:
X UCL:
X CL:
X LCL:

MR:

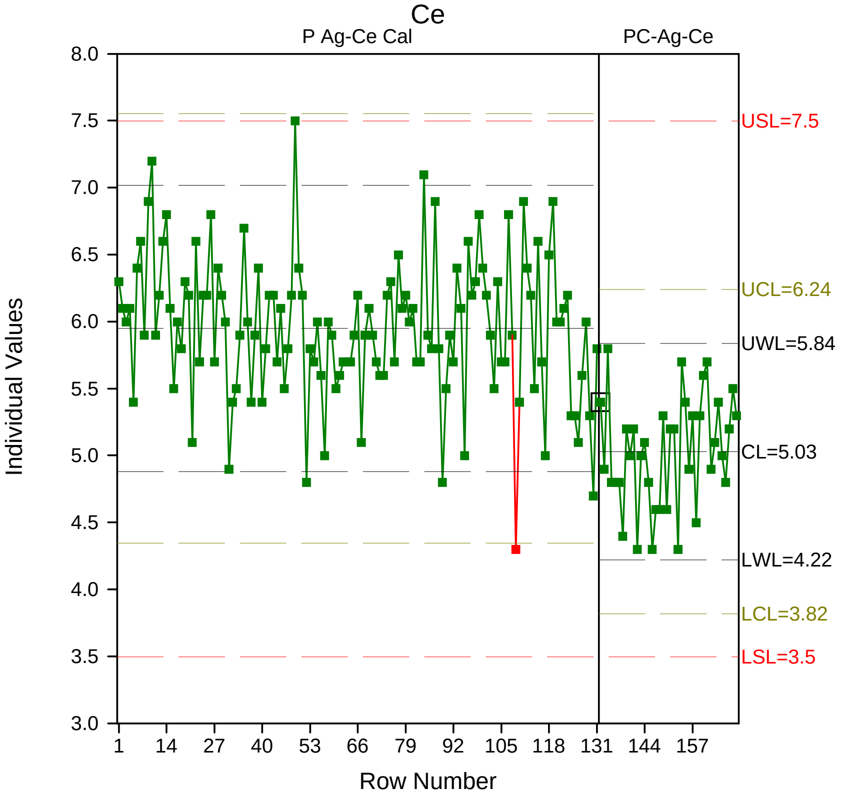


Process Statistics

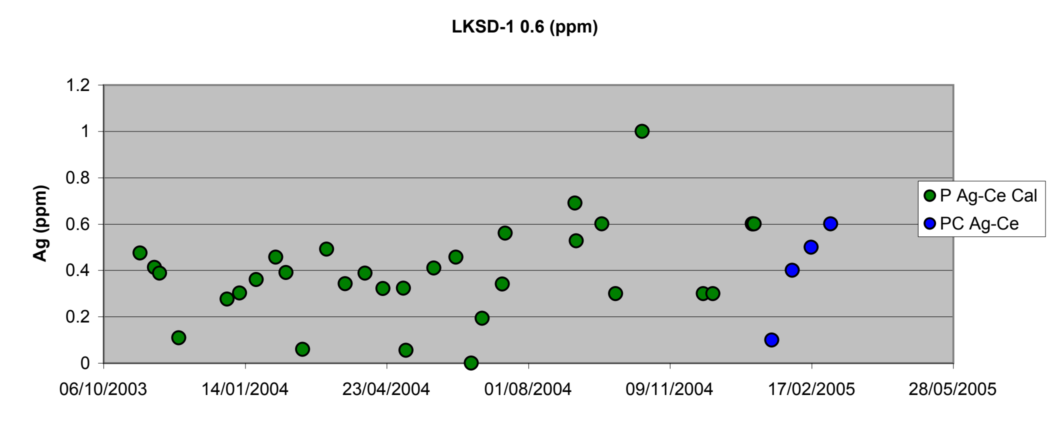
Total:	169
Rows:	All
Std Dev:	0.64
CpM:	N/A
CpK:	1.238
Est % out SL (Cap):	0.01
Act % out of SL:	0.00
Dist:	Normal
X-Bar:	5.75
Est Sigma:	0.64
Sigma Type:	N/A
MR-Bar:	0.53

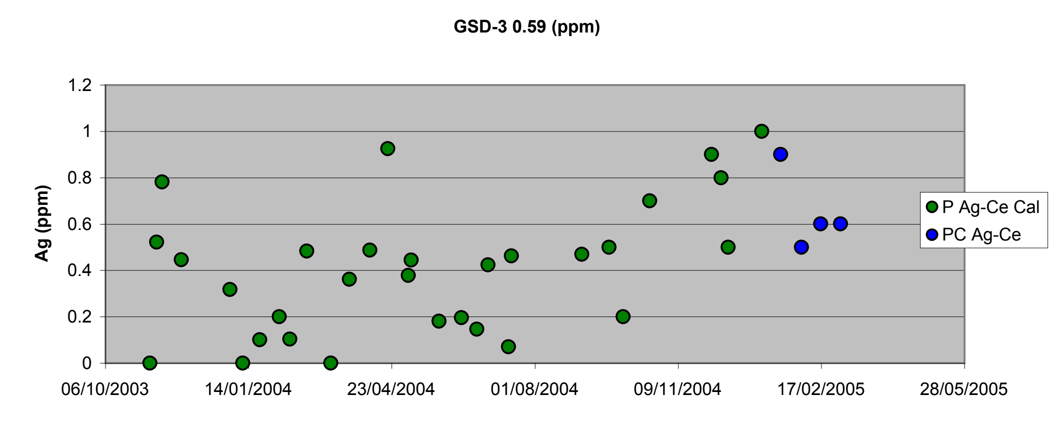
Chart Point

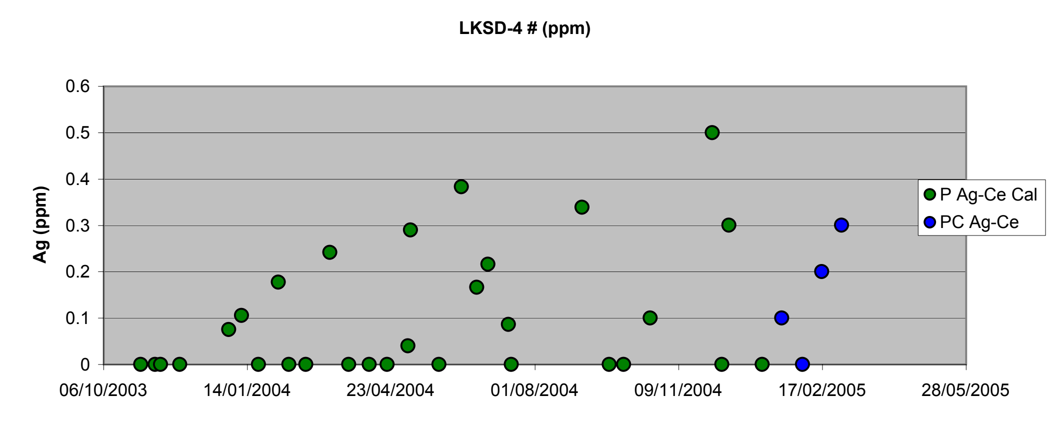
Label:	
X:	
X UCL:	
X CL:	
X LCL:	
MR:	

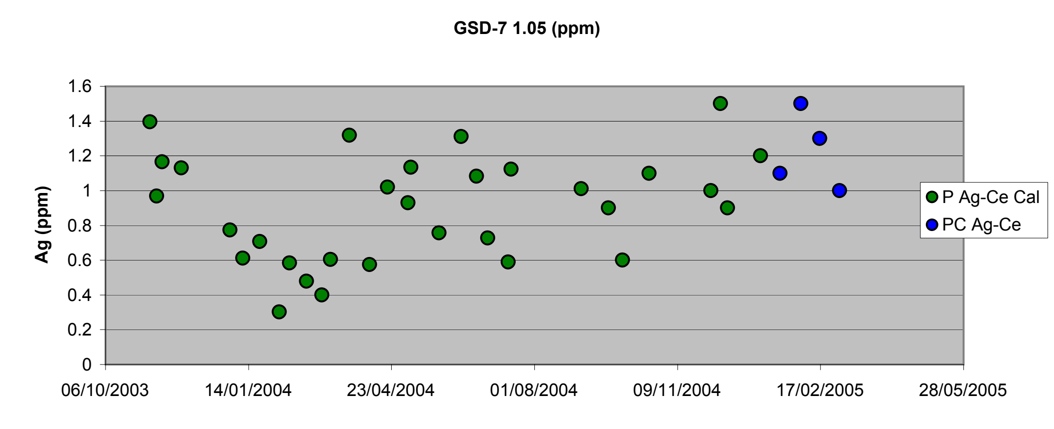


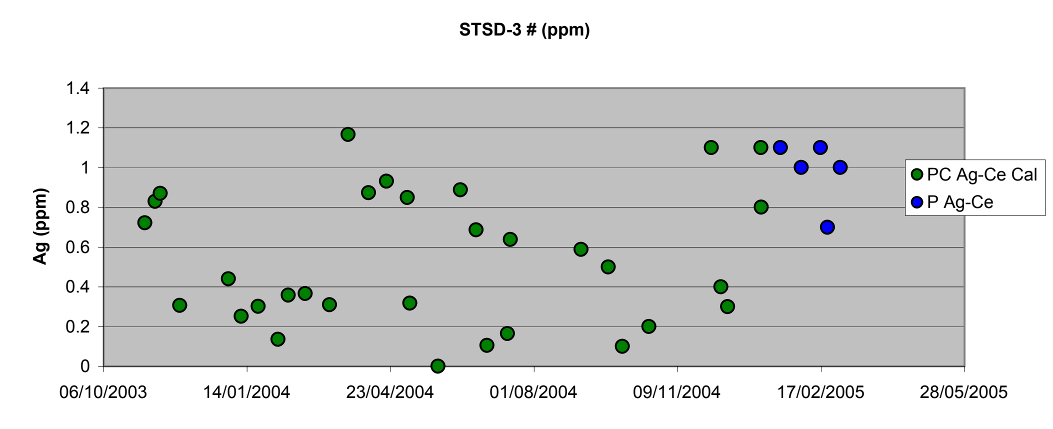
APPENDIX 12 – Reproducibility

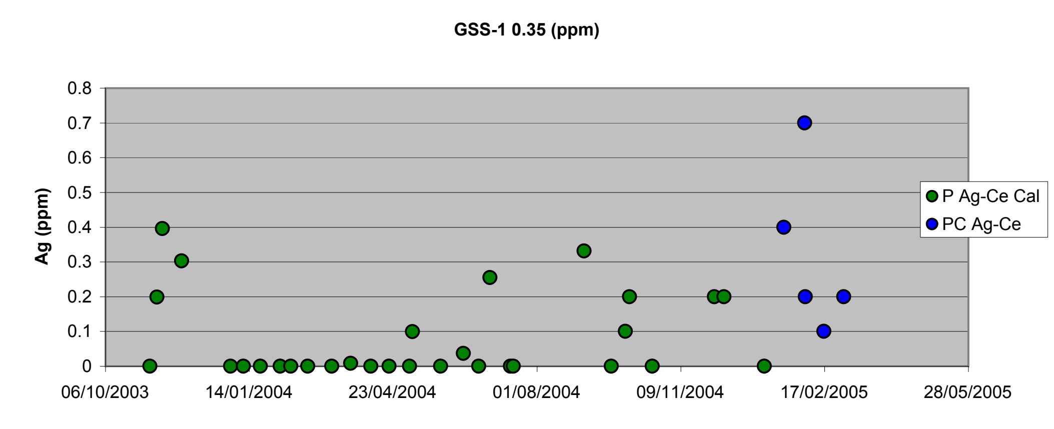

LKSD-1 0.6 (ppm)
Ag (ppm)
P Ag-Ce Cal
PC Ag-Ce
1.2
1
0.8
0.6
0.4
0.2
0
06/10/2003
14/01/2004
23/04/2004
01/08/2004
09/11/2004
17/02/2005
28/05/2005

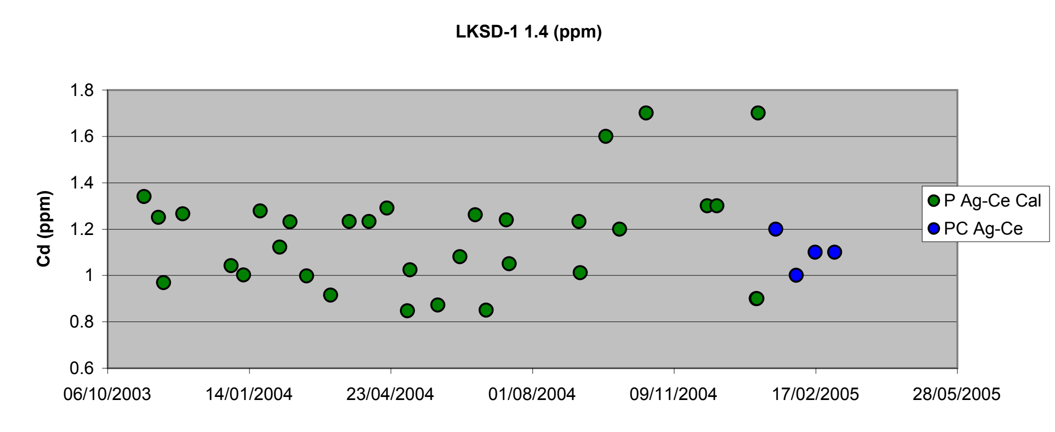

GSD-3 0.59 (ppm)
Ag (ppm)
P Ag-Ce Cal
PC Ag-Ce
1.2
1
0.8
0.6
0.4
0.2
0
06/10/2003
14/01/2004
23/04/2004
01/08/2004
09/11/2004
17/02/2005
28/05/2005

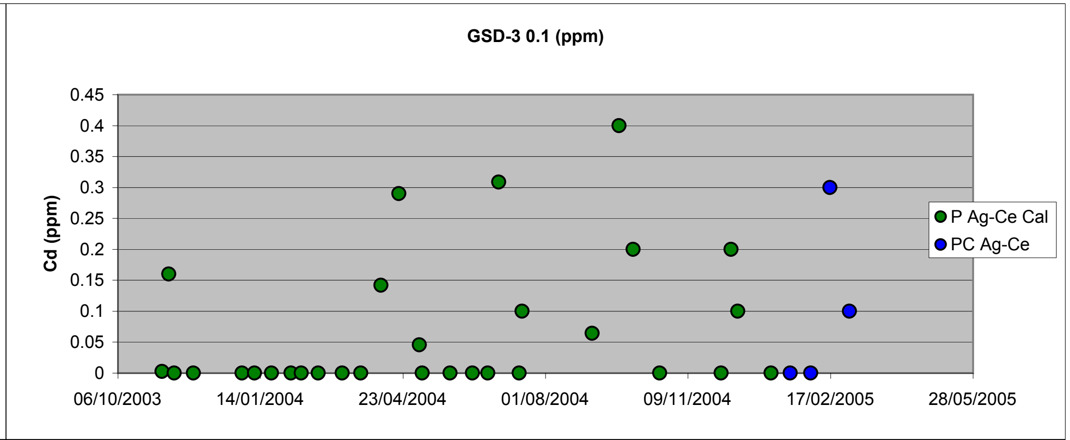

LKSD-4 # (ppm)
Ag (ppm)
P Ag-Ce Cal
PC Ag-Ce
0.6
0.5
0.4
0.3
0.2
0.1
0
06/10/2003
14/01/2004
23/04/2004
01/08/2004
09/11/2004
17/02/2005
28/05/2005

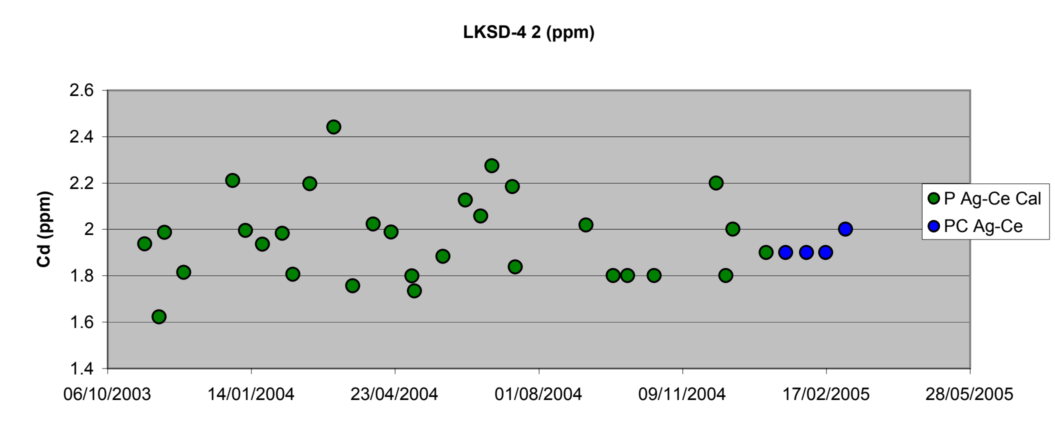

GSD-7 1.05 (ppm)
Ag (ppm)
P Ag-Ce Cal
PC Ag-Ce
1.6
1.4
1.2
1
0.8
0.6
0.4
0.2
0
06/10/2003
14/01/2004
23/04/2004
01/08/2004
09/11/2004
17/02/2005
28/05/2005

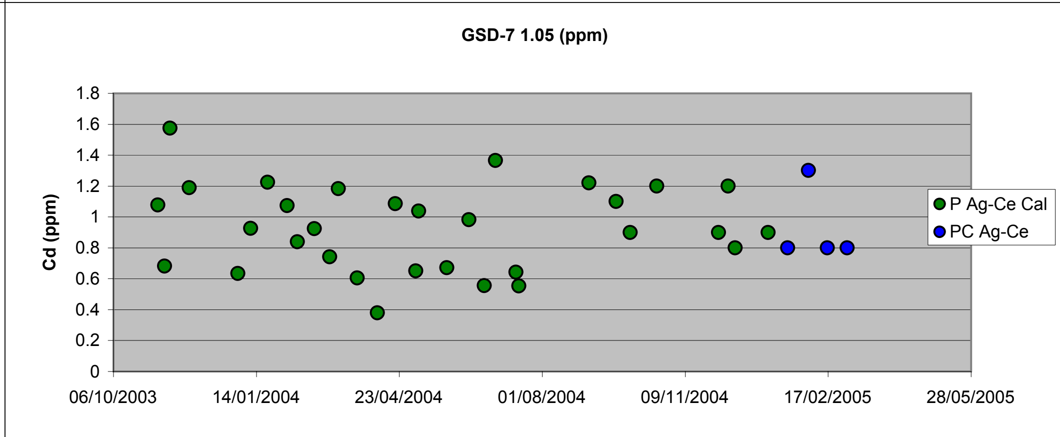

STSD-3 # (ppm)
Ag (ppm)
PC Ag-Ce Cal
P Ag-Ce
1.4
1.2
1
0.8
0.6
0.4
0.2
0
06/10/2003
14/01/2004
23/04/2004
01/08/2004
09/11/2004
17/02/2005
28/05/2005

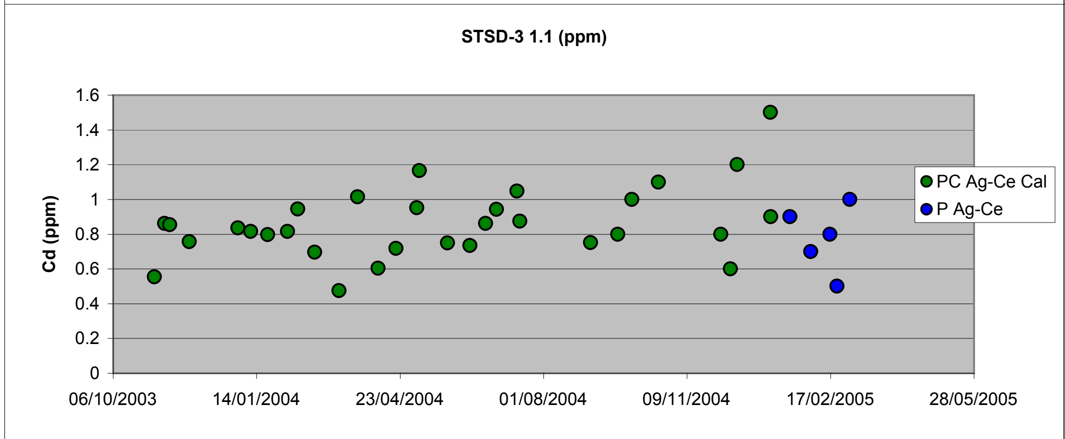

GSS-1 0.35 (ppm)
Ag (ppm)
P Ag-Ce Cal
PC Ag-Ce
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
06/10/2003
14/01/2004
23/04/2004
01/08/2004
09/11/2004
17/02/2005
28/05/2005

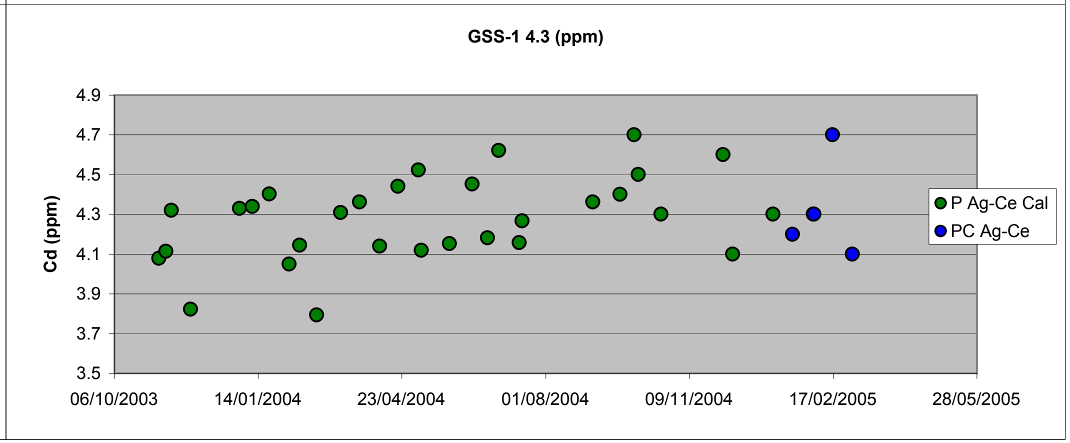

LKSD-1 1.4 (ppm)
Cd (ppm)
1.8 1.6 1.4 1.2 1 0.8 0.6
06/10/2003 14/01/2004 23/04/2004 01/08/2004 09/11/2004 17/02/2005 28/05/2005
P Ag-Ce Cal
PC Ag-Ce

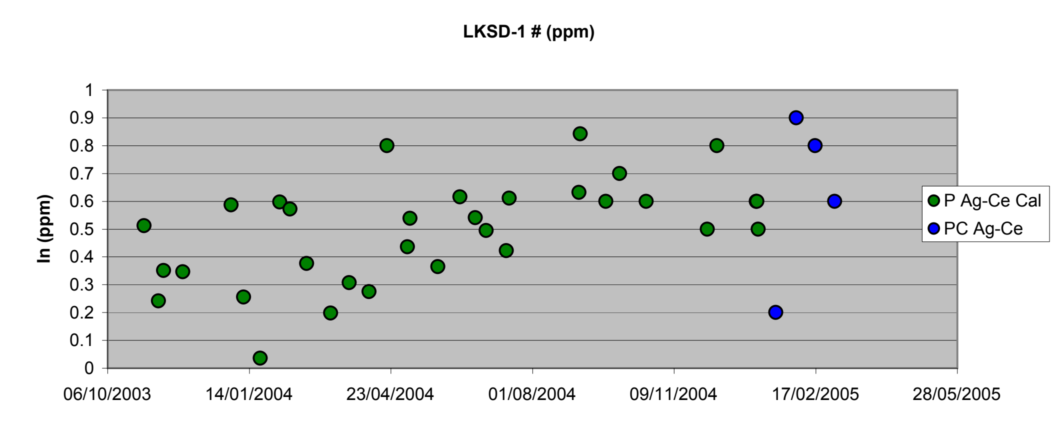

GSD-3 0.1 (ppm)
Cd (ppm)
0.45 0.4 0.35 0.3 0.25 0.2 0.15 0.1 0.05 0
06/10/2003 14/01/2004 23/04/2004 01/08/2004 09/11/2004 17/02/2005 28/05/2005
P Ag-Ce Cal
PC Ag-Ce

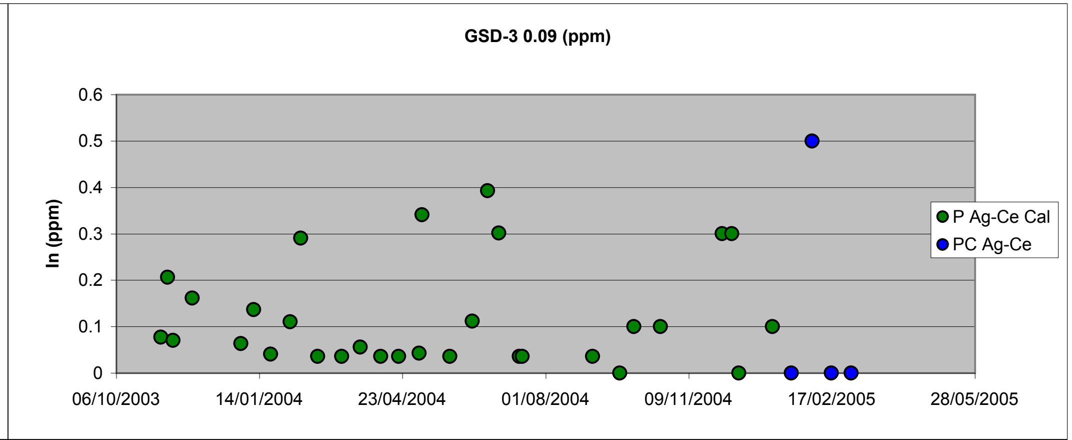

LKSD-4 2 (ppm)
Cd (ppm)
2.6 2.4 2.2 2 1.8 1.6 1.4
06/10/2003 14/01/2004 23/04/2004 01/08/2004 09/11/2004 17/02/2005 28/05/2005
P Ag-Ce Cal
PC Ag-Ce

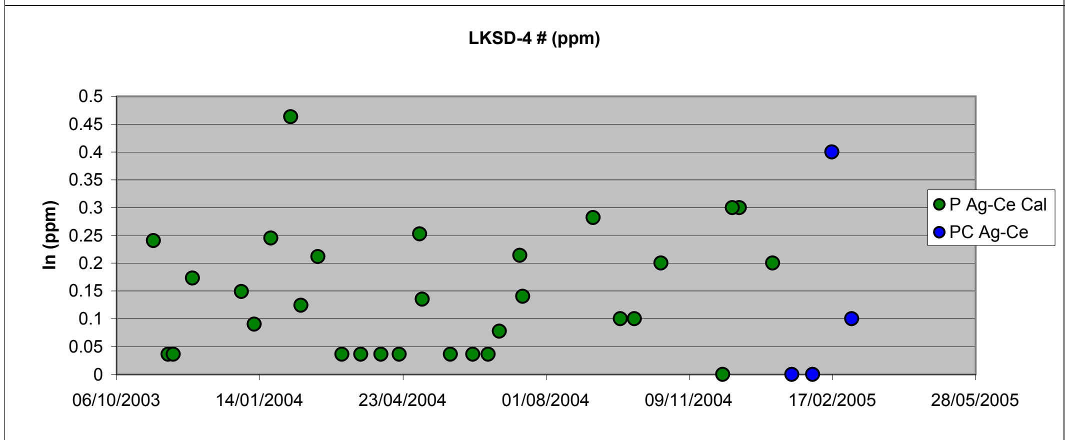

GSD-7 1.05 (ppm)
Cd (ppm)
1.8 1.6 1.4 1.2 1 0.8 0.6 0.4 0.2 0
06/10/2003 14/01/2004 23/04/2004 01/08/2004 09/11/2004 17/02/2005 28/05/2005
P Ag-Ce Cal
PC Ag-Ce

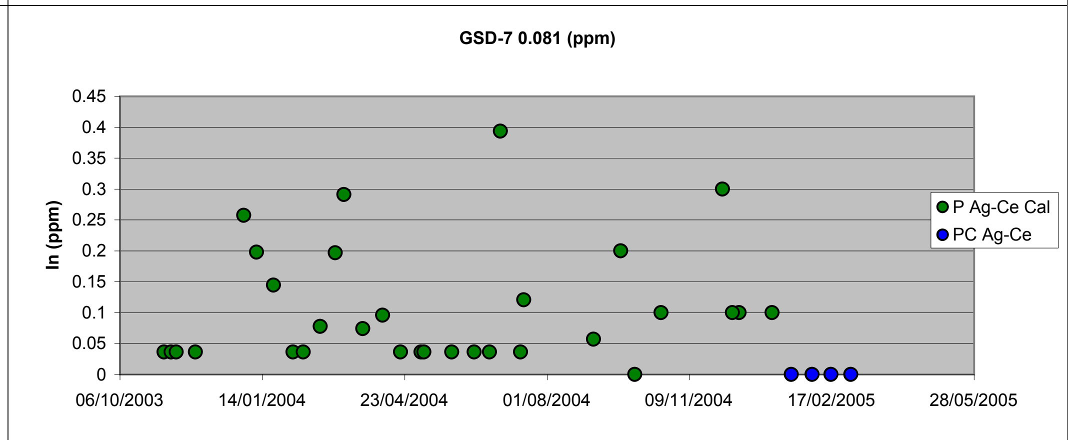

STSD-3 1.1 (ppm)
Cd (ppm)
1.6 1.4 1.2 1 0.8 0.6 0.4 0.2 0
06/10/2003 14/01/2004 23/04/2004 01/08/2004 09/11/2004 17/02/2005 28/05/2005
PC Ag-Ce Cal
P Ag-Ce

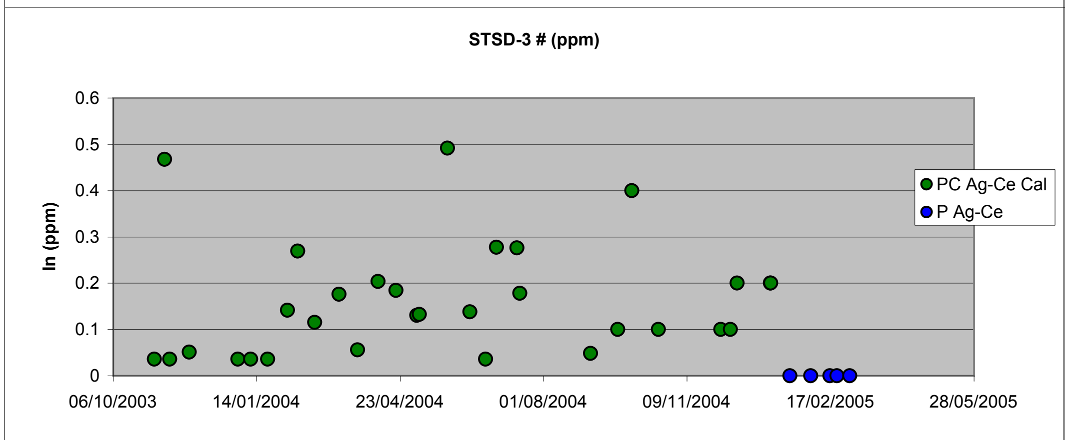

GSS-1 4.3 (ppm)
Cd (ppm)
4.9 4.7 4.5 4.3 4.1 3.9 3.7 3.5
06/10/2003 14/01/2004 23/04/2004 01/08/2004 09/11/2004 17/02/2005 28/05/2005
P Ag-Ce Cal
PC Ag-Ce

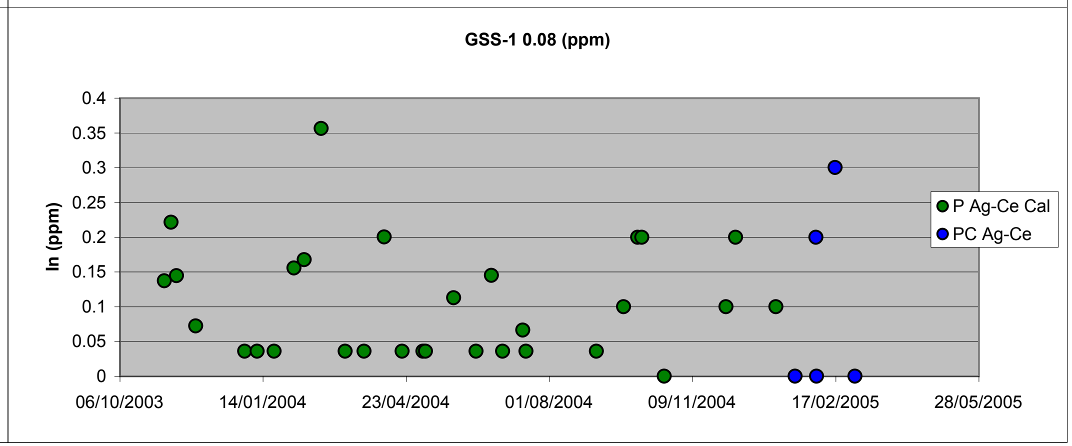

LKSD-1 # (ppm)
In (ppm)
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1
06/10/2003
14/01/2004
23/04/2004
01/08/2004
09/11/2004
17/02/2005
28/05/2005
P Ag-Ce Cal
PC Ag-Ce

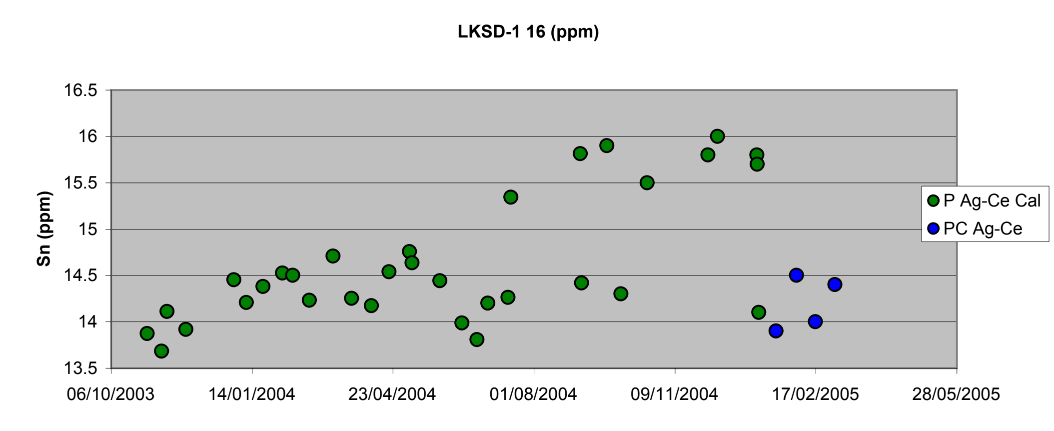

GSD-3 0.09 (ppm)
In (ppm)
0
0.1
0.2
0.3
0.4
0.5
0.6
06/10/2003
14/01/2004
23/04/2004
01/08/2004
09/11/2004
17/02/2005
28/05/2005
P Ag-Ce Cal
PC Ag-Ce

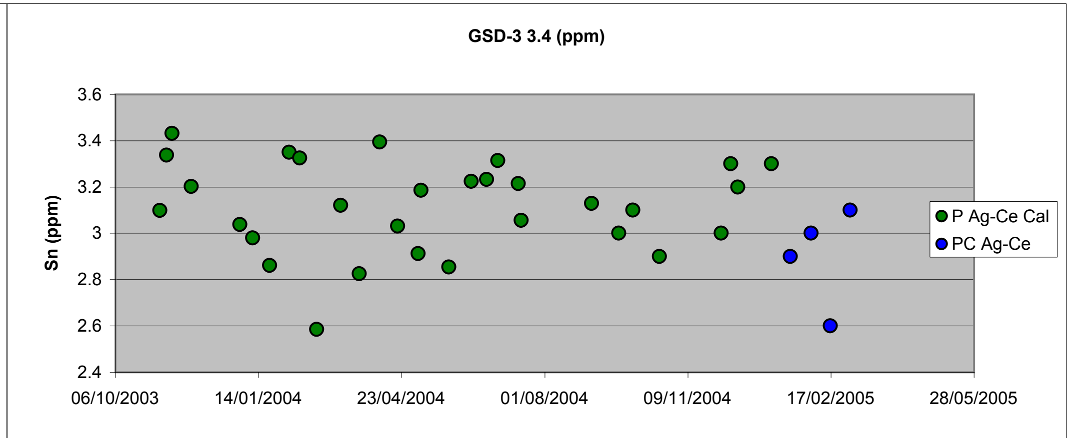

LKSD-4 # (ppm)
In (ppm)
0
0.05
0.1
0.15
0.2
0.25
0.3
0.35
0.4
0.45
0.5
06/10/2003
14/01/2004
23/04/2004
01/08/2004
09/11/2004
17/02/2005
28/05/2005
P Ag-Ce Cal
PC Ag-Ce

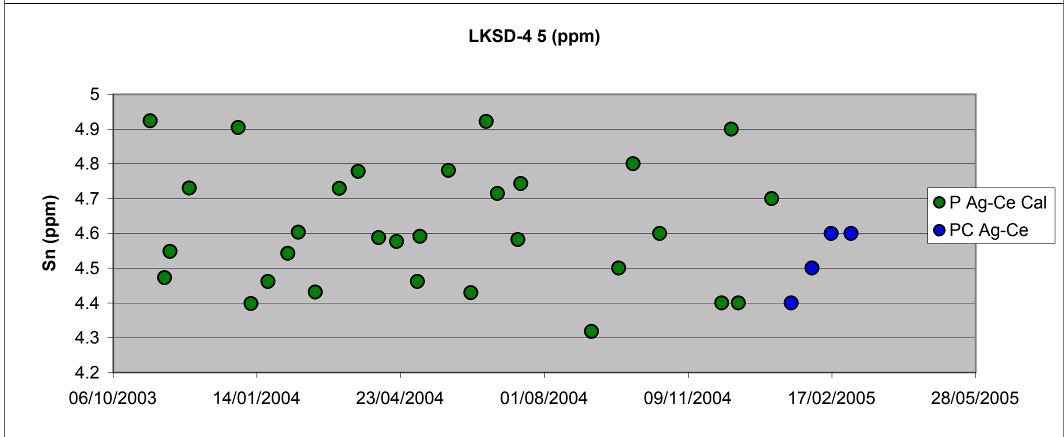

GSD-7 0.081 (ppm)
In (ppm)
0
0.05
0.1
0.15
0.2
0.25
0.3
0.35
0.4
0.45
06/10/2003
14/01/2004
23/04/2004
01/08/2004
09/11/2004
17/02/2005
28/05/2005
P Ag-Ce Cal
PC Ag-Ce

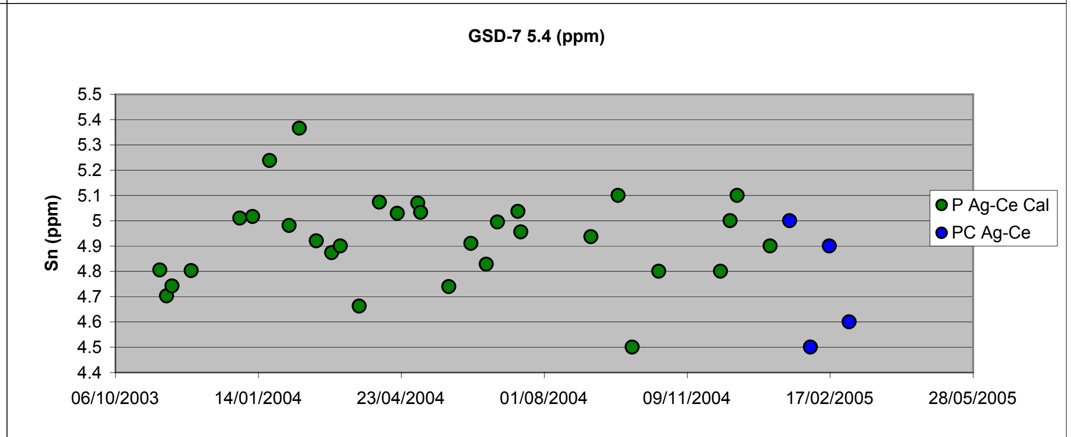

STSD-3 # (ppm)
In (ppm)
0
0.1
0.2
0.3
0.4
0.5
0.6
06/10/2003
14/01/2004
23/04/2004
01/08/2004
09/11/2004
17/02/2005
28/05/2005
PC Ag-Ce Cal
P Ag-Ce

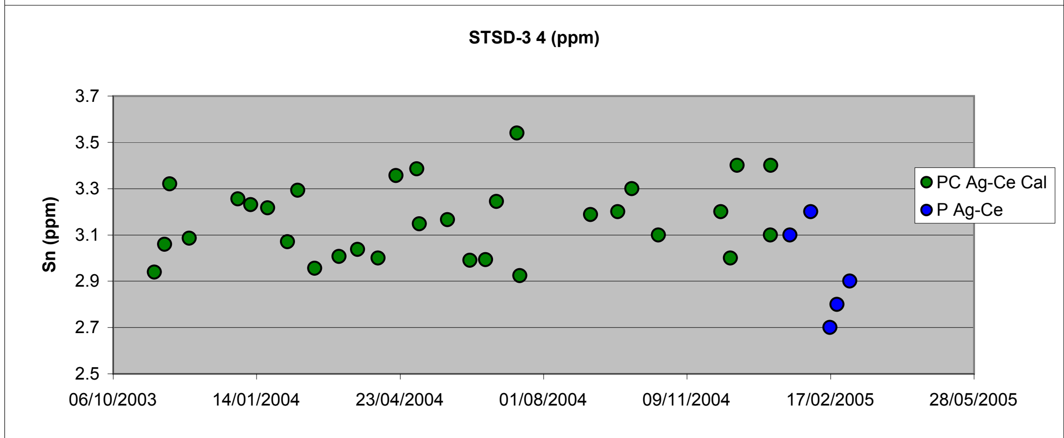

GSS-1 0.08 (ppm)
In (ppm)
0
0.05
0.1
0.15
0.2
0.25
0.3
0.35
0.4
06/10/2003
14/01/2004
23/04/2004
01/08/2004
09/11/2004
17/02/2005
28/05/2005
P Ag-Ce Cal
PC Ag-Ce

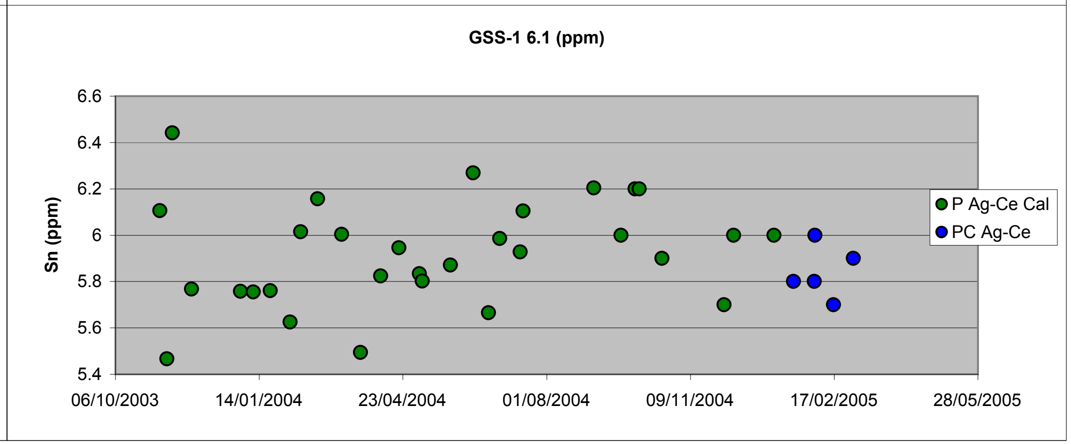

LKSD-1 16 (ppm)
Sn (ppm)
16.5
16
15.5
15
14.5
14
13.5
06/10/2003
14/01/2004
23/04/2004
01/08/2004
09/11/2004
17/02/2005
28/05/2005
P Ag-Ce Cal
PC Ag-Ce

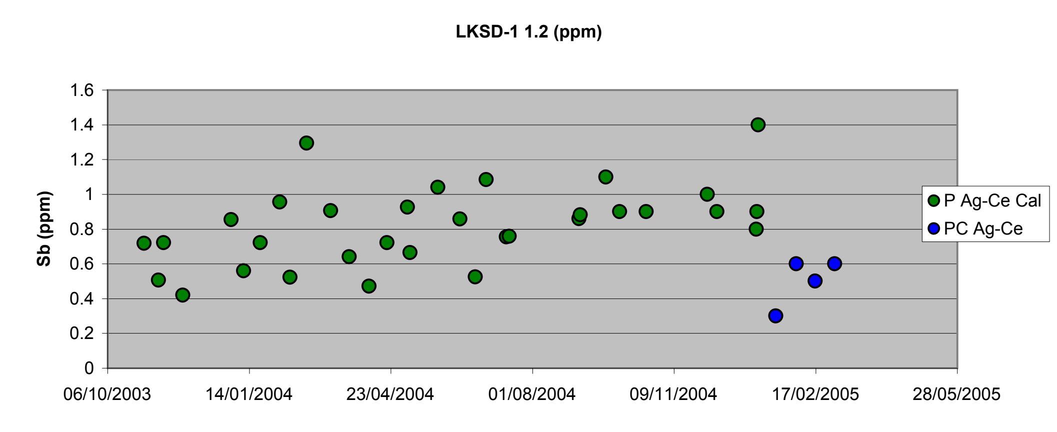

GSD-3 3.4 (ppm)
Sn (ppm)
3.6
3.4
3.2
3
2.8
2.6
2.4
06/10/2003
14/01/2004
23/04/2004
01/08/2004
09/11/2004
17/02/2005
28/05/2005
P Ag-Ce Cal
PC Ag-Ce

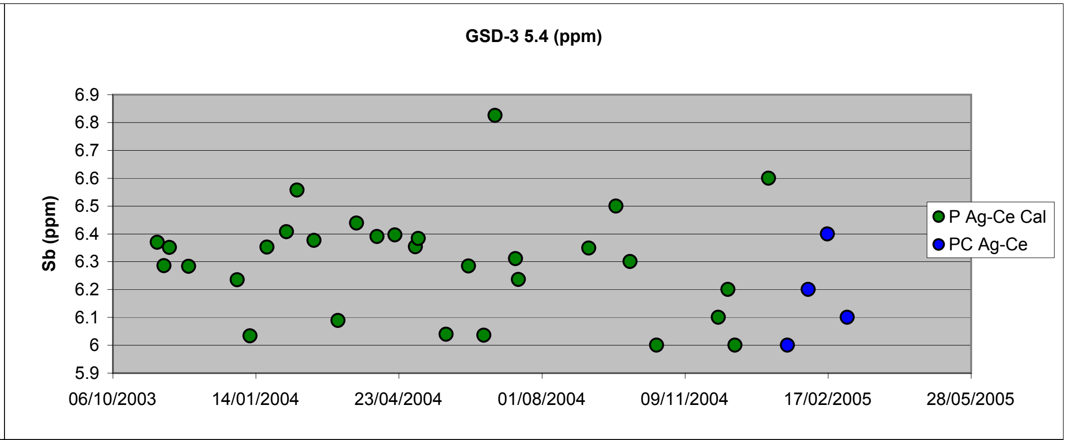

LKSD-4 5 (ppm)
Sn (ppm)
5
4.9
4.8
4.7
4.6
4.5
4.4
4.3
4.2
06/10/2003
14/01/2004
23/04/2004
01/08/2004
09/11/2004
17/02/2005
28/05/2005
P Ag-Ce Cal
PC Ag-Ce

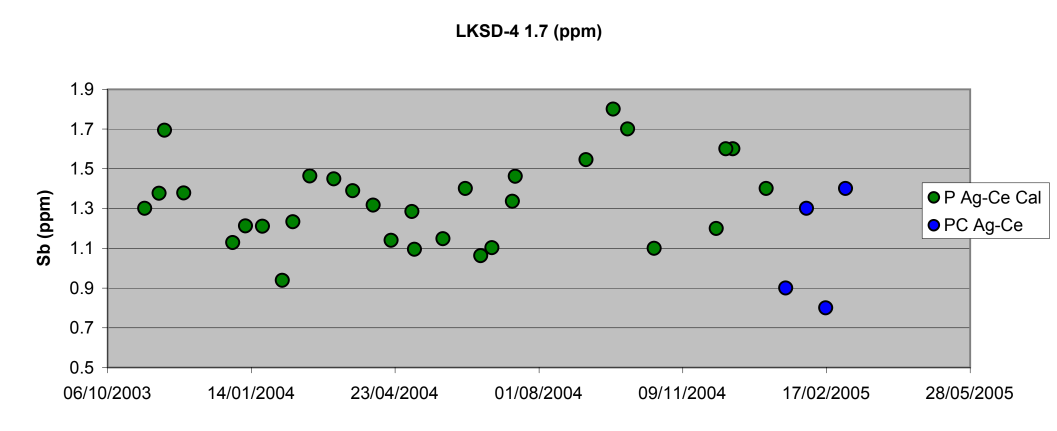

GSD-7 5.4 (ppm)
Sn (ppm)
5.5
5.4
5.3
5.2
5.1
5
4.9
4.8
4.7
4.6
4.5
4.4
06/10/2003
14/01/2004
23/04/2004
01/08/2004
09/11/2004
17/02/2005
28/05/2005
P Ag-Ce Cal
PC Ag-Ce

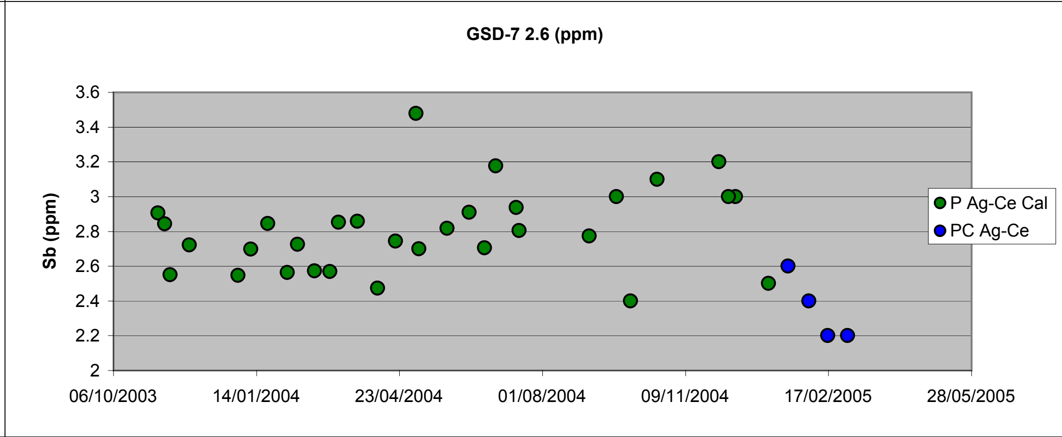

STSD-3 4 (ppm)
Sn (ppm)
3.7
3.5
3.3
3.1
2.9
2.7
2.5
06/10/2003
14/01/2004
23/04/2004
01/08/2004
09/11/2004
17/02/2005
28/05/2005
PC Ag-Ce Cal
P Ag-Ce

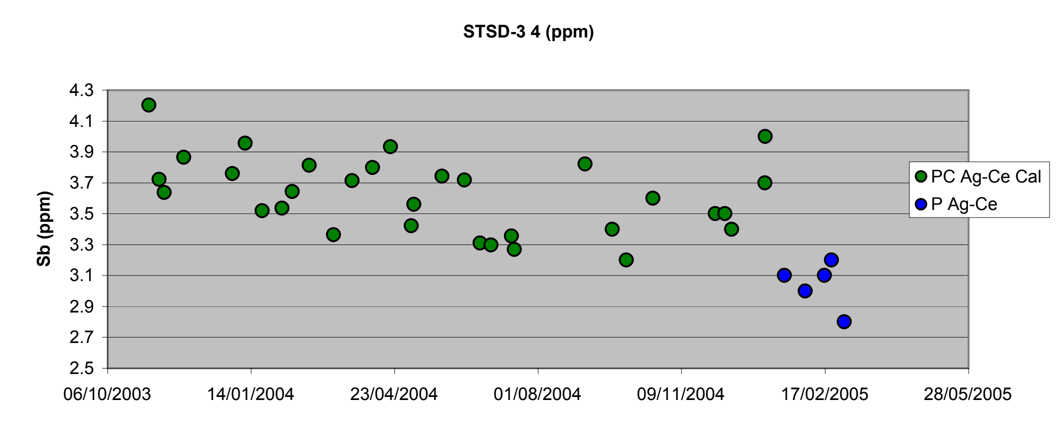

GSS-1 6.1 (ppm)
Sn (ppm)
6.6
6.4
6.2
6
5.8
5.6
5.4
06/10/2003
14/01/2004
23/04/2004
01/08/2004
09/11/2004
17/02/2005
28/05/2005
P Ag-Ce Cal
PC Ag-Ce

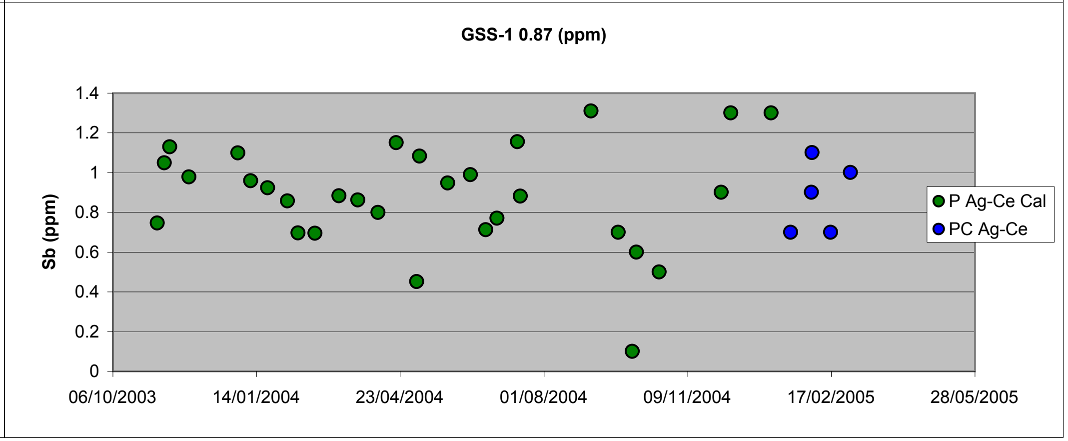

LKSD-1 1.2 (ppm)
Sb (ppm)
P Ag-Ce Cal
PC Ag-Ce
06/10/2003 14/01/2004 23/04/2004 01/08/2004 09/11/2004 17/02/2005 28/05/2005

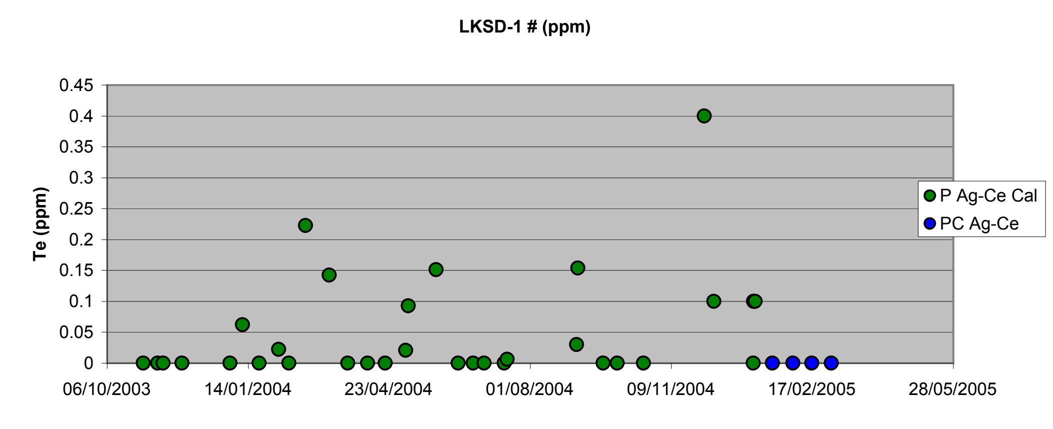

GSD-3 5.4 (ppm)
Sb (ppm)
P Ag-Ce Cal
PC Ag-Ce
06/10/2003 14/01/2004 23/04/2004 01/08/2004 09/11/2004 17/02/2005 28/05/2005

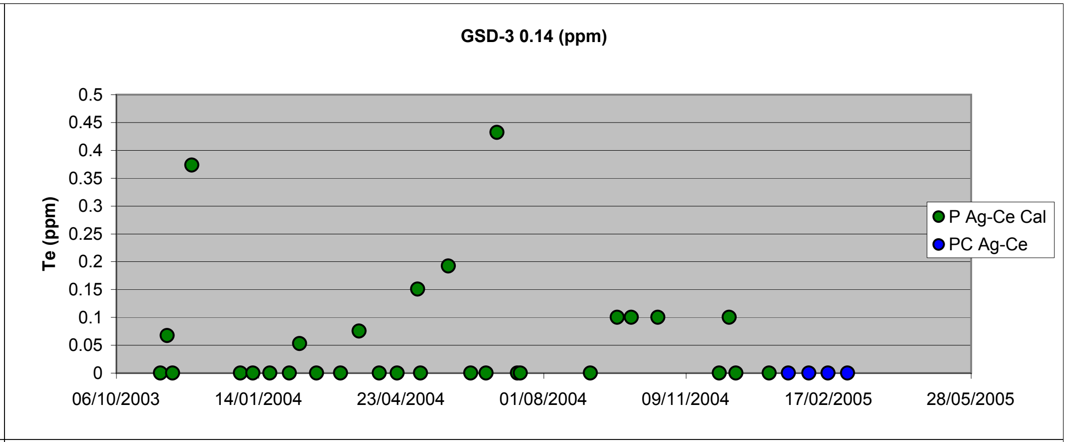

LKSD-4 1.7 (ppm)
Sb (ppm)
P Ag-Ce Cal
PC Ag-Ce
06/10/2003 14/01/2004 23/04/2004 01/08/2004 09/11/2004 17/02/2005 28/05/2005

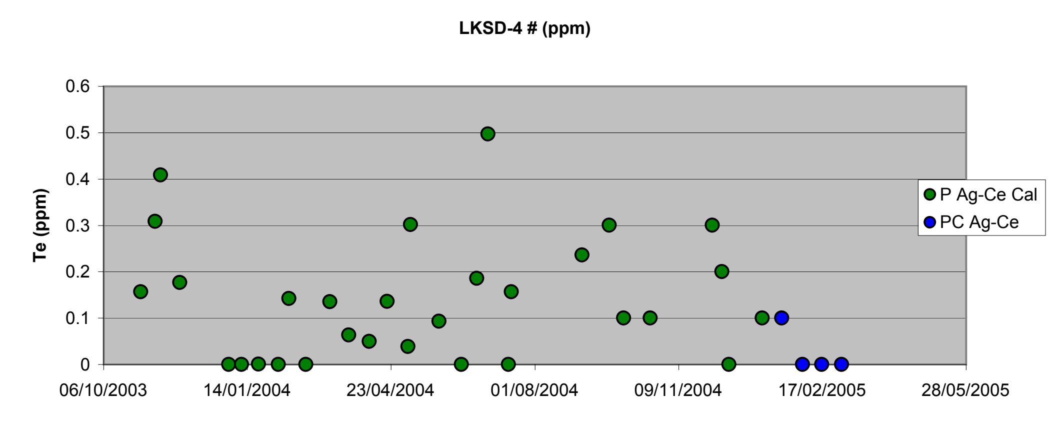

GSD-7 2.6 (ppm)
Sb (ppm)
P Ag-Ce Cal
PC Ag-Ce
06/10/2003 14/01/2004 23/04/2004 01/08/2004 09/11/2004 17/02/2005 28/05/2005

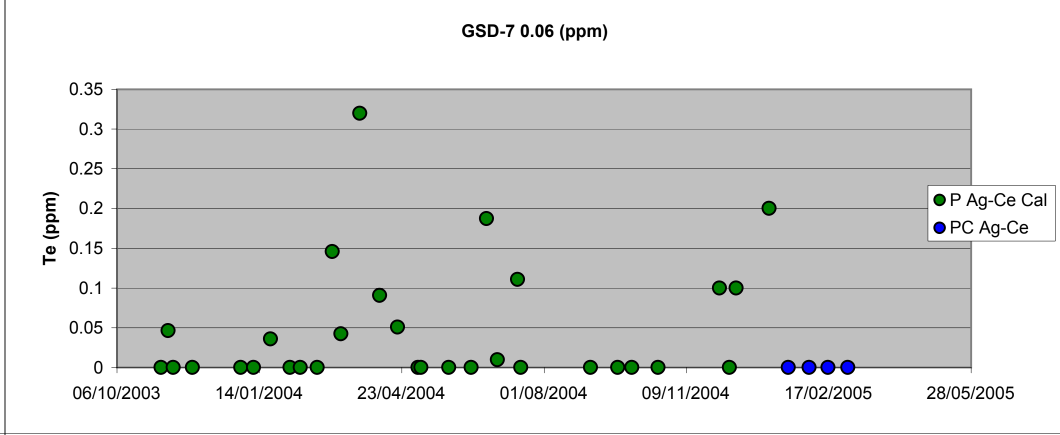

STSD-3 4 (ppm)
Sb (ppm)
PC Ag-Ce Cal
P Ag-Ce
06/10/2003 14/01/2004 23/04/2004 01/08/2004 09/11/2004 17/02/2005 28/05/2005

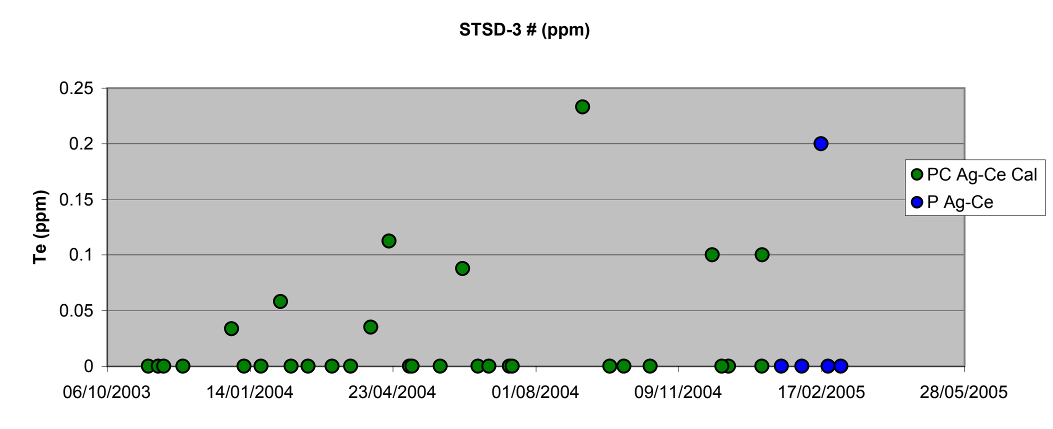

GSS-1 0.87 (ppm)
Sb (ppm)
P Ag-Ce Cal
PC Ag-Ce
06/10/2003 14/01/2004 23/04/2004 01/08/2004 09/11/2004 17/02/2005 28/05/2005

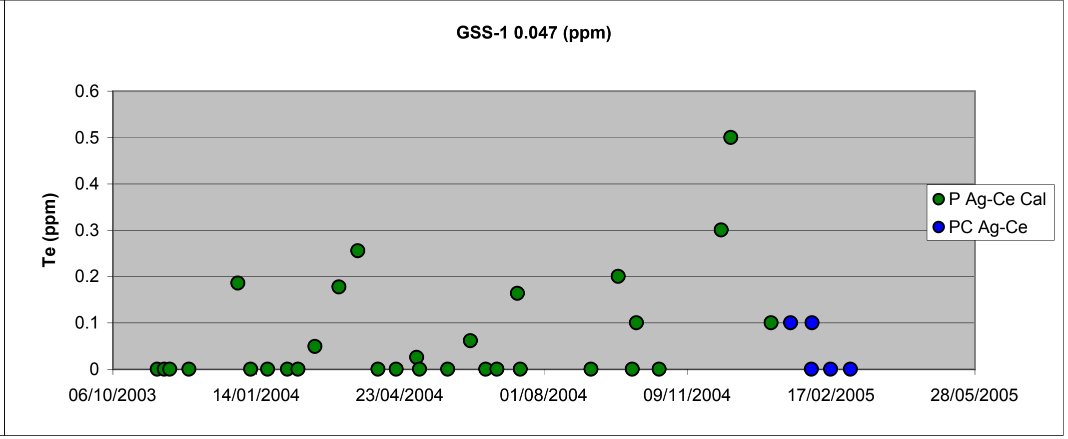

LKSD-1 # (ppm)
Te (ppm)
0.45
0.4
0.35
0.3
0.25
0.2
0.15
0.1
0.05
0
06/10/2003
14/01/2004
23/04/2004
01/08/2004
09/11/2004
17/02/2005
28/05/2005
P Ag-Ce Cal
PC Ag-Ce

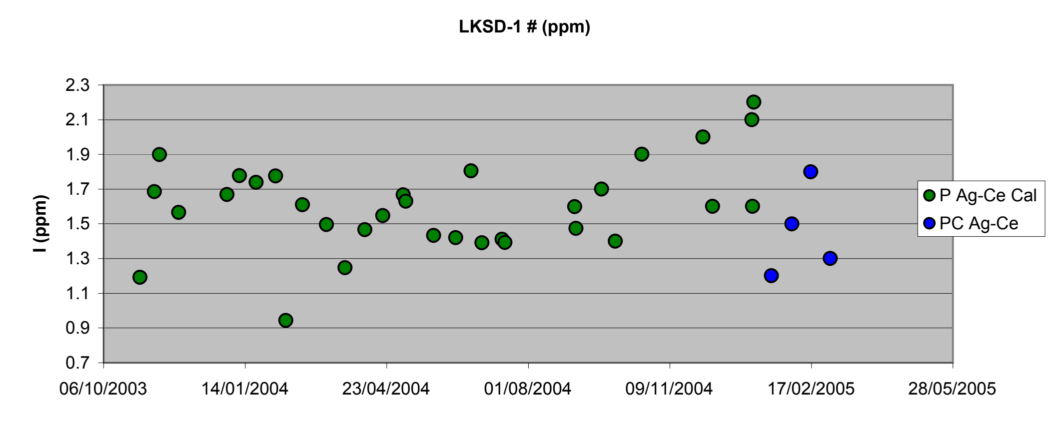

GSD-3 0.14 (ppm)
Te (ppm)
0.5
0.45
0.4
0.35
0.3
0.25
0.2
0.15
0.1
0.05
0
06/10/2003
14/01/2004
23/04/2004
01/08/2004
09/11/2004
17/02/2005
28/05/2005
P Ag-Ce Cal
PC Ag-Ce

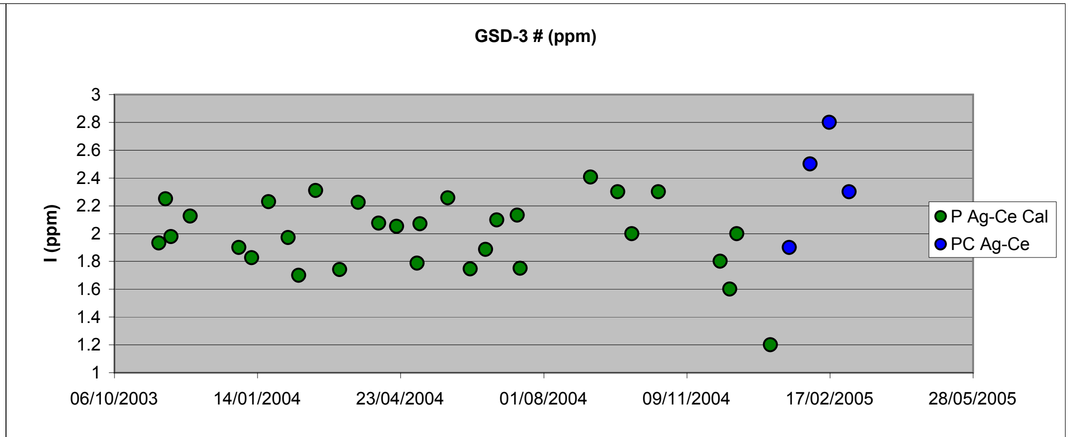

LKSD-4 # (ppm)
Te (ppm)
0.6
0.5
0.4
0.3
0.2
0.1
0
06/10/2003
14/01/2004
23/04/2004
01/08/2004
09/11/2004
17/02/2005
28/05/2005
P Ag-Ce Cal
PC Ag-Ce

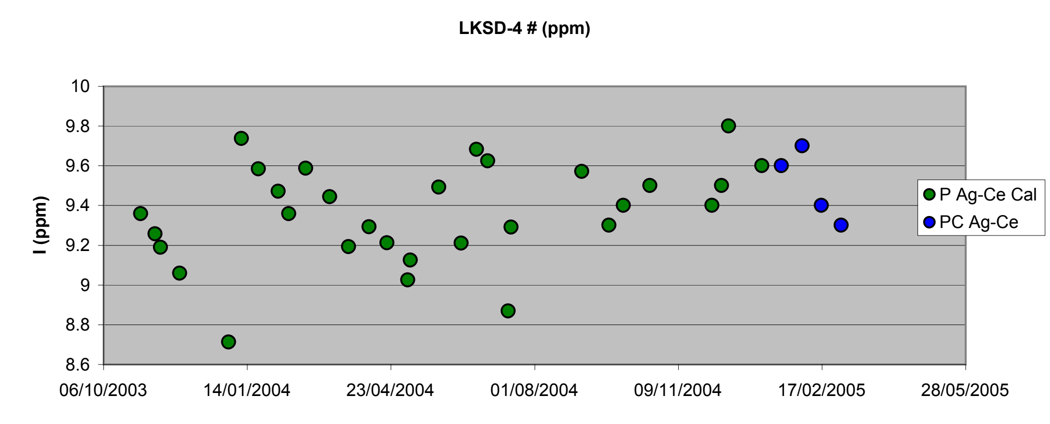

GSD-7 0.06 (ppm)
Te (ppm)
0.35
0.3
0.25
0.2
0.15
0.1
0.05
0
06/10/2003
14/01/2004
23/04/2004
01/08/2004
09/11/2004
17/02/2005
28/05/2005
P Ag-Ce Cal
PC Ag-Ce

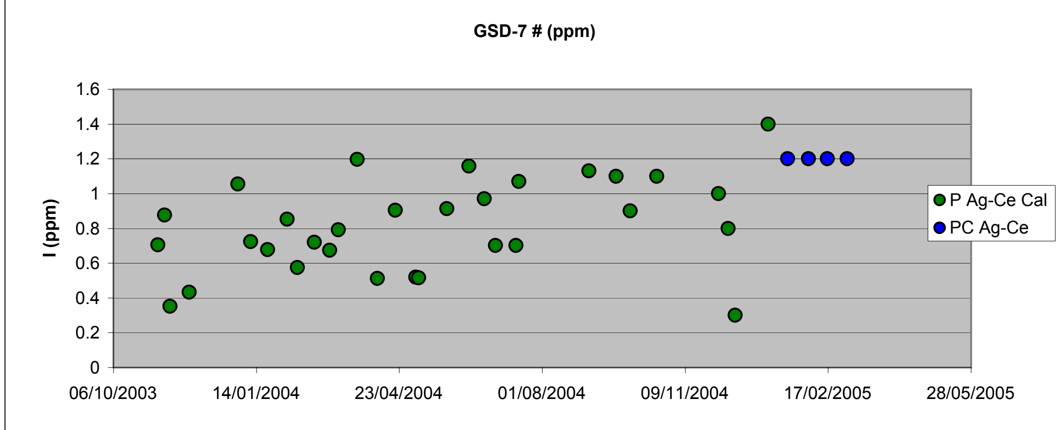

STSD-3 # (ppm)
Te (ppm)
0.25
0.2
0.15
0.1
0.05
0
06/10/2003
14/01/2004
23/04/2004
01/08/2004
09/11/2004
17/02/2005
28/05/2005
PC Ag-Ce Cal
P Ag-Ce

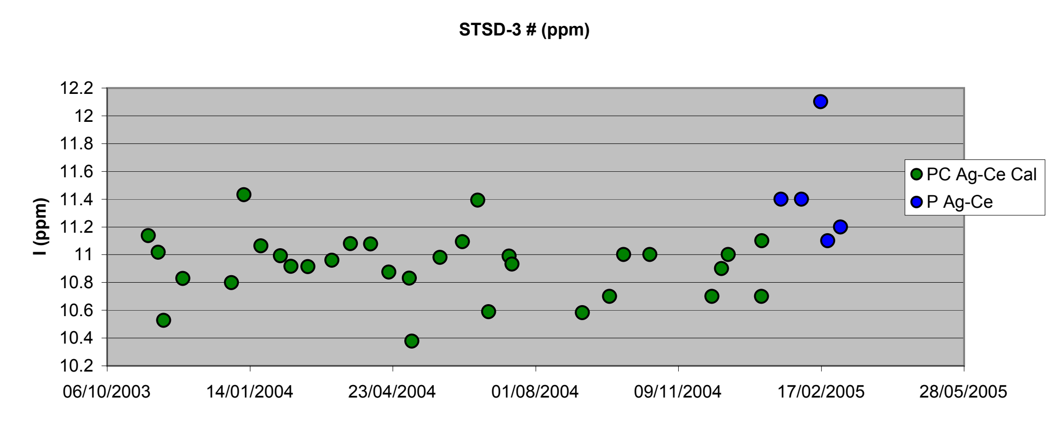

GSS-1 0.047 (ppm)
Te (ppm)
0.6
0.5
0.4
0.3
0.2
0.1
0
06/10/2003
14/01/2004
23/04/2004
01/08/2004
09/11/2004
17/02/2005
28/05/2005
P Ag-Ce Cal
PC Ag-Ce

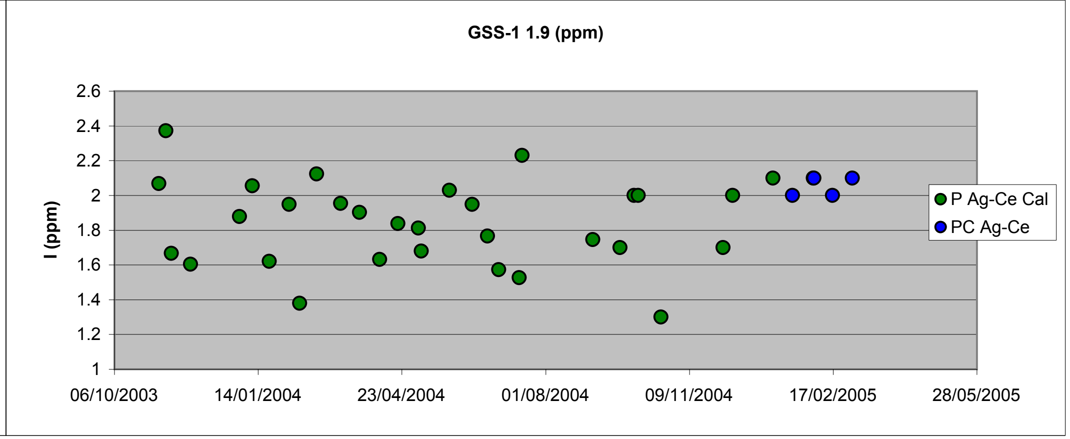

LKSD-1 # (ppm)
I (ppm)
2.3 2.1 1.9 1.7 1.5 1.3 1.1 0.9 0.7
06/10/2003 14/01/2004 23/04/2004 01/08/2004 09/11/2004 17/02/2005 28/05/2005
P Ag-Ce Cal
PC Ag-Ce

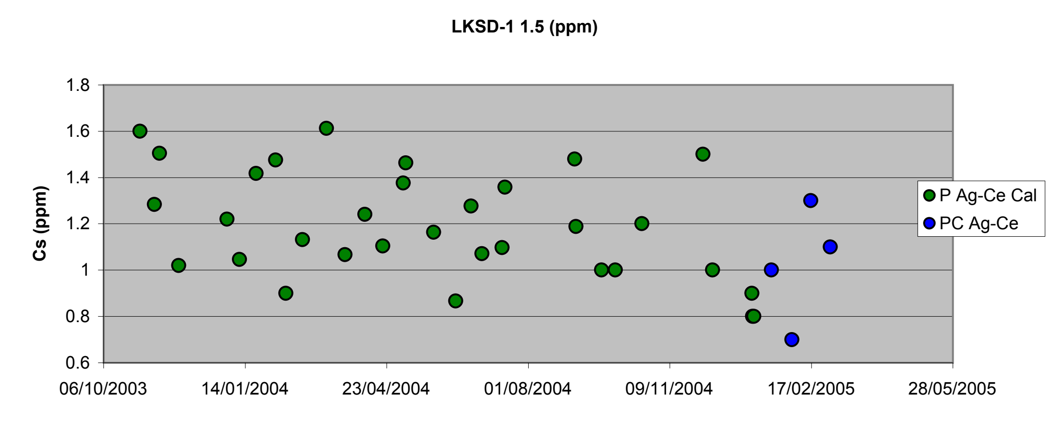

GSD-3 # (ppm)
I (ppm)
3 2.8 2.6 2.4 2.2 2 1.8 1.6 1.4 1.2 1
06/10/2003 14/01/2004 23/04/2004 01/08/2004 09/11/2004 17/02/2005 28/05/2005
P Ag-Ce Cal
PC Ag-Ce

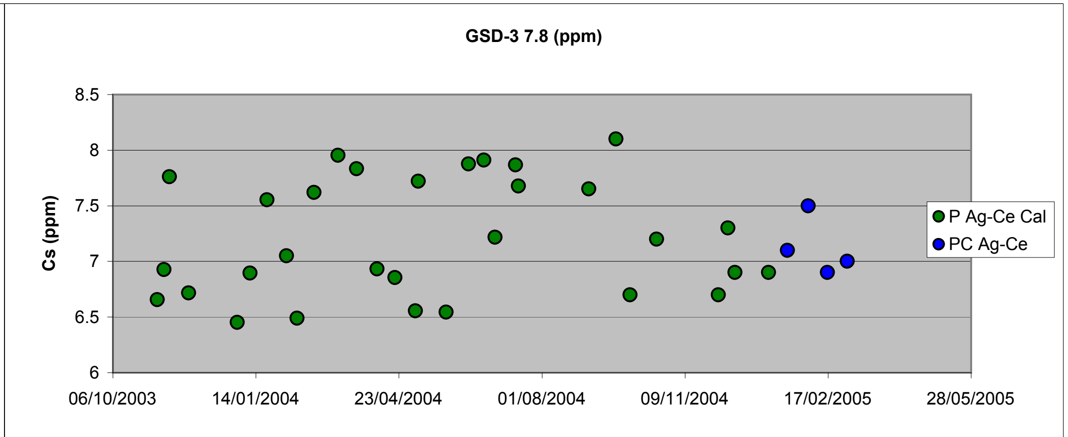

LKSD-4 # (ppm)
I (ppm)
10 9.8 9.6 9.4 9.2 9 8.8 8.6
06/10/2003 14/01/2004 23/04/2004 01/08/2004 09/11/2004 17/02/2005 28/05/2005
P Ag-Ce Cal
PC Ag-Ce

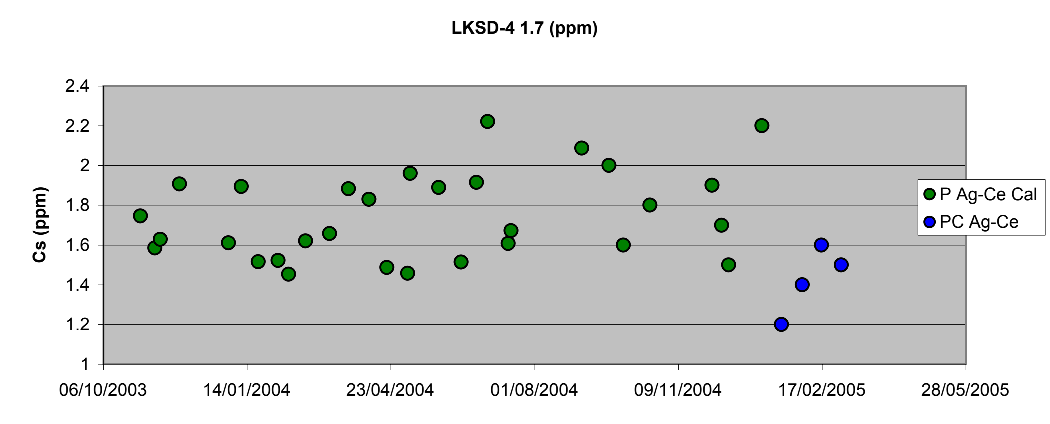

GSD-7 # (ppm)
I (ppm)
1.6 1.4 1.2 1 0.8 0.6 0.4 0.2 0
06/10/2003 14/01/2004 23/04/2004 01/08/2004 09/11/2004 17/02/2005 28/05/2005
P Ag-Ce Cal
PC Ag-Ce

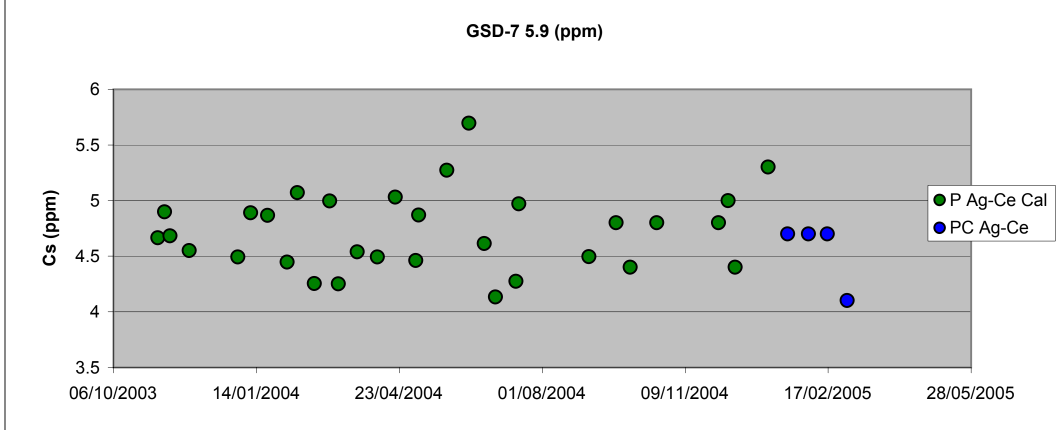

STSD-3 # (ppm)
I (ppm)
12.2 12 11.8 11.6 11.4 11.2 11 10.8 10.6 10.4 10.2
06/10/2003 14/01/2004 23/04/2004 01/08/2004 09/11/2004 17/02/2005 28/05/2005
PC Ag-Ce Cal
P Ag-Ce

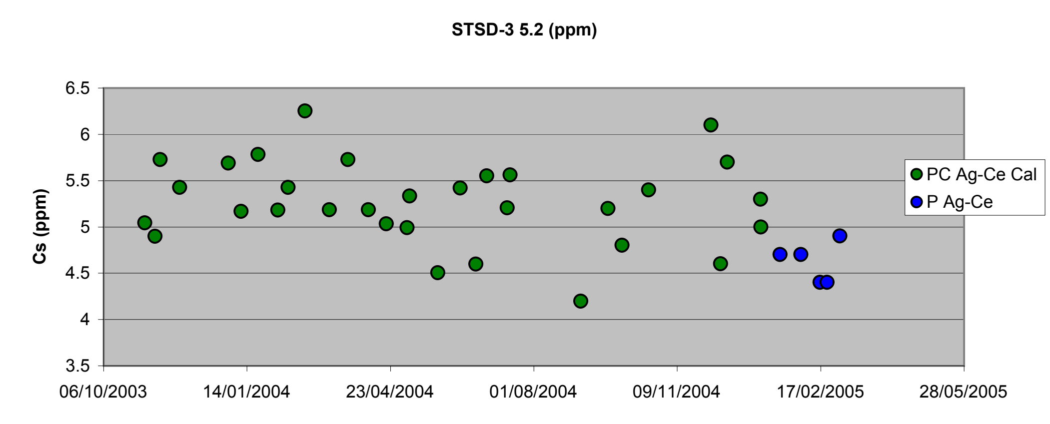

GSS-1 1.9 (ppm)
I (ppm)
2.6 2.4 2.2 2 1.8 1.6 1.4 1.2 1
06/10/2003 14/01/2004 23/04/2004 01/08/2004 09/11/2004 17/02/2005 28/05/2005
P Ag-Ce Cal
PC Ag-Ce

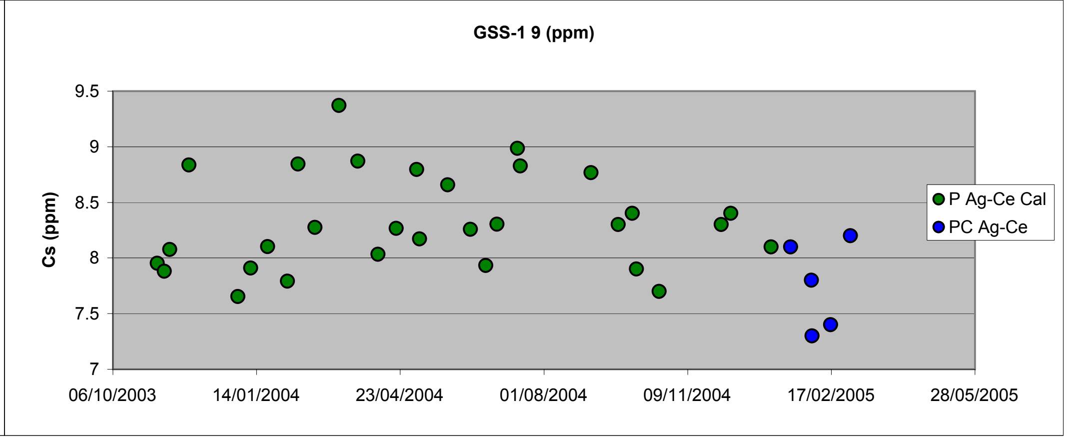

LKSD-1 1.5 (ppm)
Cs (ppm)
P Ag-Ce Cal
PC Ag-Ce
06/10/2003 14/01/2004 23/04/2004 01/08/2004 09/11/2004 17/02/2005 28/05/2005


GSD-3 7.8 (ppm)
Cs (ppm)
P Ag-Ce Cal
PC Ag-Ce
06/10/2003 14/01/2004 23/04/2004 01/08/2004 09/11/2004 17/02/2005 28/05/2005

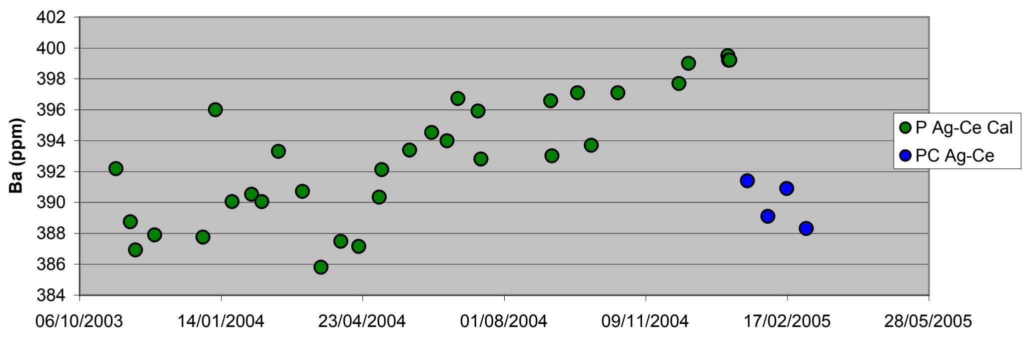

LKSD-4 1.7 (ppm)
Cs (ppm)
P Ag-Ce Cal
PC Ag-Ce
06/10/2003 14/01/2004 23/04/2004 01/08/2004 09/11/2004 17/02/2005 28/05/2005


GSD-7 5.9 (ppm)
Cs (ppm)
P Ag-Ce Cal
PC Ag-Ce
06/10/2003 14/01/2004 23/04/2004 01/08/2004 09/11/2004 17/02/2005 28/05/2005

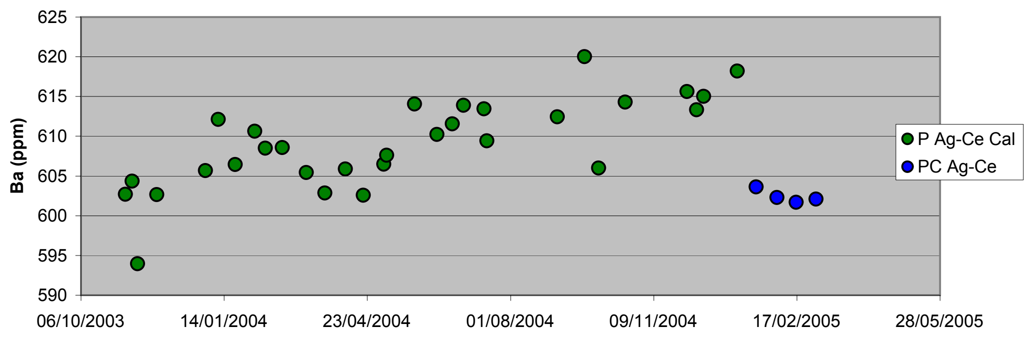

STSD-3 5.2 (ppm)
Cs (ppm)
PC Ag-Ce Cal
P Ag-Ce
06/10/2003 14/01/2004 23/04/2004 01/08/2004 09/11/2004 17/02/2005 28/05/2005


GSS-1 9 (ppm)
Cs (ppm)
P Ag-Ce Cal
PC Ag-Ce
06/10/2003 14/01/2004 23/04/2004 01/08/2004 09/11/2004 17/02/2005 28/05/2005

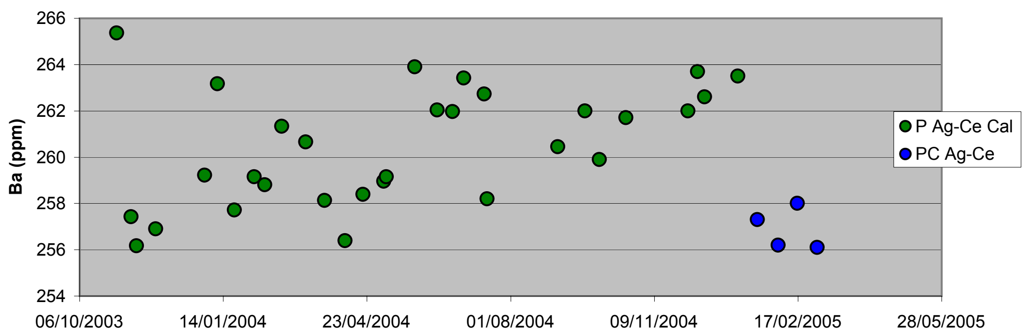
LKSD-1 430 (ppm)



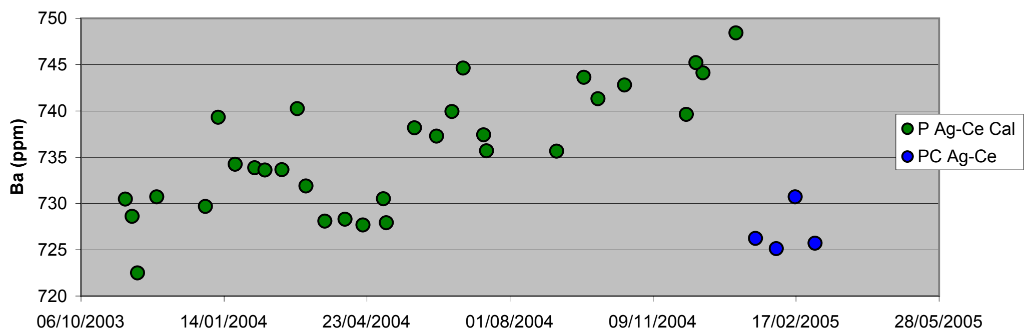
GSD-3 615 (ppm)



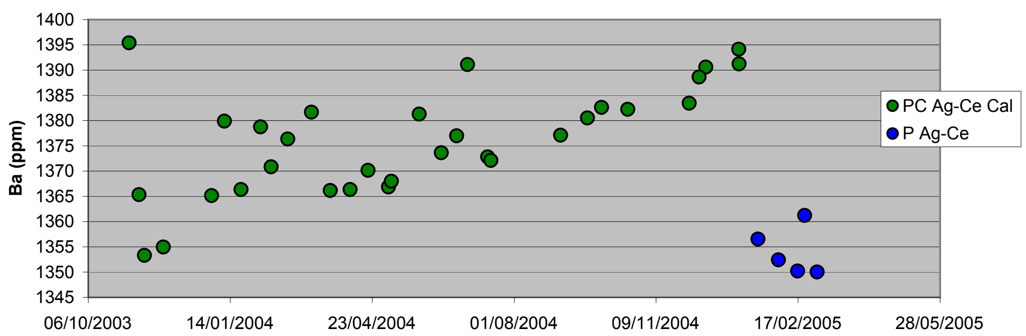
LKSD-4 330 (ppm)



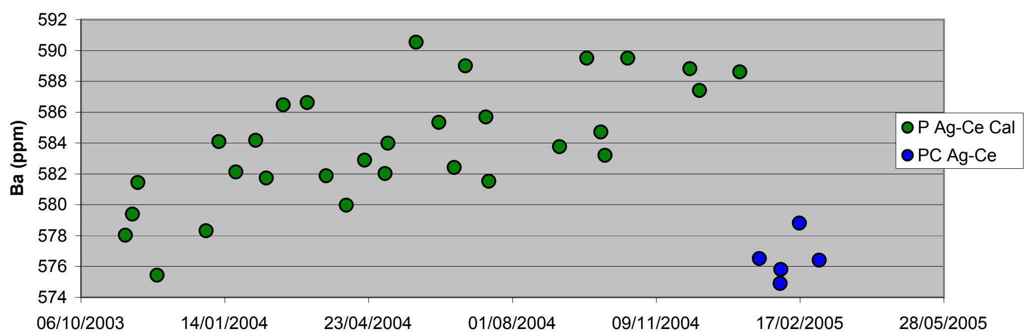
GSD-7 720 (ppm)

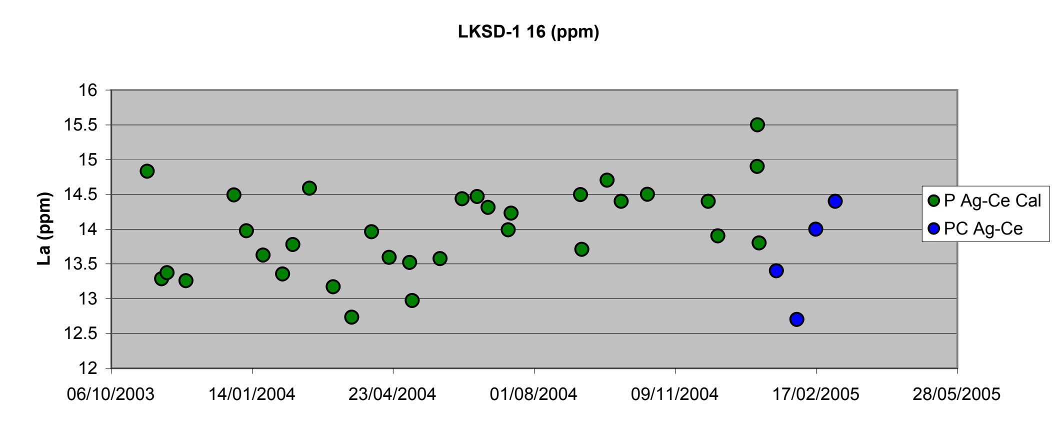


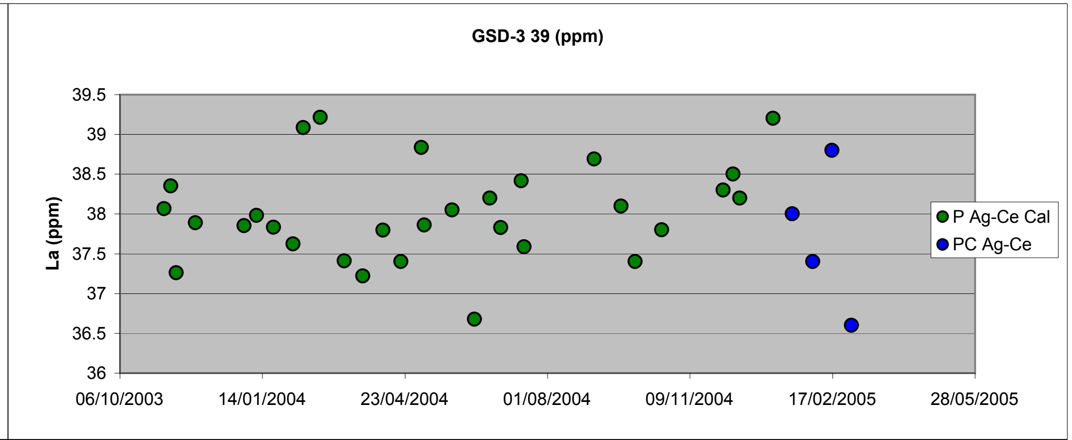
STSD-3 1490 (ppm)

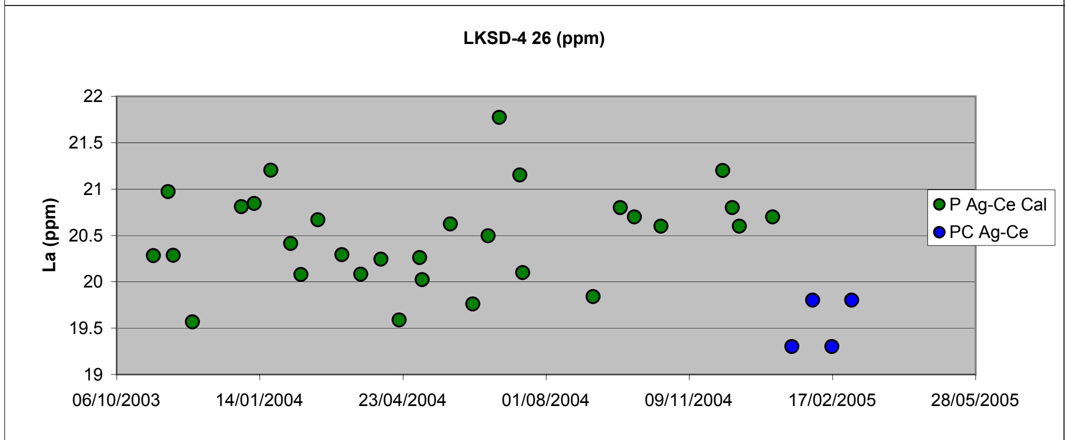


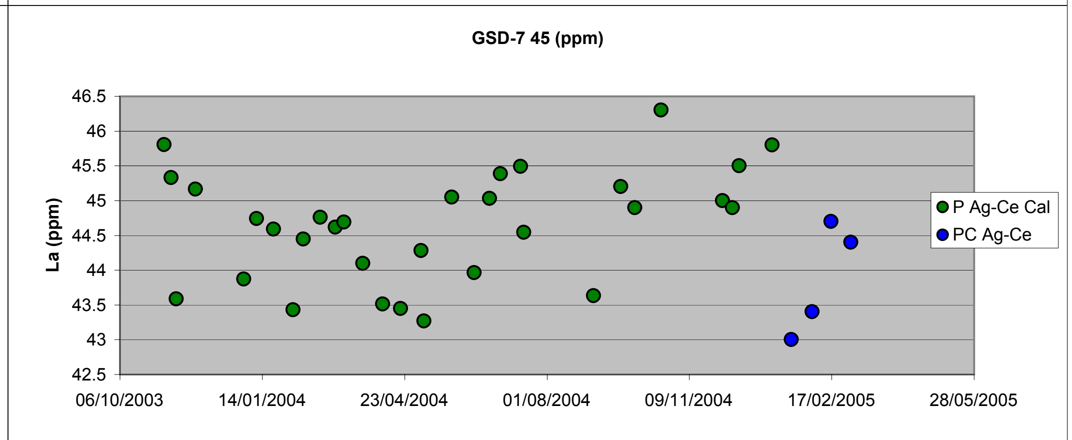
GSS-1 590 (ppm)

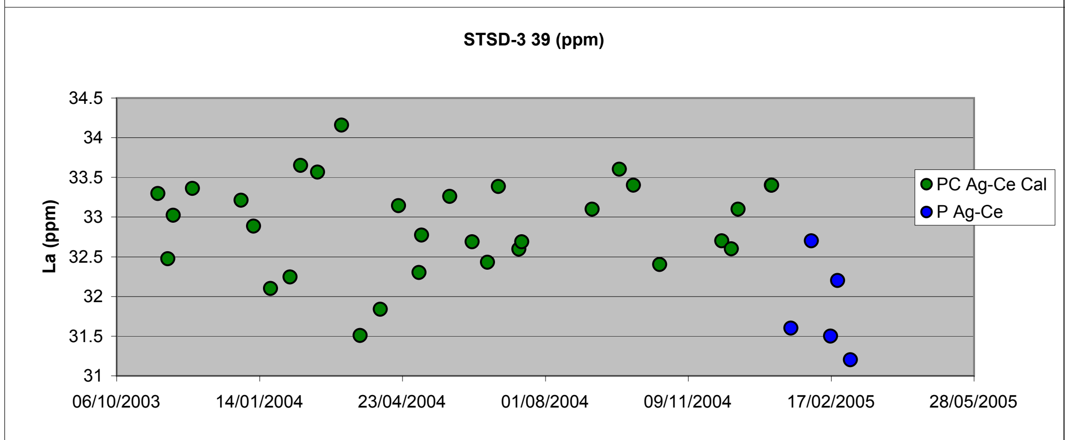


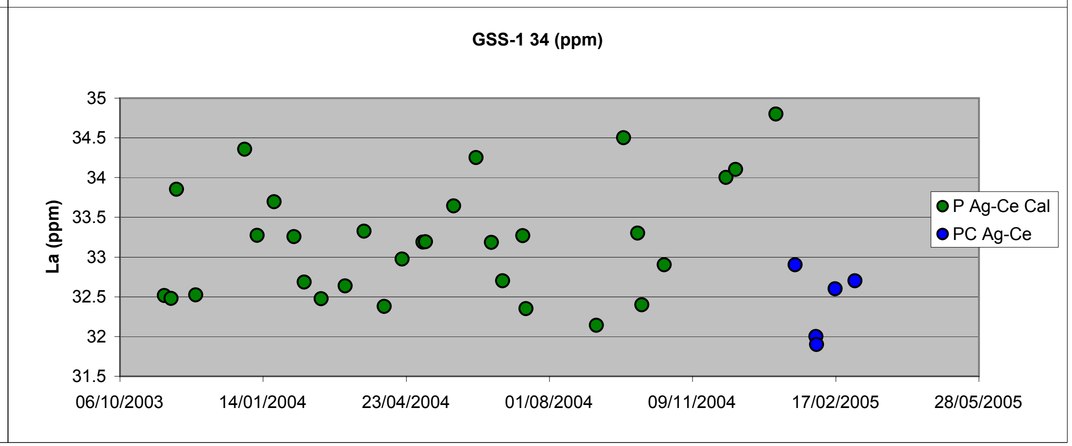

LKSD-1 16 (ppm)
La (ppm)
16
15.5
15
14.5
14
13.5
13
12.5
12
06/10/2003
14/01/2004
23/04/2004
01/08/2004
09/11/2004
17/02/2005
28/05/2005
P Ag-Ce Cal
PC Ag-Ce

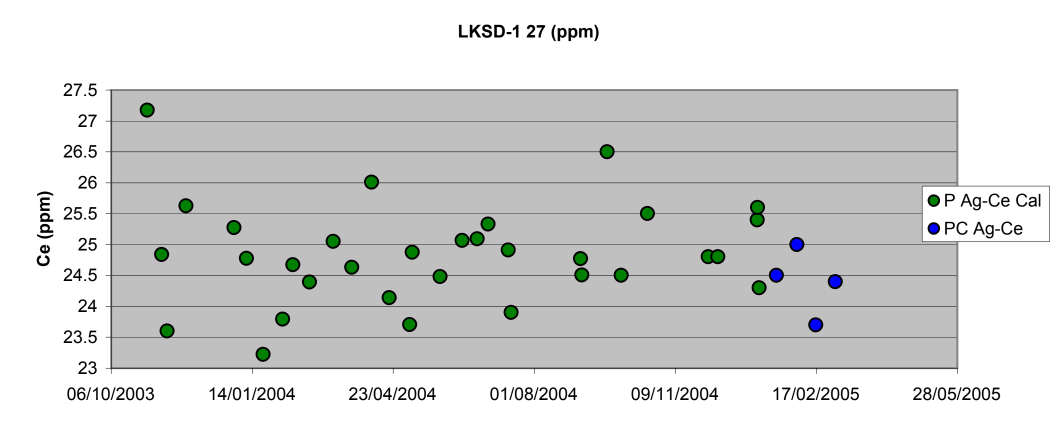

GSD-3 39 (ppm)
La (ppm)
39.5
39
38.5
38
37.5
37
36.5
36
06/10/2003
14/01/2004
23/04/2004
01/08/2004
09/11/2004
17/02/2005
28/05/2005
P Ag-Ce Cal
PC Ag-Ce

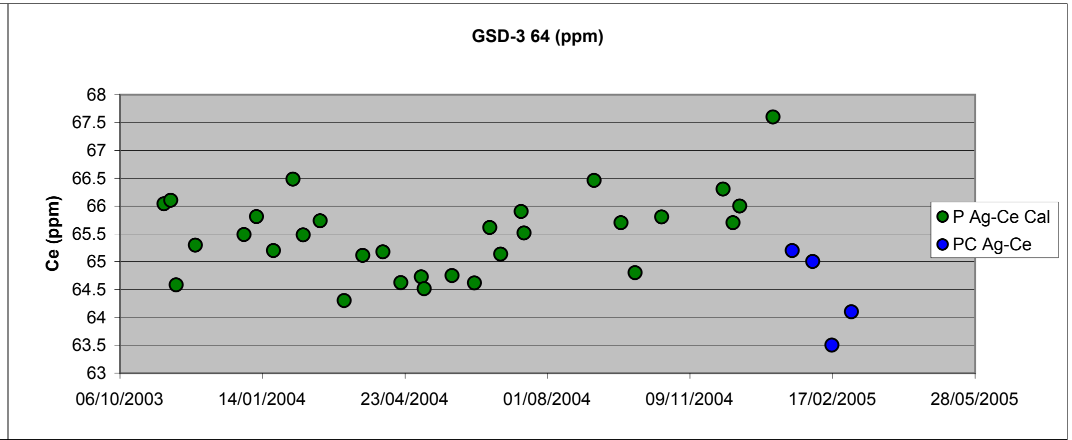

LKSD-4 26 (ppm)
La (ppm)
22
21.5
21
20.5
20
19.5
19
06/10/2003
14/01/2004
23/04/2004
01/08/2004
09/11/2004
17/02/2005
28/05/2005
P Ag-Ce Cal
PC Ag-Ce

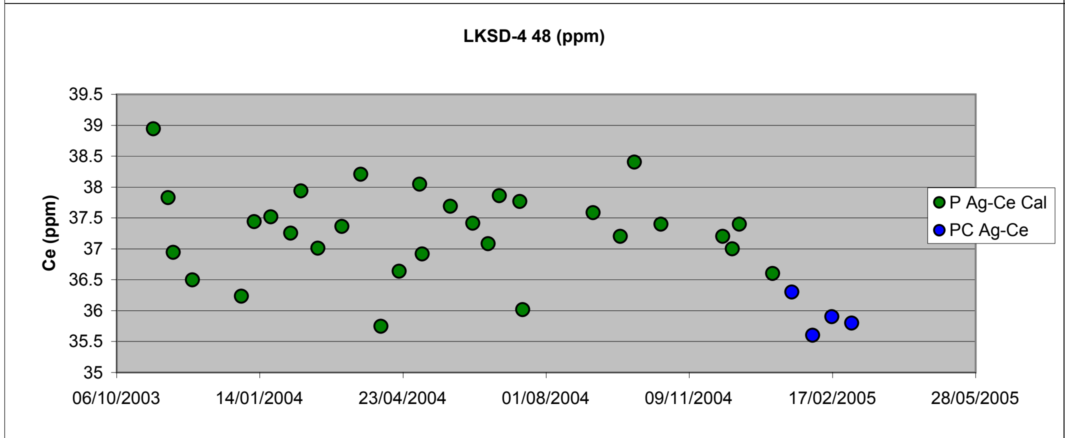

GSD-7 45 (ppm)
La (ppm)
46.5
46
45.5
45
44.5
44
43.5
43
42.5
06/10/2003
14/01/2004
23/04/2004
01/08/2004
09/11/2004
17/02/2005
28/05/2005
P Ag-Ce Cal
PC Ag-Ce

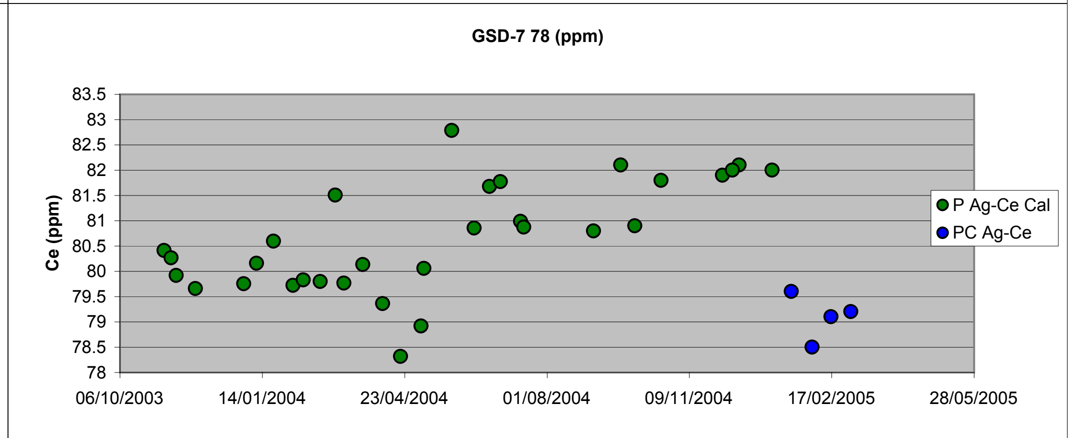

STSD-3 39 (ppm)
La (ppm)
34.5
34
33.5
33
32.5
32
31.5
31
06/10/2003
14/01/2004
23/04/2004
01/08/2004
09/11/2004
17/02/2005
28/05/2005
PC Ag-Ce Cal
P Ag-Ce

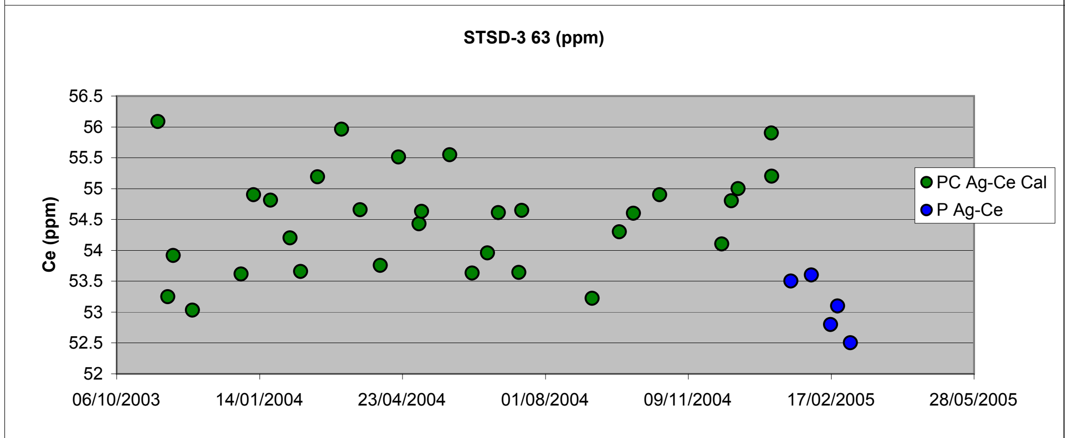

GSS-1 34 (ppm)
La (ppm)
35
34.5
34
33.5
33
32.5
32
31.5
06/10/2003
14/01/2004
23/04/2004
01/08/2004
09/11/2004
17/02/2005
28/05/2005
P Ag-Ce Cal
PC Ag-Ce

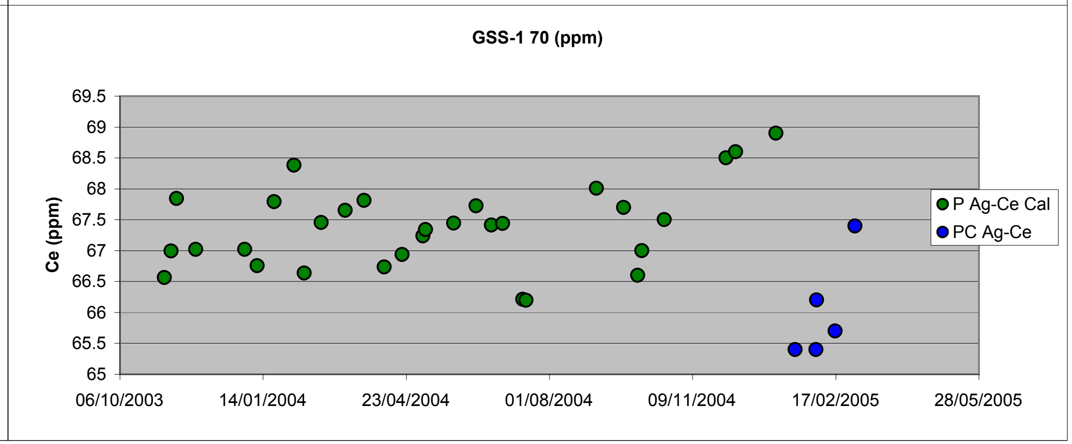

LKSD-1 27 (ppm)
Ce (ppm)
P Ag-Ce Cal
PC Ag-Ce
06/10/2003 14/01/2004 23/04/2004 01/08/2004 09/11/2004 17/02/2005 28/05/2005


GSD-3 64 (ppm)
Ce (ppm)
P Ag-Ce Cal
PC Ag-Ce
06/10/2003 14/01/2004 23/04/2004 01/08/2004 09/11/2004 17/02/2005 28/05/2005


LKSD-4 48 (ppm)
Ce (ppm)
P Ag-Ce Cal
PC Ag-Ce
06/10/2003 14/01/2004 23/04/2004 01/08/2004 09/11/2004 17/02/2005 28/05/2005


GSD-7 78 (ppm)
Ce (ppm)
P Ag-Ce Cal
PC Ag-Ce
06/10/2003 14/01/2004 23/04/2004 01/08/2004 09/11/2004 17/02/2005 28/05/2005


STSD-3 63 (ppm)
Ce (ppm)
PC Ag-Ce Cal
P Ag-Ce
06/10/2003 14/01/2004 23/04/2004 01/08/2004 09/11/2004 17/02/2005 28/05/2005


GSS-1 70 (ppm)
Ce (ppm)
P Ag-Ce Cal
PC Ag-Ce
06/10/2003 14/01/2004 23/04/2004 01/08/2004 09/11/2004 17/02/2005 28/05/2005