Standard Operation Procedure

Elemental Analysis of Solution Samples with Inductively Coupled Plasma Optical Emission Spectrometry

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October 2005, revised December 2005

1. Application

This method covers the analysis of major and minor elements in solution samples by ICP-OES (Thermo Jarrell Ash IRIS Advantage Inductively Coupled Plasma Optical Emission Spectrometry).

2. Summary of method

2.1 Principle: *An aqueous sample* is converted to aerosols via a nebulizer. The aerosols are transported to the inductively coupled plasma which is a high temperature zone (8,000–10,000ºC). The analytes are heated (excited) to different (atomic and/or ionic) states and produce characteristic optical emissions (lights). These emissions are separated based on their respective wavelengths and their intensities are measured (spectrometry). The intensities are proportional to the concentrations of analytes in the aqueous sample. The quantification is *an external multi-point linear standardization* by comparing the emission intensity of an unknown sample with that of a standard sample. Multi-element calibration standard solutions are prepared from single- and multi-element primary standard solutions. With respect to other kinds of analysis where chemical speciation is relevant (such as the concentration of ferrous iron or ferric iron), only *total elemental concentration* is analyzed by ICP-OES.

2.2 Brief procedure: Five working standard solutions are prepared from independent primary standard solutions. The newly prepared working standard solutions are confirmed against old working standard solutions and against other independent primary standard solutions. In daily operation, the ICP-OES instrument is started, brought to operation conditions and let stabilized. The sample introduction system is checked and the wavelengths are tuned. The instrument is standardized with the five working standard solutions (multi-point linear fitting). Samples are measured with standardization blanks, other kinds of blanks, drift control samples, and quality control samples. After a batch of samples are measured, the data are downloaded to an Excel spreadsheet. The data are corrected in terms of standardization blanks, other relevant

blanks, drift correction, and dilution factor application. The results are normalized to the internal reference standard if an internal reference standard is used. For several elements, a method of "wavelength switch" is used for analytes at different concentration ranges or in different matrixes

3. Safety

All relevant laboratory safety procedures are followed.

4. Interference

This method covers the analysis of over 20 elements in different kinds of samples by ICP-OES. A general discussion of interference is lengthy but not necessarily relevant to a specific element, which is especially true if the sample matrix is not specifically defined. Reading the published articles is recommended. An enormous amount of literature is available for the analysis of metals and non-metals by ICP-OES.

5. Sample collection and preservation

Containers (bottles, vials, etc) typically are soaked in 10% nitric acid overnight and rinsed with de-ionized water for several times before use. Solution samples typically are acidified with nitric acid at a ratio of 1–5 mL of concentrated nitric acid to one liter of sample. Extra cautions need to be exercised in preventing contamination and preserving samples for some specific analyses.

6. Apparatus and device

6.1 ICP-OES: Thermo Jarrell Ash IRIS Advantage Inductively Coupled Plasma Optical Emission Spectrometry.

6.2 Eight-mL polystyrene test tubes (13 mm × 100 mm. e.g. Cat #2110 by Perfector Scientific) for the ICP-OES auto-sampler are used "as is."

7. Reagents

7.1 Concentrated nitric acid (68–71% w/w. e.g. TraceMetal grade. Cat # A509-212 by Fisher Scientific).

7.2 CCV-1 multi-element primary standard set (CPI International).

7.3 ICV-2 multi-element primary standard set (SPEX).

7.4 Single-element primary standard solutions (SPEX).

8. Measurement by ICP-OES

8.1 ICP-OES working standard

8.1.1 OES_1 is a solution of 3–5% (v/v) nitric acid prepared from the concentrated nitric acid, serving as a calibration blank.

8.1.2 OES_2 is made by diluting 5 mL of Solution-A in CCV-1 primary standard to 500 mL with 3–5% nitric acid. In addition, sulfur (S) and titanium (Ti) from single-element primary standards are added, since CCV-1 does not contain these elements. OES_2 contains 27 elements, typically at 2 ppm (ppm = μg/mL = mg/L).

8.1.3 OES_3 is made by diluting 5 mL of ICV-2 primary standard to 500 mL with 3–5% nitric acid. Phosphorus (P), sulfur (S), titanium (Ti) and antimony (Sb) from single-element primary standards are added. OES_3 contains 25 elements ranging from 1–20 ppm.

8.1.4 OES_4 contains 19 elements, typically at 100 ppm. This is made by diluting

single-element primary standards in a 500 mL volumetric flask with 3–5% nitric acid.

8.1.5 OES_5 contains 9 elements, particularly for elements at high concentration ranges. This is made by diluting single-element primary standards in a 500 mL volumetric flask with 3–5% nitric acid.

8.1.6 The details of the standards are listed in Table 1: Multi-element working standards for ICP-OES.

Note: The analysis by ICP-OES is flexible and is easily expanded to other elements. These working standards may not cover the concentration ranges of several elements in samples. Therefore, these working standards may be augmented with some additional standard solutions.

8.2 Preparing sample solutions

8.2.1 Transfer "routine" samples to 8-mL polystyrene test tubes directly.

8.2.2 Prepare "none-routine" samples in some other methods, depending on the requested analyses, sample matrix, analyte concentrations, etc. For example, low-volume or "over-concentrated" samples are diluted before analysis. Turbid samples are left to stand overnight so that particles settle down to the bottom, or the samples are centrifugated so that particles are separated from the samples.

8.2.3 Yttrium (Y) may be used as an internal reference standard. After a given amount of sample (weight or volume) is spiked with a given amount of yttrium, the concentration ratio of (analyte/ytterium) is later used for quantification. Any further dilution does not change the concentration ratio (see Appendix 1: Internal reference standard).

8.3 ICP-OES measurement

The detailed list of start and shut-down steps is given in Appendix 2: Standard start and shut down operation procedure for Jarrell Ash IRIS Advantage ICP-OES. Other instrument conditions are listed in Table 2: ICP-OES instrument conditions.

9. Data processing after ICP-OES analysis

9.1 After the instrument is standardized, the software generates concentration values already. However, these values are further processed.

9.2 Download all of the concentration data into an in-house Microsoft Excel spreadsheet "SPAL" program.

9.3 The results of all QC water measurements are arranged together. Based on these results, the drift (with time) per element is calculated. This drift is corrected for each sample, assuming the drift is linear within two bracketing QC water measurements.

9.4 If applicable, the results are corrected based on an internal reference standard (IRS). Yttrium is used as an IRS.

9.5 The results of the measurement blanks are averaged. This averaged blank is subtracted from all of the other samples.

9.6 If relevant, use the digestion blank(s) to correct the digest blank for digested samples, or use the appropriate blank(s) for some other kind of blank correction.

9.7 Check the analyte results against their respective detection limits.

9.8 Apply dilution factors if appropriate.
9.9 Generate out-going reports.

10. Quality assurance (QA) and quality control (QC)

An ICP-OES instrument is used for broad applications in unlimited situations. A general discussion about QA/QC practice is not specific to a particular application, yet detailed discussions about various applications become too lengthy and are beyond the scope of this procedure. Presented here are some basic operations. The details are presented in Appendix 3: Strategies and implementation of quality assurance (QA) and quality control (QC) in the elemental analysis of solution samples with inductively coupled plasma optical emission spectrometry

10.1 The in-house ICP-OES working standards are made from primary standards of several independent sources. These working solutions are confirmed by using some other independent primary standards. A new set of working standards are checked and confirmed against a previous set of working standards. Where applicable, the working standard solutions are confirmed by using ICP-MS.

10.2 In-house quality control waters (msQC water at ppb level and QC water at ppm level) are analyzed each time after the instrument is standardized. The results of these measurements are confirmed against the expected values. The expected values are compiled from the side-by-side analysis of this msQC water with NIST 1643d water, the historical results of this msQC water by the ICP-OES and ICP-MS analysis, and the historical results of this msQC water and QC water by the ICP-OES analysis.

10.3 The result of the QC water serves as a primary checking point against events such as clogged nebulizer, power abruption, low-argon gas supply, auto-sampler failure, etc. The samples after these events are re-analyzed.

10.4 Samples are diluted to different ratios and measured. The results are used to evaluate matrix effects and (calibration) dynamic ranges.

10.5 Samples are analyzed by using the calibration of internal standard addition.

10.6 Identical samples are analyzed multiple times within one-day's acquisition sequence and are analyzed in different-day's acquisitions. The results are used to evaluate the repeatability of the analysis.

10.7 The ICP-OES analytical results are confirmed by the analysis of ICP-MS.

10.8 Some basic performance or data are listed in Table 3: The analysis by ICP-OES. The RSD (relative standard deviation) is generally better than 5% if an analyte concentration is about 10 times higher than the relevant limit of detection.

10.9 It should be reminded that the time in setting/evaluating the QA/QC criteria is well spent only when the sample matrix is defined, the instrument and its condition are defined, and the target element and concentration range are defined.

– End –

Table 1: Multi-element working standards for ICP-OES

Primary standards			Element	Working standards				
CPI	SPEX	SPEX		OES_1	OES_2	OES_3	OES_4	OES_5
CCV-1	ICV-2	single-element			from CCV1	from ICV2		
ppm	ppm	ppm		ppm	ppm	ppm	ppm	ppm
	100	1000	Ag	0		1	2	
200	1000	10000	Al	0	2	10	100	
200	500		As	0	2	5		
200		1000	B	0	2		10	
100	1000		Ba	0	1	10		
100	100		Be	0	1	1		
200		1000	Bi	0	1 (note)		2	
200	2000	10000	Ca	0	2	20	100	400
100	100		Cd	0	1	1		
100	500		Co	0	1	5		
50	200		Cr	0	0.5	2		
200	200	1000	Cu	0	2	2	20	
200	1000	10000	Fe	0	2	10	100	
500	2000	10000	K	0	5	20	100	500
200		1000	Li	0	2		10	
200	2000	10000	Mg	0	2	20	100	300
100	100	10000	Mn	0	1	1	4	40
200		1000	Mo	0	1 (note)		10	
	2000	10000	Na	0		20	100	
200	500		Ni	0	2	5		
500		10000	P	0	5	20	100	400
200	500		Pb	0	2	5		
		10000	S	0	2	20	100	400
		1000	Sb	0		2	5	
200	500		Se	0	2	5		
		1000	Si	0			5	10
200		1000	Sr	0	2			4
		1000	Ti	0	2	5		
200	500		Tl	0	2	5		
100	500		V	0	1	5		
		1000	Y	0			5	10
100	100	1000	Zn	0	1	1	20	

STD_1: zero concentration. Calibration blank.
STD_2: 5 mL of CPI CCV-1 diluted to 500 mL. Sulfur and titanium were spiked.
STD_3: 5 mL of SPEX ICV-2 diluted to 500 mL. Antimony, phosphorus, sulfur, and titanium were spiked.
STD_4, and STD_5: from 1,000 or 10,000 ppm single element primary standards.

Note: Mo and Bi in CPI is 100 ppm (not 200 ppm as claimed).

Table 2: ICP-OES Instrument Conditions

ICP-OES	TJA IRIS Advantage ICP-OES
Plasma forward power	1150 W
Plasma height	Yttrium bullet halfway between coil top and torch top
Coolant gas flow rate	Instrument default
Auxiliary gas flow rate	Low
Nebulizer	Glass Expansion Sea Spray
Nebulizer pressure	26 psi
Spray chamber	Glass Expansion Tracey Cyclonic
Pump rate	100 rpm
Tubing	Orange-orange
Sample uptake rate	1.2 mL/min
Sample uptake time	30 s
Acquisition	30 s low wave length range, 10 s high wave length range. Twice
Wash solution	De-ionized water or very diluted nitric acid (< 1% v/v)
Wash time	15 s

Element			Background		Tune	Element			Background		Tune
	Wavelength	Order	Left	Right	ppm		Wavelength	Order	Left	Right	ppm
Ag	reserved for future use					Mn	257.61	130	3		5
Al	308.22	109	3	14	50	Mn	293.93	114	1	15	
As	189.04	177	1		30	Mo	202.03	166	4		15
B	249.68	135	1		10	Na	589.59	57	3	14	5
B	249.77	134	3			Ni	231.60	145		15	10
Ba	455.40	74	1	15	4	Ni	232.00	145		12	
Be	reserved for future use					P	177.50	188	3		30
Bi	reserved for future use					Pb	220.35	152	1	15	20
Ca	183.80	182	1	15	40	S	182.03	184	4		50
Ca	184.01	182	1	15		Sb	reserved for future use				
Cd	228.80	147		13	10	Se	196.09	171	4	15	40
Co	228.62	147		15	10	Si	251.61	134	4	13	5
Cr	267.72	126	4	13	10	Sr	407.77	82	1	15	2
Cu	324.75	103	4		10	Ti	334.94	100	3		5
Fe	238.20	141	4	15	30	Tl	reserved for future use				
Fe	271.44	124	1			V	310.23	108	2		4
K	766.49	44	1	15	40	Y	319.56	105	3	13	10
Li	670.78	50	2	13	2	Zn	213.86	157	3		10
Mg	285.21	117	4		10						
Mg	285.21	118	2	14							

Table 3: The Analysis by ICP-OES

	LOD	2% nitric	Bovine serum			Human urine			Soft water			Hard water		
	ppm		ppm	sd	rsd	ppm	sd	rsd	ppm	sd	rsd	ppm	sd	rsd
Al	0.05	<LOD	<1.8			<0.5	0.2		<LD	0.03		<LD	0.01	
As	0.03	<LOD	<0.9			<0.3	0.1		<LD	0.005		<LD	0.012	
B	0.03		(for high Fe samples such as soil samples)											
B	0.002	<LOD	0.16	0.04	22	2.06	0.01	0.3	0.007	0.001	12	0.005	0.002	53
Ba	0.0002	<LOD	0.120	0.001	1	<0.002	0.001		<LD	0.000		0.014	0.000	1.9
Ca	0.01	<LOD	97	2	2	184	3	1	0.12	0.08	71	66	0.2	0.3
Cd	0.004	<LOD	<0.12			<0.04	0.01		<LD	0.001		<LD	0.014	
Co	0.003	<LOD	<0.09			<0.03	0.01		0.003	0.001	45	<LD	0.001	
Cr	0.001	<LOD	<0.06			<0.01	0.01		<LD	0.000		<LD	0.001	
Cu	0.005	<LOD	0.90	0.04	5	0.07	0.01	16	0.030	0.004	14	0.028	0.002	5
Fe	0.001	<LOD	2.02	0.06	3	0.02	0.01	33	0.041	0.002	6	0.136	0.003	2
K	0.03	<LOD	186	3	2	1918	3	0.2	<LD	0.04		0.94	0.04	4
Li	0.0005	<LOD	<0.03			0.011	0.002	14	0.002	0.000	9	0.002	0.000	17
Mg	0.007	<LOD	20.8	0.4	2	107	0	0.3	1.91	0.02	0.9	35.7	0.1	0.3
Mn	0.0003	<LOD	< 0.03			<0.003	0.001		0.003	0.000	5	0.009	0.001	9
Mo	0.005	<LOD	0.34	0.05	14	0.18	0.27	151	<LD	0.002		<LD	0.005	
Na	0.006	<LOD	3026	48	2	2651	4	0.2	133	1	0.5	2.29	0.04	1.6
Ni	0.004	<LOD	<0.09			<0.03	0.02		<LD	0.004		<LD	0.002	
Ni	0.02		(for high Fe samples such as soil samples)											
P	0.05	<LOD	125	2	2	790	6	0.7	<LD	0.03		<LD	0.02	
Pb	0.02	<LOD	<0.6			<0.2	0.1		<LD	0.004		<LD	0.004	
S	0.05	<LOD	779	11	1	653	3	0.5	6.05	0.06	1	5.87	0.09	2
Se	0.04	<LOD	<1.2			2	3	160	0.04	0.04	99	<LD	0.010	
Si	0.007	<LOD	1.39	0.20	14	13.9	0.0	0.2	6.95	0.02	0.3	7.16	0.01	0.2
Sr	0.0001	<LOD	0.09	0.00	2	0.212	0.000	0.2	<LD	0.000		0.056	0.000	0.5
Ti	0.002	<LOD	<0.06			0.015	0.003	23	<LD	0.001		<LD	0.000	
V	0.004	<LOD	<0.12			<0.03	0.02		<LD	0.002		<LD	0.001	
Y	0.01	<LOD				<0.08	0.02		0.023	0.004	16	<LD	0.004	
Zn	0.001	<LOD	1.12	0.08	7	0.61	0.25	41	0.01	0.02	239	0.002	0.001	58

Note

LOD: Limit of the detection = 3 times of the standard deviation of the repeated analysis of 1% nitric acid.
The samples were measured and the results were averaged (n = 6).
sd (ppm) = 1 sd. rsd (%) = 100 X (sd/average).

The rsd was greater than 10% when the measured concentrations were close to the detection limits.

2% nitric: 2% (v/v) nitric acid.
Bovine serum: diluted by 30 times. The dilution factor is applied already.
Human urine: diluted by 10 times. The dilution factor is applied already.
Soft water: Madison City tap water after residential water softener.
Hard water: Madison City tap water.

Appendix 1: Internal Reference Standard

1. Internal reference standard (IRS)

An instrumental analysis is a process of comparing an unknown sample's signal with a standard's signal. If the signal of Cu in a milk sample is 100 and the signal of 10 ppm Cu in a 1% nitric acid is 100, the milk sample contains 10 ppm of Cu. Because of matrix effects (sample viscosity, presence of other inorganic or organic material, etc.), these two signals are usually different from each other. If both samples are spiked with equal amounts of yttrium (Y) as the internal reference standard (IRS), the signal ratios of Cu/Y of both samples are less affected by matrix effects. The reliable comparison between an unknown sample and a standard is greatly improved.

Using an internal standard is a common practice in ICP-OES and in ICP-MS applications. An internal standard is used to correct between sample variations – such as the differences in sample matrix, as mentioned above. It is used to correct short-term and long-term instrument drift with time caused by plasma fluctuation and other instrumental fluctuations. An important advantage is to correct the volume inaccuracy during sample preparation, as given below in section 4: A practical use of internal reference standard – correction for volume inaccuracy.

2. Disadvantages of IRS technique

Any signal is measured with some degree of uncertainty. In direct signal comparison, it is the process of comparing an unknown's (signal±uncertainty) with the standard's (signal±uncertainty). In the IRS technique, it is the process of comparing the ratio of (signal±uncertainty)/(signal± uncertainty) of an unknown sample with the ratio of (signal±uncertainty)/(signal± uncertainty) of the standard. In principle, a larger margin of error is introduced by using the IRS technique since more uncertainties are involved in the calculation. In practice, this problem is less important with respect to the benefit of correcting matrix effect and of correcting instrument drift by using IRS.

3. Precautions in using IRS

There are precautions to take when selecting an internal standard. Its original or natural amount in a sample should be so low that it can be ignored with respect to the spiked amount (e.g. original amount <1% of spiked amount). If 0.04 mL of 10,000 ppm of yttrium is spiked to 0.5 gram of sample, and is subsequently diluted to 50 mL, this is equivalent to 800 ppm of yttrium in solid sample ($0.04 \times 10000/0.5 = 800$ ppm) or 8 ppm in solution. Plant tissue samples and soil samples contain less than 10 mg/kg of yttrium. Therefore, the natural yttrium in a plant sample or a soil sample is insignificant with respect to the spiked yttrium.

An internal standard should also be so selected that it does not interfere with targeted elements. This has to be confirmed for each element at the given concentrations of the IRS (e.g. 8 ppm of yttrium in a solution) and at the expected concentrations of other elements.

The fundamental requirement in using IRS is that the signals of a target element and the IRS element (e.g. yttrium) are enhanced or suppressed, equally, so that the signal ratios (of target element/reference element) are always the same no matter how other conditions change. In a multi-element method, this is usually true but not always. The worst scenario is that a target element

and the reference element behave in opposite directions. For example, from 1% nitric acid to milk, the signal of element X is enhanced by 10% but the signal of reference R is suppressed by 10%. Without the IRS technique, the error of X might be +10%. With the IRS technique, the error could be +20%. In this case, an IRS should not be used at all. Therefore, a method with IRS could be more deceiving than a plain method without IRS.

Similarly, instrument drift (with time) is usually element-specific. The drift correction based on an IRS alone could also be deceiving, as pointed out above, if a target element and the reference element drift in opposite directions. Alternatively, the drift (with time) might be corrected by inserting a drift control sample containing all of the target elements between unknown samples.

4. A practical use of internal reference standard – correction for volume inaccuracy

After a sample is spiked with an IRS (e.g. 0.04 mL of 10,000 ppm of yttrium to 0.5 gram of sample), the concentration ratios of target elements to the reference element are fixed, no matter whether the sample is later diluted by 10 times or by 100 times. Since the concentration ratios (actually the signal ratios) are used in later data processing, the volume accuracy of a container is irrelevant in the subsequent dilutions and a sample could be freely diluted.

This "free dilution" without strict volume accuracy requirement has several practical advantages. Some QA/QC protocols require the use of Class A volumetric flasks (although in many cases of environmental or agricultural analysis, rarely that is required). Plastic lab-wares are preferred in metal analysis, especially in trace analysis or when hydrofluoric acid is used. Class A glass volumetric flasks are generally available but Class A plastic volumetric flasks are scarce. Another advantage is that an analyst could make the subsequent dilutions quickly and easily without introducing any unintentional "volumetric" error. And lastly, if one target element in a particular sample is over a standardization range, that sample is "freely" diluted and re-analyzed for that element without paying too much attention to volume accuracy or to dilution factor. For example, given a solution of 150 ppm of zinc and 8 ppm of yttrium, the zinc concentration is over a standardization range of 40 ppm. This solution is easily diluted by 10 times to contain 15 ppm of zinc and 0.8 ppm of yttrium. The calculation, since it is based on concentration ration (actually signal ratio), treats this sample as if the sample were not diluted.

As one may deduce from the above example, a sample is diluted "freely" in theory but "limited" in practice. In other words, a concentration ratio is always the same no matter how much a sample is diluted, but a signal ratio is not and depends on the overall sample matrix and instrument response. Therefore, all of the samples should be diluted to the same extent as much as possible so that a signal ratio is still proportional to a concentration ratio consistently for all of the samples and standards.

– End –

Appendix 2: Standard Start and Shut down Operation Procedure for Jarrell Ash IRIS Advantage ICP-OES

1 Per first day of a month

1.1 Replace all peristaltic pump tubings.
1.2 Refill water to the argon gas humidifier.
1.3 Refill the washing water.

2 Daily start procedure

2.1 Check the liquid nitrogen and the liquid argon. Order if needed.
2.2 Check the CID temperature (-90ºC).
2.3 Confirm that the exhaust fan is on.
2.4 Lock peristaltic pump platens down.
2.5 Drain the spray chamber if needed.
2.6 Ignite the plasma. Confirm that the waste is being pumped out.
2.7 If the plasma is not lit, most likely either there is a leak of air into the sample introduction system, or the purge was insufficient. Find the leak or increase the purge time. Try one or two more times. If the plasma is still not lit, find the cause and fix it. Options are: hard reset, reboot the computer, and reboot the instrument and the computer.
2.8 Warm up for at least 30 minutes.
2.9 Per first day of a month: Record the operation power level (LCD on the right panel).
2.10 Per first day of a month: select the mercury lamp as the source, acquire at several wavelengths, and record the intensities.

3 Daily operation procedure

3.1 Aspire a 1,000 ppm yttrium solution to the system, check and confirm that the yttrium bullet is half way between the coil top and the torch top. The bullet position is adjusted by setting the nebulizer pressure. If the pressure is significantly out of "normal" range, find the cause and fix it.
3.2 Use an in-house tune solution (containing 1–50 ppm of multi-elements), carry out "Auto peak adjustment." Still use the same tune solution and measure as one sample. Check the analyte peaks of this measurement with the peaks of previous measurements. The peaks may shift left or right, but the peak height should be about the same for the identical tune solution. When the method is switched to a different one, either carry out auto peak adjustment or run one sample to confirm the peak position.
3.3 Aspire 10–30% nitric acid for one to two minutes to clean the system. Set up the ICP-OES working standards, measure, and carry out the standardization. Check and confirm the standardization result by checking the slopes, intercepts, and correlation coefficients. If the slopes deviate from "normal" values significantly, find the cause and fix it.
3.4 Measure a 3–5% nitric acid solution for two times as the measurement blanks. Measure one msQC water (quality control water at low concentration – ppb level). Measure one QC water (quality control water at high concentration – ppm level). Check these results against established results.
3.5 Confirm the autosampler's alignment before using it. Set the sample rack(s) into place. Start the whole acquisition sequence.
3.6 The QC water (at ppm level) is measured after every 20 samples.

4 Daily shutdown procedure

4.1 Thoroughly rinse the sample introduction system by aspiring de-ionized water for 5–10 minutes.
4.2 Shutdown the instrument (i.e. extinguish the plasma and shut down the RF generator).
4.3 Release the peristaltic pump.

– End –

Appendix 3: Strategies and Implementation of Quality Assurance (QA) and Quality Control (QC) in the Elemental Analysis of Solution Samples with Inductively Coupled Plasma Optical Emission Spectrometry

1. Introduction

There are different ways in developing an analytical method and implement QA/QC strategies in using an instrument with multi-element capability such as an ICP-OES. This appendix, in loosely-connected sections, provides the relevant information and rational for the development of "Elemental analysis of solution samples with ICP-OES."

2. Selection of elements

A multi-element method ideally includes as many elements as possible. However, neither is this necessary nor practical in reality. Two main factors are considered in selecting or deselecting elements – requested analysis and instrument capability.

2.1 Primary elements – Al, As, B, Ca, Cd, Co, Cr, Cu, Fe, K, Li, Mg, Mn, Mo, Na, Ni, P, Pb, S, Se, and Zn (21 elements). These are frequently requested elements for the agricultural, environmental, biomedical, and other applications.

2.2 Secondary elements – Ag, Ba, Be, Bi, Sb, Si, Sr, Ti, Tl, V, and Y (11 elements). These elements are requested less frequently for analysis. However, the instrument potentially provides good performance in terms of detection limit, linear range, and stability for the following elements: Ag, Ba, Be, Si, Sr, Ti, V, and Y. These elements are readily available in working standard solutions (see section Working standards): Ag, Ba, Be, Bi, Sr, Tl, and V. The inclusion of these secondary elements does not prolong the analysis time of the primary elements. since the TJA IRIS ICP-OES runs simultaneously on all elements.

2.3 Other elements are deselected. Some elements do not have sensitive wavelengths (e.g. Cs), do not have less-interfered wavelengths (e.g. rare earth elements), are never requested for analysis (e.g. Ru, Sc, and Te), are not readily available in standard solutions (e.g. Rb, Sn, and Zr), and/or are not compatible with other elements (e.g. iodine). The SPAL's ICP-MS instrument (VG PQ2T Plus ICP-MS) provides a much better analysis for most of these elements in terms of detection limit and interference reduction (e.g. Cs, Ge, and U) than the analysis by ICP-OES.

2.4 Selected elements in alphabetical order – Ag, Al, As, B, Ba, Be, Bi, Ca, Cd, Co, Cr, Cu, Fe, K, Li, Mg, Mn, Mo, Na, Ni, P, Pb, S, Sb, Se, Si, Sr, Ti, Tl, V, Y, and Zn (32 elements).

2.5 Selected elements in mass order – Li, Be, B, Na, Mg, Al, Si, P, S, K, Ca, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Se, Sr, Y, Mo, Ag, Cd, Sb, Ba, Tl, Pb, and Bi.

3. Working standards

There are several potential ways in making multi-element working standard solutions by using standards from single-element primary standards, multi-element primary standards, custom-style primary standards, and/or a combination of single-element and multi-element primary standards. The criteria are easy, error-proof and economic.

In making 32-element working standards from single-element primary standards, an analyst needs to transfer different amounts of standards from approximately 40 bottles of standard solutions (some primary standards at 1,000 ppm and some at 10,000 ppm) to 4–6 volumetric flasks. This process is very time consuming and is prone to mistakes. In addition, it is difficult to control and/or trace the quality of 40 bottles of primary standards. The primary standards are expensive and yet only a tiny portion of these standards may be used. Often, a good portion of the standards still remains long after their expiration dates.

Multi-element primary standards are available commercially. However, these solutions usually do not have the desired element combinations and/or the desired concentration ranges for a specific analysis. For example, digested plant solutions contain high concentrations of P, K, Ca, Mg and S (> 100 ppm), but low concentrations of B, Cu and Zn (< 1 ppm).

Custom-designed primary standards are available commercially. Desired combination of elements and desired concentration ranges are specified by customers. However, the cost of these standards is simply too high.

A practical, economical, and reliable approach is to make low-concentration working standards from multi-element primary standards (covering about 30 elements) and to make high-concentration working standards from single-element primary standards (about 10 elements). Two multi-element primary standards are purchased from two different sources: Solution-A in the set of CCV-1 from CPI International and ICV-2 from SPEX. Other single-element primary standards are purchased from SPEX. From these primary standard solutions, five working standard solutions are made: OES_1, OES_2, OES_3, OES_4, and OES_5.

The primary standards Solution-A in CCV-1 (for OES_2) and ICV-2 (for OES_3) are from different sources and, therefore, are expected to be independent. The two working standards (OES_2 and OES_3) are prepared with a very minimum operation (i.e. very low chance to introduce operational errors). Therefore, these two standards are planned to be used to confirm each other's claimed concentrations.

4. Calibration strategy choice – 1: Single point (actually one blank point and one high concentration point) linear fitting or multi-point linear fitting

A calibration curve, in most cases, is the shape of an over-stretched "S" – from very low concentrations to very high concentrations. An instrument response is generally considered as being linear from zero to a certain point of concentration and non-linear from that point on. Linear or non-linear is relative. There is no sudden jump from a linear response to a non-linear response. A response viewed by one analyst as linear may be viewed as non-linear by another analyst. The linear response of ICP-OES is generally accepted to be over 5 orders of magnitude from sub-ppb to ppm levels.

In principle, one point (i.e. one zero and one high) linear fitting is no worse than multi-point linear fittings in the linear range. Two points define a line. Several points also define a line and do not necessarily define a "superior" line. In reality, operational errors and instrumental errors, whether systematic or random, are unavoidable. A multi-point

linear fitting would catch the majority of these errors. From this standpoint, a multi-point linear fitting is superior to a single-point linear fitting. This concept is implemented in making the working standards for the primary elements. For example, the linear fitting of cadmium (Cd) contains 3 points: one blank point (OES_1) and two 1-ppm points (OES_2 and OES_3).

5. Calibration strategy choice – 2: Curve fitting, linear fitting, or wavelength switching in a wide concentration range (i.e. Assumed to be non-linear range)

Within a linear response range, a multi-point linear fitting is no better than a one-point linear fitting in theory. However, a multi-point linear fitting is more reliable, in reality, due to operational and instrumental errors. In a non-linear response range, a multi-point linear fitting is no better than a one-point linear fitting, either in theory or in reality. Instead, the harm created by a multi-point linear fitting may be more extreme because it is prejudged that the result by a multi-point fitting is better than a one-point fitting.

Would a multi-point curve fitting be better than anything else? This is not absolutely true. Mathematically, there are no formulas which define a straight line at one end and a curve at the other end. Approximation is unavoidable and errors are introduced. These kinds of errors are less intuitive and usually more difficult to catch than errors introduced during a linear fitting.

The TJA IRIS ICP-OES is a simultaneous instrument–the analysis time is independent of the number of wavelengths. Therefore, two wavelengths per element are selected for elements with wide concentration ranges (such as Ca [0–400 ppm], Fe [0–100 ppm], Mg [0–300 ppm], and Mn [0–40 ppm]). One wavelength is for the low concentration range and the other for the high concentration range. All are linear fittings. The blank point (OES_1) is excluded from the linear fitting in the high concentration ranges. An external calibration, by its nature, is a comparison process. Standards at low concentration ranges are not necessary for analyses at very high concentration ranges.

6. Calibration strategy choice – 3: Standardization or calibration

The TJA IRIS ICP-OES instrument is prepared in two ways: standardization and calibration ("Standardization" as defined in the TJA IRIS ICP-OES manual is a linear fitting "calibration" as we normally say. "Calibration" as defined in the TJA IRIS ICP-OES manual is actually a way of curve fitting "calibration").

6.1 Standardization: Linear fitting based on a set of working standards The standardization is carried out daily or each time before sample analysis with a whole set of standards.

6.2 Advantage of standardization: Quantification is based on a linear relationship. The calculation is simple. This relationship is direct and easy to diagnose in case something is inaccurate. Standardization can be based on just two points.

6.3 Disadvantage of standardization: Instrument response is usually not linear at very low concentration ranges or at very high concentration ranges. During each sample analysis, the whole set of standards (whether being two or ten) also have to be analyzed.

6.4 Calibration: Curve fitting based on a set of working standards (minimum – 4 standards). The curve is adjusted

(normalized) daily or before each sample analysis with a "low-end" standard and a "high-end" standard.

6.5 Advantage of calibration – Better instrument response in a wide concentration range than a linear fitting. Only two "Norm" standards are needed for each sample analysis.

6.6 Disadvantage of calibration – A curve fitting is less intuitive and makes it difficult to diagnose a problem. The calibration is less adaptive to a significant instrument change. Some examples include: auto-peak adjustment where the peak of an element can be shifted either to left or to right, nebulizer change, and plasma power change.

6.7 "Standardization" is selected over "calibration" by primarily considering that a "calibration" is less tolerant to instrument condition changes and less intuitive. However, these two terms are not distinguished in other sections of this appendix.

7. Validation of the working standard

It is a widely accepted practice to use NIST SRMs (standard reference materials) to validate various kinds of laboratory operations. However, NIST SRMs are not readily available to validate these working standards due to the unique concentration ranges and element combinations. Alternatively, several different approaches are used.

7.1 First of all, these multi-element working standards are purposely made from primary standards of independent sources. An agreement between these primary standards themselves is an indication that the claimed concentrations are valid.

7.2 When a new set of working standard solutions are made, the new set of standards are measured against the old set of standards. One example is given in Table Appendix 3-1: Validation of working standard - comparison of new set with old set. This agreement is better than 100±3% in most cases.

7.3 After the instrument is standardized with these working standards, an independent set of primary standard solutions, CLMS-1, CLMS-2 and CLMS-4 (all from SPEX), which contain 10 ppm of most elements, are measured either "as is" or diluted by 10 times. The results are given in Table Appendix 3-2: Validation of working standard - based on independent SPEX primary standards. For most elements, the agreement is better than 100±5%. However, the recoveries of some elements are significantly out of the above range. MS1 contains 17 elements, MS2 contains 29 elements and MS4 contains 12 elements. A certain extent of inter-element interference is possible but this is not fully examined. The five OES working standard solutions are designed to cover high concentrations ranges for some elements such as K, Fe, Al and S. The concentrations of these elements in MS1, MS2, and MS4 solutions, especially after dilution, may not be in the optimum calibration ranges of these OES working standard solutions. SPEX MS-4 contains trace amount of HF acid. This may explain the extraordinarily high concentrations of Si (measured 19 ppm vs. claimed 10 ppm), since the sample introduction system is not HF-resistant.

7.4 Eight other independent standard solutions from four different sources

are measured based on these five OES working standards. These eight solutions are diluted by 10 or 20 times and then analyzed. The recovery ratios (the measured concentrations to the claimed concentrations of these eight independent standard solutions) are better than 100±5% for most of the elements (see Table Appendix 3-3: Validation of working standard - based on other eight primary standard solutions). The exceptions might be caused by potential inter-element interferences and/or improper dilutions.

7.5 The consistency between these working standards and other standard solutions is also confirmed by using ICP-MS for several elements where applicable. The mechanisms of inter-element interferences of ICP-OES are different from those of ICP-MS. For example, the concentration of molybdenum in Solution-A of CCV-1 (from CPI international) is found to be 100 ppm rather than as the claimed concentration of 200 ppm, based on several different analyses. Solution-A of CCV-1 is used to make the OES_2 working standard.

8. Analytical merit – limit of detection (LOD), calibration blank (cBlk) and blank correction

8.1 A solution of 3–5% nitric acid is consecutively measured 12 times in one day. The average and the standard deviation (SD) of these measurements are calculated. The limit of detection (LOD) is three times the standard deviation (LOD = 3 × SD). Six sets of LODs are so collected on six different days. The average of these six sets of LODs is taken as the instrument's LOD and listed in Table Appendix 3-4: Analytical merits.

8.2 There have been extensive and endless discussions about the way of obtaining and the way of applying the limit of detection (LOD). There are also discussions about other "confusing" terms, such as: instrument detection limit, method detection limit, and limit of quantification, etc. Overall, the LOD and other terms depend on their respective definitions and depend on the conditions under which a sample is measured. The LOD and other terms should be used as general reference but not an absolute judge point.

8.3 An analogy to limit of detection is the achievable speed by a race car. Every effort is made to achieve the maximum speed of a race car. The achievable speed of a race car does provide a lot of information but does not provide all of information. If some one thinks about three types of vehicles (race car, regular car and all-terrace vehicles) in three types of fields (car-race field, regular highway and off-road), the maximally achievable speed by a race car tells virtually very little, or is not considered as critical at all.

8.4 A quick suggestion is that a researcher may need to interpret a value cautiously if the value is close to the limit of detection. It is advised to design a research to avoid such an uncertain situation. Alternatively, a different instrumentation or different analytical methods may better be used. For example, the SPAL's ICP-MS service is recommended for the analysis of minor and trace elements (the heavy metal list) in plant tissue samples. Hydride generation technique is better for arsenic and selenium in

most types of samples rather than conventional nebulization (ICP-OES or ICP-MS).

9. Calibration blank (cBlk) and blank correction

9.1 A solution of 3–5% nitric acid is measured every time after the instrument is standardized. All of these measurements (in one year, about 140 sets of data) are pooled, the average (Avg) and three times the standard deviation (3sd) are calculated and also listed in Table Appendix 3-4: Analytical merits.

9.2 The 3sd values are apparently higher than the respective LODs of each element. This makes sense since the 3sd values are calculated from the pooled measurements of blank samples over a long period of time while the LOD values are based on samples measured within a very short period of time. This 3sd values in one way may be viewed as the realistic detection limits achievable in any day's analysis.

9.3 The average values of the blank sample (cBlk, 3–5 % nitric acid) are close to zero, which makes sense since these values should be zero statistically. However, the measured values of the cBlk sample on any particular day could be fairly away from zero. The equivalent concentrations may be negative or positive simply based on the mathematics of the calculation.

9.4 These equivalent concentrations of the cBlk sample, whether positive or negative, are corrected from all of the other samples. This correction is important for elements at low concentration levels (ppb levels), such as: iron or copper in water samples, but it is undetectable for elements at high concentration levels (ppm levels), such as: calcium or magnesium in hard water samples.

9.5 On the other hand, this blank correction in effect does not change the analytical conclusion, when the equivalent concentrations of the cBlk sample are significantly less than their respective LODs (as listed in Table Appendix 3-4: Analytical merits), although the two procedures (with and without correction) are conceptually different.

10. In-house quality control water (msQC water at ppb levels and QC water at ppm levels)

Several NIST waters might be used as quality control solutions for trace analysis at ppb levels, but are not applicable to major and minor analysis at ppm levels. It is also expensive to include NIST waters in day-to-day analysis. Other kinds of quality control solutions are available commercially with similar problems: not matching and/or not economical.

10.1 An in-house quality control (QC) water is made by adding standard solutions to a 20-liter glass jar, diluting with 3–5% nitric acid, and sub-bottling it in 2.5-liter glass bottles. These 2.5-liter glass bottles are reagent bottles which were used for Trace Metal Grade nitric acid (Fisher). No more leaching-out of metals is expected from these bottles by 3 – 5% nitric acid. The 3–5 % nitric acid prevents absorption and precipitation of metals. The metals are at 5–40 ppm concentration levels and an interaction between these metals is not expected. Therefore, this QC water is expected to be stable for years.

10.2 An in-house quality control (msQC) water is made similarly but at ppb levels.

10.3 The in-house msQC and QC waters are used to confirm the instrument standardization in day-to-day analysis. The QC water is also used to correct instrument's within-day drift.

11. Long term consistency (day to day analysis)

After the TJA IRIS ICP-OES is standardized, the msQC water and the QC water are analyzed. The results of msQC water (from July 2004 to December 2005) are shown in Figure Appendix 3-1: Analysis of elements at ppb level. The results of QC water (from June 2003 to December 2005) are shown in Figure Appendix 3-2: Analysis of elements at ppm level. The respective averages and standard deviations are listed in Table Appendix 3-4: Analytical merits.

11.1 The msQC water contains minor and trace elements at ppb levels. The data quality of each element needs to be evaluated after considering what the LOD is, how high the concentration is or how big the difference is between the concentration and the LOD, and how the msQC water is stored. Some examples are given below.

11.1.1 The vertical scales of the plots of Al, Cu are the same in Figure Appendix 3-1. Both average concentrations of Al and Cu are about 90 ppb. By looking at the respective plots, it can be concluded immediately that the data quality of Cu is much better than that of Al. This is because the concentration of Al in the msQC water is about as twice as Al's LOD, but the concentration of Cu is about 20 times higher than Cu's LOD.

11.1.2 Other examples may be seen from the elements of Ba, Co, Cr, Li, Mo, Ni, Sr, Ti, V and Y where the vertical scales are the same. Generally, the magnitude of standard deviation (SD, listed in Table Appendix 3-4) of data points is positively related to the magnitude of the respective LOD for each element.

11.1.3 Relative standard deviation (RSD), another term for quality evaluation, is the ratio of the standard deviation to the average concentration of an element. The RSD generally decreases with the increasing concentration of an element.

11.1.4 The concentrations are apparently different before and after the msQC water in two sub-bottles were measured, respectively, for Ca, Fe, Li, Na and especially Si. This is because the msQC water contains trace amount of HF acid. These elements are released from the glass bottles with time.

11.2 The QC water contains most elements at ppm levels. As such, the detection limit is usually not the main factor in controlling data quality. As such, the data quality is consistent across different elements for a long period of time (several years).

11.2.1 In this period of time, the working standard solutions are renewed for three times. The whole laboratory is relocated to a different place. The QC water is analyzed from different sub-bottles. The consistent results as shown in Figure Appendix 3-2 demonstrate the successful practice of this QA/QC implementation.

11.2.2 On the other hand, the concentrations of Al, Ca, Na, and Si increase significantly with time or vary

significantly in different sub-bottles. This is quite contrary to an initial thought that these concentrations would be stable for years. It is expected that a solution of 3–5% of nitric acid would not release metals from the glass bottle. However, several solutions which were used for making the QC water contain HF acid and it might be this HF acid that releases these Al, Ca, Na, and Si elements from the glass bottle.

11.2.3 Since the QC water contains elements at ppm level and more standard solutions (and more HF acid) are used than the solutions used for making the msQC water, the release of these elements from the glass bottles is more significant than that of the msQC water.

11.2.4 The release of Al from the bottles of msQC water is not obviously observed. This might be either because the release is insignificant with respect to the release of Al in the QC water bottles, or because the release of Al is blurred by the huge scattering of the data points as seen from Figure Appendix 3-1.

11.3 The evaluation on the data quality of a multi-element analysis is not easy or straightforward. Many factors have to be considered simultaneously. Each and every element has to be considered and evaluated individually. A cross-board expectation of data quality for all of elements is just simply impractical.

11.4 The result presented in Figures Appendix 3-1 and 3-2 provide a visual estimation of data quality for different elements at different concentration levels. The numerical values are provided in Table Appendix 3-4.

12. Short term consistency (within day analysis)

Immediately after the instrument is standardized, the QC water is measured. This QC water is also measured at every 20 sample intervals. The ratios of subsequent concentrations to the first concentration in a time sequence indicate how much the instrument drifts over time.

12.1 This TJA IRIS ICP-OES instrument is typically used for 5–10 hours each time after standardization. Most of the time (>80–90%), the ratios are between 0.95 and 1.05, or the drift is less than 5%. In the first example (Table Appendix 3-5: Short term stability as seen from the drift of QC water), the instrument is standardized and used for 17 hours. The ratios are roughly one.

12.2 The drift sometimes can be quite significant, as seen from the second example in Table Appendix 3-5. This second example also indicates that the drift is element-dependent, changes in opposite directions (up or down), and varies at different rates.

12.3 This element-dependent drift makes the drift-correction a challenge. Using an internal reference standard (a common practice in ICP-OES) would not help much in correcting this type of drift. Actually, the correction based on an internal reference standard makes the drift-introduced error even larger, if the internal reference standard and the target element drift in opposite directions.

12.4 Assuming that the drift is linear within a short period of time between two check points (i.e. between two QC

water analyses), the drift of other samples/elements could be corrected based on the drift of the QC water. After the instrument's output is loaded into an Excel spreadsheet, an in-house computer program is used to carry out this correction. Listed in Table Appendix 3-6: Results of short-term drift correction are some examples. Typically in one day, the tenth sample (i.e. the mid-point sample between the first QC measurement and the second QC measurement) is measured again at the end of the day's analysis (i.e. just before the last QC measurement). As seen from Table Appendix 3-6, the results of duplicate analyses are repeatable.

12.5 The nature of this drift correction is equivalent to the normalization of the instrument with the QC water after every 20 samples.

13. Ending

The data quality is judged in terms of accuracy and precision. The accuracy and precision of the SPAL's analysis is generally better than 100±5 %. However, there are exceptions.

In a single-element method, experimental conditions are optimized to the best conditions for that specific element in a specific matrix. In a multi-element method, it is impossible to select the best conditions for all of the elements in various kinds of matrix, since one best condition for one element could be a worst condition for another element. A multi-element method virtually is a multi-compromising method. Therefore, there are differences between data quality obtained via a single-element method and data quality obtained via a multi-element method. And there are differences in data quality between results of elements obtained by one analytical method.

The selection of a dilution factor is a very good example here. Samples contain components in a large concentration range from trace, minor, to major. With a limited sample preparation (e.g. one dilution factor for all), some components fall into the best concentration range for an analytical method, while other component's concentrations are either too high or too low. Consequently, the data qualities are different for different elements.

What are the criteria in accepting/rejecting an analytical result? It depends. The data quality of 0.02±0.01 ppm for selenium may be as good as the data quality of 2000±60 ppm for sulfur, although the relative standard deviation (RSD) of Se's result (50%) is way higher than that of S (3%). It is improper to compare the data quality of trace elements (such as Se) with the data quality of major elements (such as S). The best criteria are to consult the research literature. If the common RSD for Se found in literature is about 50% for results at 0.02 ppm level obtained by using an ICP-OES method in a multi-element analysis, the quality of the result (0.02±0.01 ppm Se) could be judged as accurate and be well accepted.

Although an analyst may be proud of his/her performance in obtaining such "accurate" data, a client may not be happy because s/he needs to know whether the concentration of Se is 0.01 ppm or 0.03 ppm. In that case, a different analytical procedure has to be sought. For example, the SPAL offers the analysis of Se with hydride generation stable isotope dilution – ICP-MS, which offers a detection limit of 0.001 ppm of Se in plant

tissue. The detection limit, offered by the ICP-OES method, is 4–7 ppm.

As discussed in section *11. Long term consistency*, the interpretation and application of multi-element analyses is complicated and requires the consideration of many factors/parameters: sample type, sample preparation, element, concentration range, detection limit, contamination, and instrument performance to that specific element. The time, effort, and resources for a project are wisely spent only after these factors/parameters are well considered and controlled beforehand.

– End –

Table Appendix 3-1: Validation of working standard - comparison of new set of standard with old set of standard.

	Intended concentration				Measured concentration				Measured concentration							
	All units are ppm				Set made on 06/24/2003				Set made on 05/27/2004				Ratio of new to old			
	oes2	oes3	oes4	oes5	oes2	oes3	oes4	oes5	oes2	oes3	oes4	oes5	oes2	oes3	oes4	oes5
Al	2	10	100		2	11	98		2	10	99		97	97	101	
As	2	5			2	5			2	5			102	101		
B	2		10		2		10		2		10		102		102	
Ba	1	10			na = not added				1	10						
Ca	2	20	100	400	2	20	103	406	2	20	104	402	100	99	102	99
Cd	1	1			1	1			1	1			101	100		
Co	1	5			1	5			1	5			100	101		
Cr	0.5	2			0.5	2			0.5	2			101	101		
Cu	2	2	20		2	2	20		2	2	20		107	103	101	
Fe	2	10	100		2	10	100		2	11	101		102	109	101	
K	5	20	100	500	5	20	99	498	5	20	101	500	106	100	102	100
Li	2		10		2		10		2		10		102		96	
Mg	2	20	100	300	2	20	107	298	2	19	108	296	101	92	101	100
Mn	1	1	4	40	1	1	4	40	1	1	4	40	104	104	103	100
Mo	1		10		1		10		1		10		103		102	
Na		20	100			20	97			21	99			106	103	
Ni	2	5			2	5			2	5			100	101		
P	5	20	100	400	5	21	106	405	5	22	107	403	103	103	101	99
Pb	2	5			2	5			2	5			98	99		
S	2	20	100	400	2	20	101	406	2	20	101	405	102	102	100	100
Se	2	5			2	5			2	5			101	100		
Si			5	10							5	10				
Sr	2			4					2			na				
Ti	2	5			na = not added				2	5						
V	1	5							1	5						
Y			5	10							5	10				
Zn	1	1	20		1	1	20		1	1	20	0	103	104	103	

	All units are ppm				Set made on 05/27/2004				Set made on 06/14/2005				Ratio of new to old			
Al	2	10	100		2	10	99		2	10	97		103	99	98	
As	2	5			2	5			2	5			99	100		
B	2		10		2		10		2		10		100	103	99	
Ba	1	10			1	10			1	10			100	100		
Ca	2	20	100	400	2	20	104	402	2	20	104	400	99	100	99	99
Cd	1	1			1	1			1	1			100	99		
Co	1	5			1	5			1	5			100	100		
Cr	0.5	2			0.5	2			0.5	2			100	100		
Cu	2	2	20		2	2	20		2	2	20		101	100	99	
Fe	2	10	100		2	11	101		2	11	99		99	98	98	
K	5	20	100	500	5	20	101	500	5	20	100	492	100	100	99	98
Li	2		10		2		10		2		10		100		98	
Mg	2	20	100	300	2	19	108	296	2	19	107	292	100	100	98	99
Mn	1	1	4	40	1	1	4	40	1	1	4	40	100	100	97	99
Mo	1		10		1		10		1		10		99		99	
Na		20	100			21	99			21	98			100	99	
Ni	2	5			2	5			2	5			100	99		
P	5	20	100	400	5	22	107	403	5	22	106	397	100	100	99	99
Pb	2	5			2	5			2	5			100	100		
S	2	20	100	400	2	20	101	405	2	20	100	399	95	100	99	99
Se	2	5			2	5			2	5			99	99		
Si			5	10			5	10			5	10			99	99
Sr	2			4	2			na	2			4	100			
Ti	2	5			2	5			2	5			99	100		
V	1	5			1	5			1	5			102	99		
Y			5	10			5	10			5	10			99	98
Zn	1	1	20		1	1	20	0	1	1	20	0	100	100	99	

Table Appendix 3-2: Validation of working standard - based on independent SPEX primary standards

	Claimed SPEX CLMS1, CLMS2 and CLMS4 concentration. All units are ppm.			Measured "as is" based on the set made on 05/27/2004. Data are the average of three measurements on three days.			Measured after 10 times dilution based on the set made on 06/14/2005. One measurement.		
	ms1	ms2	ms3	ms1	ms2	ms3	ms1	ms2	ms4
Al		10			11.2			10.7	
As		10			10.9			10.1	
B			10			10.5			9.8
Ba		10						10.5	
Ca		10			10.5			10.1	
Cd		10			10.1			10.0	
Co		10			10.4			10.2	
Cr		10			10.5			10.4	
Cu		10			10.5			10.2	
Fe		10			11.8			10.7	
K		10			10.1			9.1	
Li		10			10.0			9.7	
Mg		10			10.7			9.8	
Mn		10			11.0			10.4	
Mo			10			10.9			10.0
Na		10			10.5			10.2	
Ni		10			11.1			10.5	
P			10			10.7			9.6
Pb		10			10.7			10.2	
S			10			9.9			8.8
Se		10			10.9			9.7	
Si			10			18.6			12.3
Sr		10						10.7	
Ti			10			10.8			9.9
V		10						10.1	
Y	10						10.5		
Zn		10			10.7			10.4	

Table Appendix 3-3: Validation of working standard - based on other eight primary standard solutions

	Claimed concentrations in the 8 standards. All ppm								Measured based on the set made on 05/27/2004 after 10 times of dilution. All recovery ratio %							
	1A	3	7	240	A	B	ES	CPI	1A	3	7	240	A	B	ES	CPI
Al			100	20	500	600	650	200			111	114	102	104	104	98
As	100	20	100	20				200	102	101	97	105				98
B	20			20				200	100			100				102
Ba	10			20	5	4		100	103			103	103	105		102
Ca	100			20	350	260	80	200	98			101	98	99	98	100
Cd	20		100	20				100	97		101	103				101
Co			100	20				100			99	97				101
Cr			100	20		15		50			98	99		105		103
Cu	20		100	20				200	99		103	96				101
Fe			100	20	200	400	350	200			98	102	99	99	98	101
K		100	100	100	200	200	150	500		103	100	102	102	103	102	101
Li		20		20				200		103		103				100
Mg			100	20	65	120	100	200			102	105	103	105	104	102
Mn	20	20	100	20		6	4	100	102	102	99	101		102	101	102
Mo		20		20				200		92		97				97
Na		20	100	20	70	55	200			106	106	103	104	101	106	
Ni		20	100	20				200		95	94	94				98
P		100		100	10	10	5	500		100		97	96	93	86	96
Pb			100	20				200			97	96				100
S		100								104						
Se	50			20				200	97			96				98
Si				100	3000	3000	3000					92	104	104	104	
Sr				20				200				102				100
Ti				20				200				98				98
V				20				100				102				102
Y			600								96					
Zn			100	20	1	5		100			98	99	87	98		100

	Measured based on the set made on 06/14/2005 after 20 times of dilution. All recovery ratio %							
	1A	3	7	240	A	B	ES	CPI
Al			92	103	98	97	97	106
As	104	105	109	103				109
B	99			105				103
Ba	99			107	100	99		101
Ca	103			99	105	104	106	105
Cd	105		104	102				103
Co			104	106				103
Cr			106	105		100		101
Cu	99		98	109				102
Fe			109	103	105	105	106	109
K		95	96	101	98	97	97	99
Li		93		99				95
Mg			101	100	100	99	99	103
Mn	104	104	107	107		103	104	108
Mo		101		102				104
Na		98	99	107	99	102	98	
Ni		106	106	106				103
P		104		105	105	101	96	108
Pb			106	106				104
S		94						
Se	98			99				105
Si				108	94	94	95	
Sr				106				92
Ti								
V				104				100
Y			106					
Zn			107	107	115	106		106

Table Appendix 3-4: Analytical merits

	LOD	cBlk		msQC water		QC water	
	ppm	avg	3sd	avg	sd	avg	sd
Al	0.05	-0.0015	0.07	0.090	0.017	14.8	
As	0.03	-0.0002	0.05	0.061	0.012	4.7	0.1
B	0.03	-0.0005	0.04	(for high Fe samples such as soil samples)			
B	0.002	-0.0024	0.007	0.175	0.002	5.5	0.1
Ba	0.0002	-0.0002	0.0003	0.046	0.001	3.0	0.0
Ca	0.01	0.0002	0.02	0.810		18.8	
Cd	0.004	-0.0001	0.006	0.112	0.003	4.5	0.1
Co	0.003	-0.0003	0.005	0.017	0.002	4.9	0.1
Cr	0.001	0.0000	0.002	0.042	0.001	4.4	0.1
Cu	0.005	-0.0009	0.009	0.095	0.003	5.7	0.1
Fe	0.001	0.0002	0.007	0.227		6.3	0.1
K	0.03	-0.0106	0.05	0.137	0.011	17.8	0.3
Li	0.0005	0.0001	0.0008	0.030		4.4	0.2
Mg	0.007	-0.0004	0.014	0.264	0.015	35.1	0.6
Mn	0.0003	-0.0003	0.0008	0.051	0.001	11.2	0.2
Mo	0.005	-0.0034	0.021	0.022	0.003	5.0	0.1
Na	0.006	-0.0070	0.015	0.299		15.2	
Ni	0.004	-0.0014	0.010	0.018	0.002	6.1	0.1
Ni	0.02	-0.0002	0.12	(for high Fe samples such as soil samples)			
P	0.05	-0.0056	0.07	3.080	0.093	20.1	0.5
Pb	0.02	-0.0005	0.02	0.068	0.007	5.2	0.1
S	0.05	-0.0147	0.19	4.611	0.103	19.4	0.4
Se	0.04	-0.0031	0.08	0.059	0.009	5.6	0.2
Si	0.007	-0.0019	0.011	2.856		35.2	
Sr	0.0001	0.0000	0.0003	0.044	0.001	4.7	0.1
Ti	0.002	0.0001	0.003	0.026	0.001		
V	0.004	-0.0010	0.008	0.037	0.002		
Y	0.009	-0.0006	0.014	0.029	0.003		
Zn	0.001	-0.0010	0.003	0.052	0.002	10.9	0.2

Table Appendix 3-5: Short term (within-day) stability as seen from the drift of QC water

Example 1: Stability in 17 hours (360 samples)																		
Time	10:39	11:39	12:40	13:39	14:41	15:46	16:46	17:47	18:48	19:48	20:50	21:51	22:53	23:55	0:56	1:55	2:55	3:27
Al	1.00	1.00	1.02	0.99	1.00	0.99	0.99	1.00	1.01	0.99	0.98	0.99	0.98	0.98	0.99	1.00	0.98	0.99
As	1.00	0.99	1.00	0.99	0.99	0.97	0.98	0.98	0.96	0.93	0.93	0.93	0.93	0.90	0.93	0.92	0.91	0.91
B	1.00	1.01	1.01	1.00	1.02	1.01	1.00	1.02	1.00	1.02	1.00	1.00	1.00	1.01	1.01	1.02	1.02	1.02
Ba	1.00	1.00	1.01	0.99	0.98	0.98	0.98	0.99	1.00	0.97	0.97	0.98	0.96	0.96	0.96	0.97	0.96	0.96
Ca	1.00	1.01	1.02	1.01	1.02	1.02	1.00	1.01	0.98	0.98	0.97	0.98	0.97	0.96	0.97	0.99	0.98	0.98
Cd	1.00	0.99	1.01	0.99	1.01	1.00	0.99	1.00	0.99	0.99	0.98	0.98	0.98	0.98	0.99	1.00	1.00	1.00
Co	1.00	1.01	1.01	1.01	1.01	1.01	1.00	1.01	0.99	0.99	0.98	0.99	0.98	0.97	0.98	0.99	0.99	0.99
Cr	1.00	1.01	1.02	1.01	1.02	1.02	1.01	1.02	1.00	1.00	0.99	0.99	0.99	0.99	0.99	1.01	1.00	1.01
Cu	1.00	1.00	1.00	0.98	0.98	0.97	0.97	0.98	0.99	0.97	0.97	0.97	0.96	0.96	0.96	0.97	0.96	0.96
Fe	1.00	1.02	1.02	1.01	1.03	1.02	1.01	1.02	1.00	1.00	0.99	0.99	0.99	0.99	1.00	1.01	1.01	1.01
K	1.00	0.99	1.01	0.98	0.98	0.97	0.97	0.99	1.00	0.98	0.97	0.98	0.97	0.97	0.97	0.99	0.98	0.99
Li	1.00	0.99	1.00	0.97	0.96	0.97	0.97	0.99	1.00	0.99	0.99	0.99	0.98	0.98	0.98	0.99	0.98	0.99
Mg	1.00	0.99	1.00	0.97	0.96	0.96	0.96	0.97	0.98	0.95	0.96	0.96	0.94	0.93	0.94	0.95	0.93	0.93
Mn	1.00	1.00	1.01	0.98	0.97	0.97	0.96	0.97	0.98	0.94	0.94	0.94	0.93	0.91	0.93	0.93	0.92	0.92
Mo	1.00	0.99	1.02	0.98	0.99	0.98	0.98	0.99	0.97	0.95	0.94	0.95	0.94	0.94	0.94	0.95	0.94	0.94
Na	1.00	1.00	1.02	1.00	1.00	0.99	0.99	1.01	1.02	1.02	1.00	1.01	1.01	1.01	1.01	1.03	1.03	1.03
Ni	1.00	1.00	1.01	1.00	1.00	1.00	0.98	0.99	0.98	0.96	0.96	0.96	0.95	0.95	0.95	0.96	0.96	0.96
P	1.00	1.02	1.03	1.00	1.02	0.98	0.97	0.97	0.93	0.94	0.93	0.94	0.93	0.91	0.92	0.93	0.92	0.92
Pb	1.00	0.99	1.02	1.00	1.01	1.00	0.99	1.00	0.97	0.97	0.97	0.97	0.96	0.95	0.97	0.98	0.98	0.96
S	1.00	0.99	1.02	0.99	1.00	0.98	0.97	0.98	0.96	0.96	0.96	0.97	0.94	0.94	0.95	0.97	0.98	0.96
Se	1.00	1.08	1.02	1.06	1.09	1.08	1.07	1.08	1.04	1.02	1.01	1.02	1.01	1.01	0.99	1.00	1.00	1.02
Si	1.00	1.00	1.02	1.00	1.01	1.01	1.00	1.01	1.00	1.00	0.99	1.00	0.99	0.99	1.00	1.01	1.01	1.01
Ti	1.00	1.00	1.01	0.98	0.97	0.97	0.96	0.97	0.98	0.95	0.95	0.96	0.94	0.93	0.94	0.94	0.93	0.93
V	1.00	1.00	1.01	0.99	0.98	0.98	0.98	0.99	0.99	0.97	0.97	0.97	0.96	0.94	0.95	0.97	0.95	0.95
Y	1.00	1.02	1.03	1.02	1.03	1.01	1.02	1.03	1.02	1.02	1.00	1.01	1.00	1.01	1.00	1.03	1.02	1.02
Zn	1.00	0.99	1.01	0.99	1.00	0.99	0.99	0.99	0.98	0.98	0.97	0.97	0.95	0.94	0.95	0.98	0.95	0.95

Example 2: Stability in 3 hours				
Time	10:31	11:33	12:33	13:27
Al	1.00	0.99	1.01	1.03
As	1.00	1.03	1.06	1.13
B	1.00	0.99	1.01	1.04
Ba	1.00	0.98	1.00	1.02
Ca	1.00	1.04	1.08	1.17
Cd	1.00	1.02	1.04	1.09
Co	1.00	1.00	1.03	1.08
Cr	1.00	0.99	1.02	1.07
Cu	1.00	0.99	1.00	1.02
Fe	1.00	1.01	1.03	1.09
K	1.00	0.99	1.00	1.02
Li	1.00	0.97	0.96	0.96
Mg	1.00	1.00	1.02	1.05
Mn	1.00	1.01	1.03	1.08
Mo	1.00	1.03	1.05	1.10
Na	1.00	0.97	0.98	0.99
Ni	1.00	1.02	1.04	1.10
P	1.00	1.06	1.09	1.17
Pb	1.00	1.02	1.05	1.13
S	1.00	1.04	1.05	1.11
Se	1.00	1.00	1.03	1.09
Si	1.00	0.99	1.01	1.05
Ti	1.00	1.00	1.02	1.06
V	1.00	0.99	1.01	1.05
Y	1.00	1.00	1.03	1.09
Zn	1.00	1.01	1.03	1.08

The QC water is analyzed right after standardization and after every 20 samples.
The concentration ratios of the subsequent analyses to the first analysis are listed.

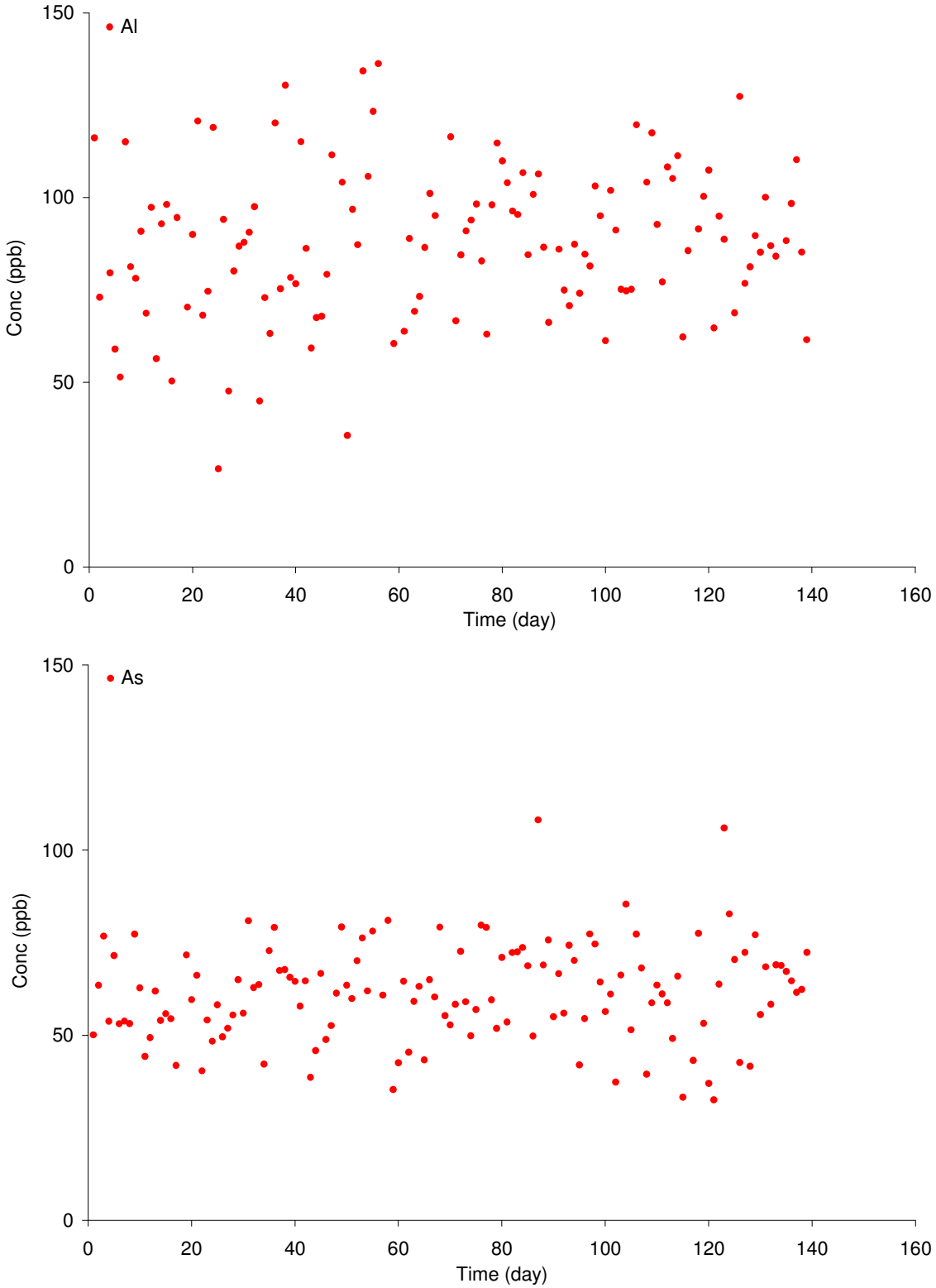
Table Appendix 3-6: Results of short-term drift correction

In a day, a sample is randomly selected for this short-term repeability check purpose.
The sample is mesured twice within one day (within one standardization).
The drift is corrected based on the result of QC water.

	water 1		water 2		soil		plant 1		plant 2		plant 3		plant 4	
	1st and 2nd measuring time (hour:minute)													
	1st	2nd	1st	2nd	1st	2nd	1st	2nd	1st	2nd	1st	2nd	1st	2nd
	13:24	15:09	10:34	15:13	8:53	14:41	13:29	13:32	12:19	12:22	11:07	11:10	9:27	13:13
	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm
Al	155	155	1.5	1.4	11837	11538	287	275	182	177	1007	1018	23	28
B	0.31	0.29	0.15	0.15	39	40	0.74	0.68	5.7	5.5	3.6	4.0	52	53
Ca	97	99	14	14	30207	33813	365	361	490	488	528	508	22158	21538
Cu	0.029	0.038	0.17	0.18	18	17	0.80	0.94	0.61	0.80	3.1	2.7	5.5	5.1
Fe	124	123	1.95	1.96	13969	14242	370	371	164	164	1009	1019	80	81
K	26	26	495	506	2165	2042	1526	1508	1064	1068	3685	3659	20958	23008
Mg	75	74	10	10	22247	21184	190	190	170	171	403	398	4250	4489
Mn	3.9	3.9	1.3	1.3	457	463	14	14	30	30	23	23	75	76
Na	9.5	9.3	1.7	1.7	197	182	38	37	18	18	50	54	62	69
P	4.9	5.3	34	34	685	753	394	393	347	348	1475	1495	2229	2233
S	9.7	9.9	21	21	419	457	440	437	353	344	1389	1404	1237	1229
Zn	1.1	1.2	0.47	0.47	51	54	13	13	13	18	58	59	104	109

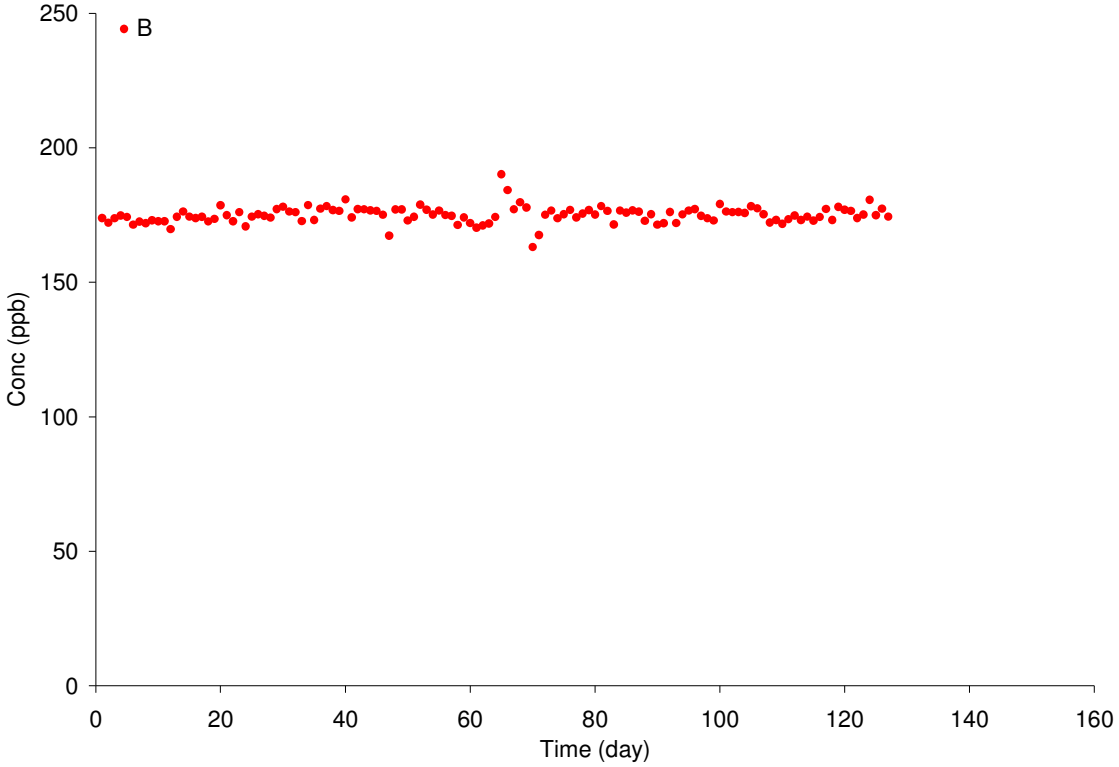
	plant 5		plant 6		plant 7		plant 8		plant 9		plant 10		plant 11	
	1st and 2nd measuring time (hour:minute)													
	1st	2nd	1st	2nd	1st	2nd	1st	2nd	1st	2nd	1st	2nd	1st	2nd
	8:26	11:02	9:07	14:53	8:52	14:18	10:54	13:58	9:56	13:09	8:20	12:35	11:23	14:42
	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm
Al	5.7	6.4	69	69	39	38	106	117	4.6	< 3	64	84	40	44
B	35	36	7.7	7.5	37	37	61	63	22	23	7.5	8.3	9.9	9.3
Ca	16083	16132	1978	1964	10561	10486	12177	12403	14703	13922	7136	7111	5741	5295
Cu	9.6	10.4	12	12	3.0	3.4	2.5	2.5	3.9	3.3	14	14	17	18
Fe	112	113	23	32	121	120	347	350	10	10	136	148	101	93
K	21521	23353	9827	9847	5509	5505	4475	4574	18871	20005	14248	14058	28464	28736
Mg	4254	4528	1944	1946	3299	3307	3321	3361	4867	4933	7887	7811	4595	4565
Mn	50	50	25	25	357	358	647	645	6.4	6.7	48	48	60	58
Na	52	57	107	107	14	14	61	66	352	377	101	142	55	59
P	2904	2935	2182	2194	1694	1688	1924	1961	4069	3953	4271	4256	4611	4364
S	1649	1696	1014	1016	1121	1065	1316	1336	4690	4555	2390	2367	1855	1771
Zn	45	50	24	29	35	36	36	37	147	146	30	31	82	82

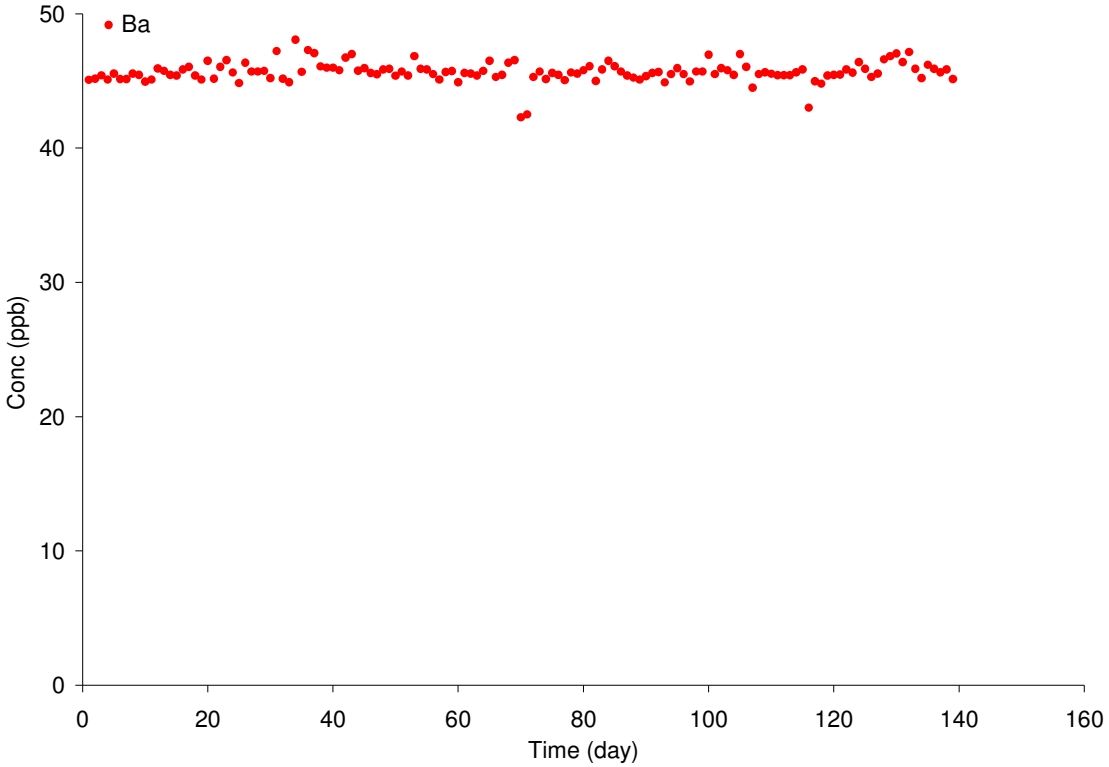
Figure A3-1: Analysis of elements at ppb level by TJA Iris ICP-OES



First day: 07/15/04. Day 25: Bottle switch. Day 94: Standard switch. Last day: 12/01/05.

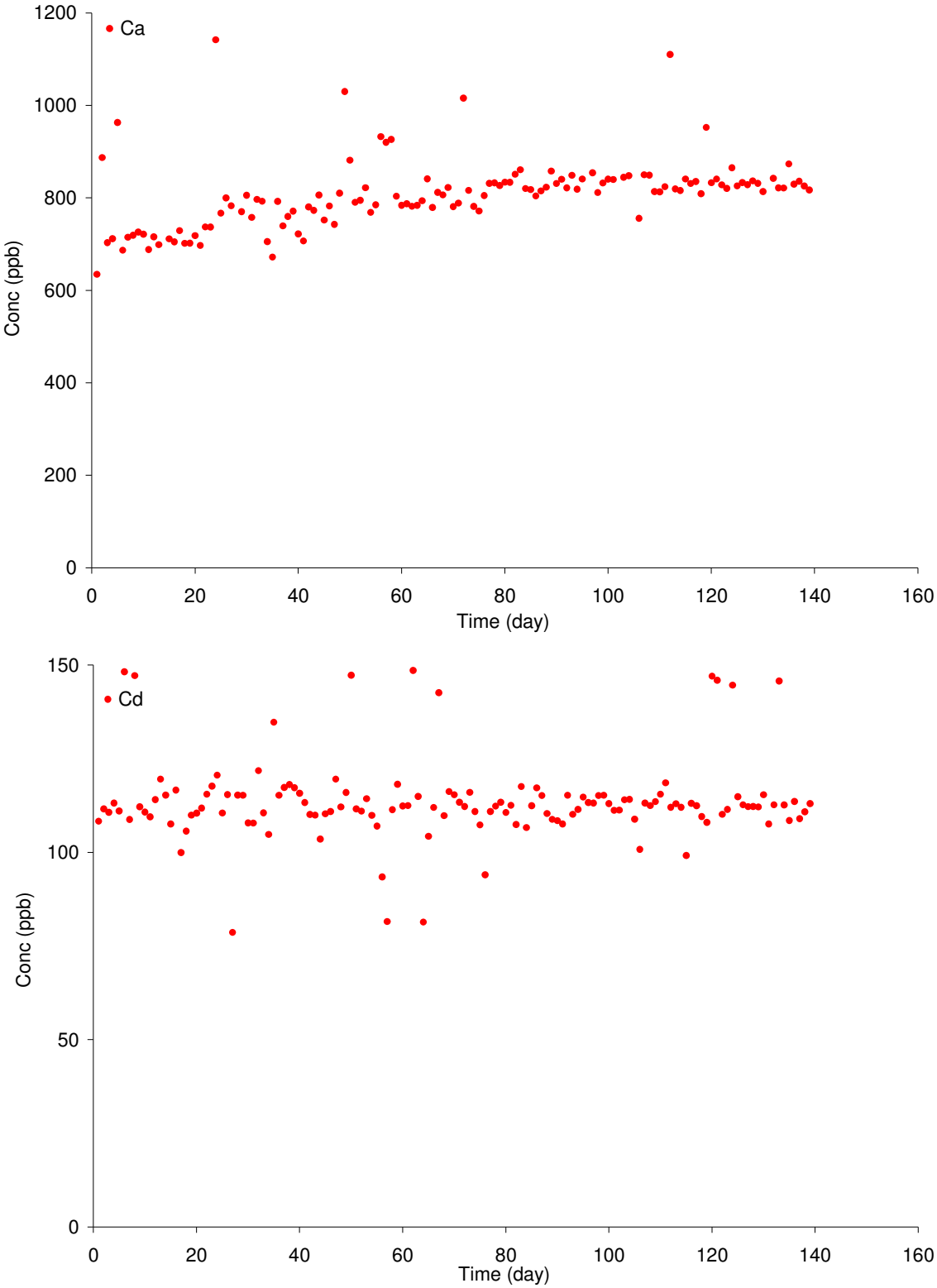
Figure A3-1: Analysis of elements at ppb level by TJA Iris ICP-OES (cont'd)





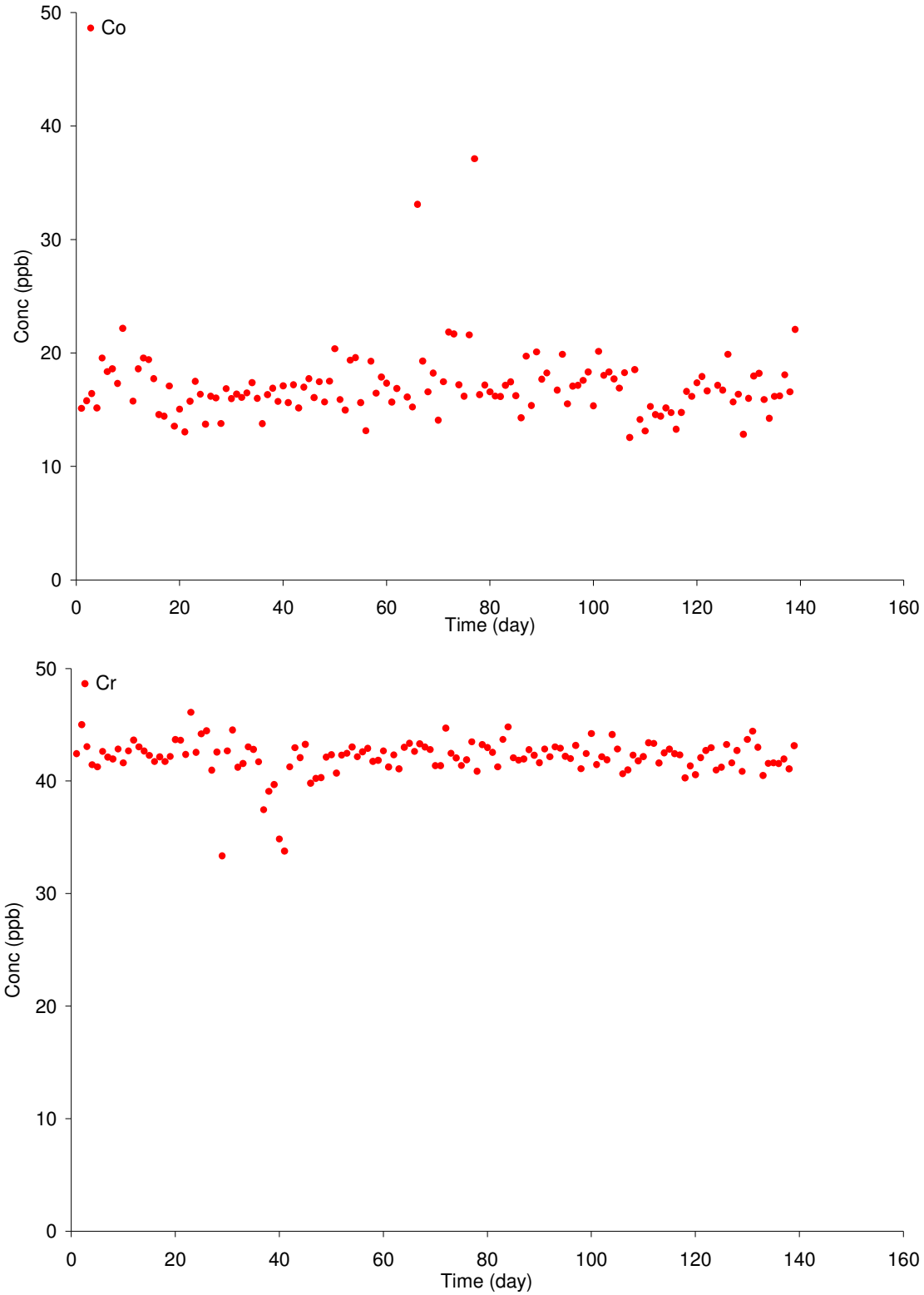
First day: 07/15/04. Day 25: Bottle switch. Day 94: Standard switch. Last day: 12/01/05.

Figure A3-1: Analysis of elements at ppb level by TJA Iris ICP-OES (cont'd)



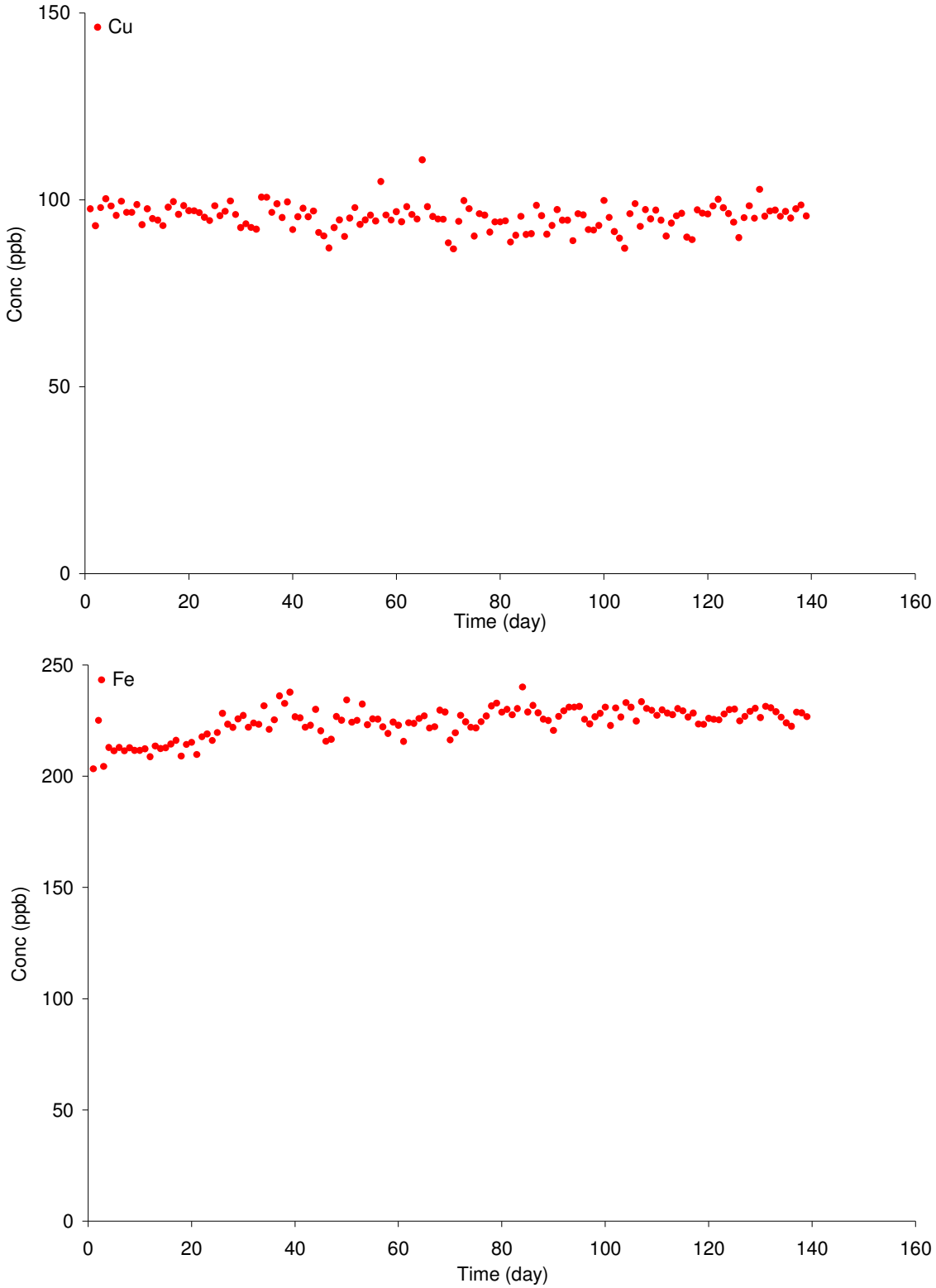
First day: 07/15/04. Day 25: Bottle switch. Day 94: Standard switch. Last day: 12/01/05.

Figure A3-1: Analysis of elements at ppb level by TJA Iris ICP-OES (cont'd)



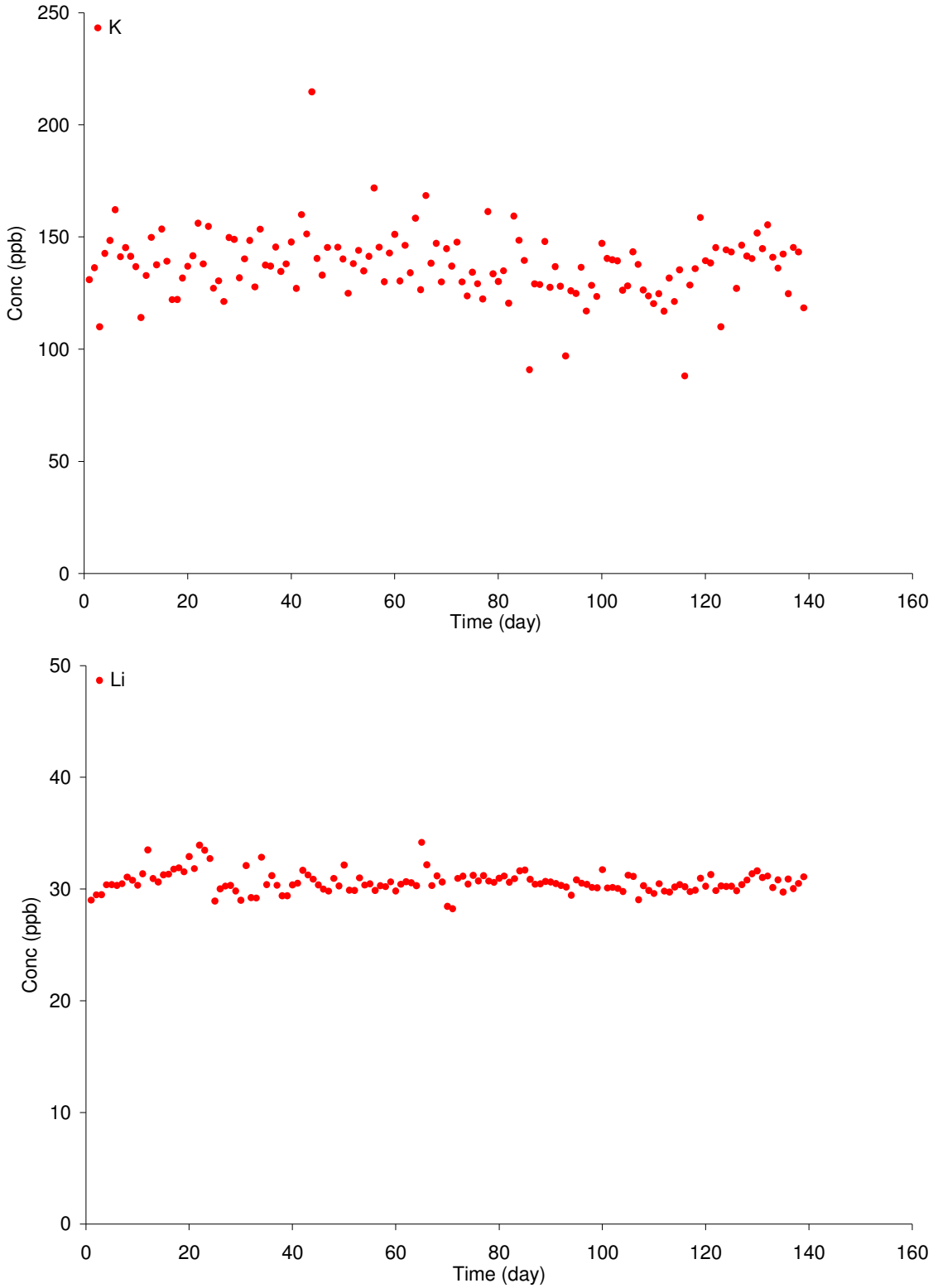
First day: 07/15/04. Day 25: Bottle switch. Day 94: Standard switch. Last day: 12/01/05.

Figure A3-1: Analysis of elements at ppb level by TJA Iris ICP-OES (cont'd)



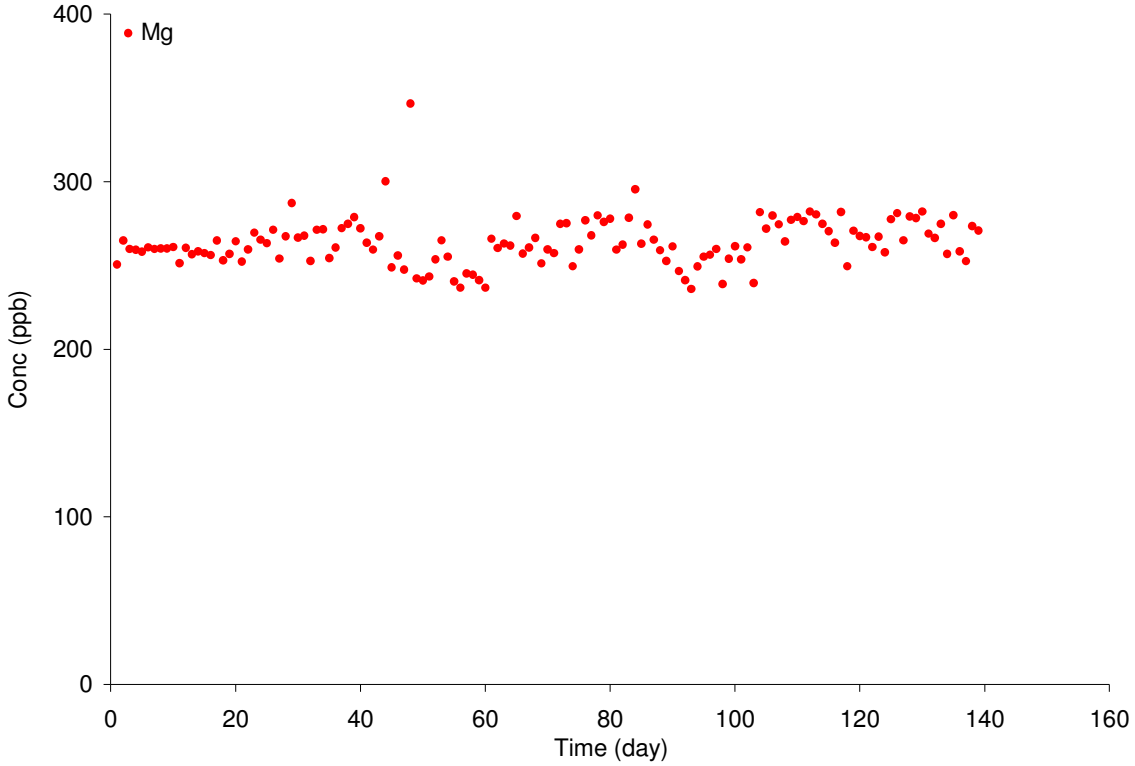
First day: 07/15/04. Day 25: Bottle switch. Day 94: Standard switch. Last day: 12/01/05.

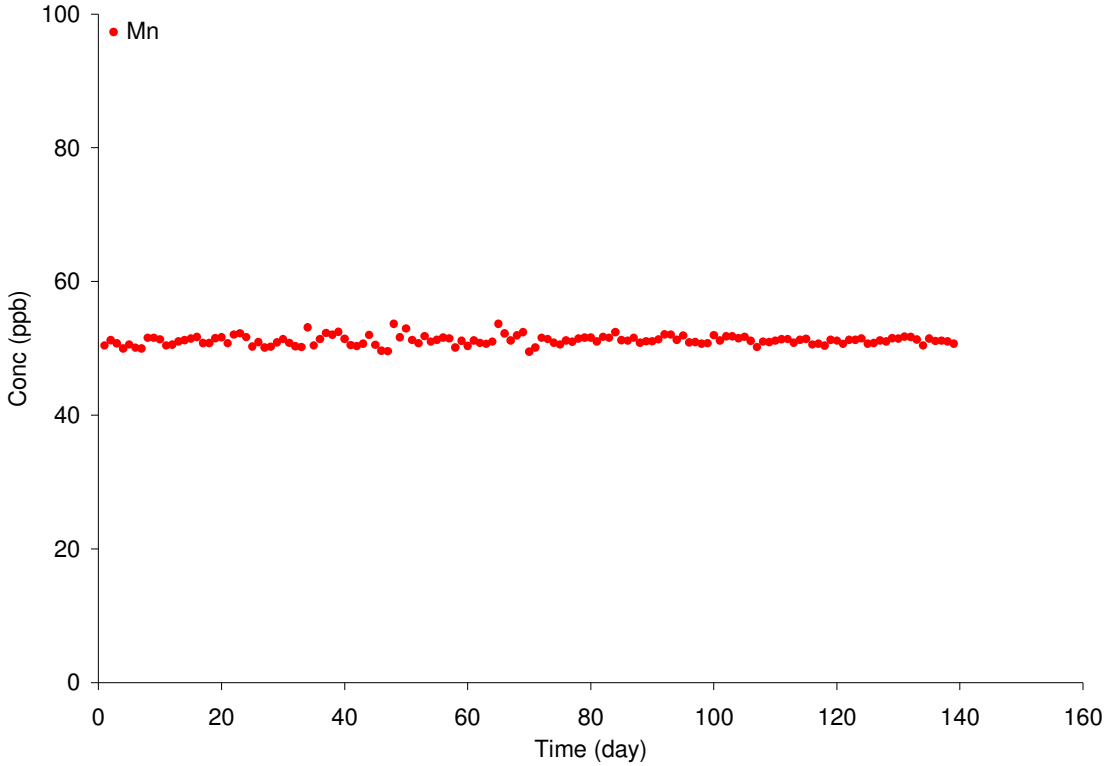
Figure A3-1: Analysis of elements at ppb level by TJA Iris ICP-OES (cont'd)



First day: 07/15/04. Day 25: Bottle switch. Day 94: Standard switch. Last day: 12/01/05.

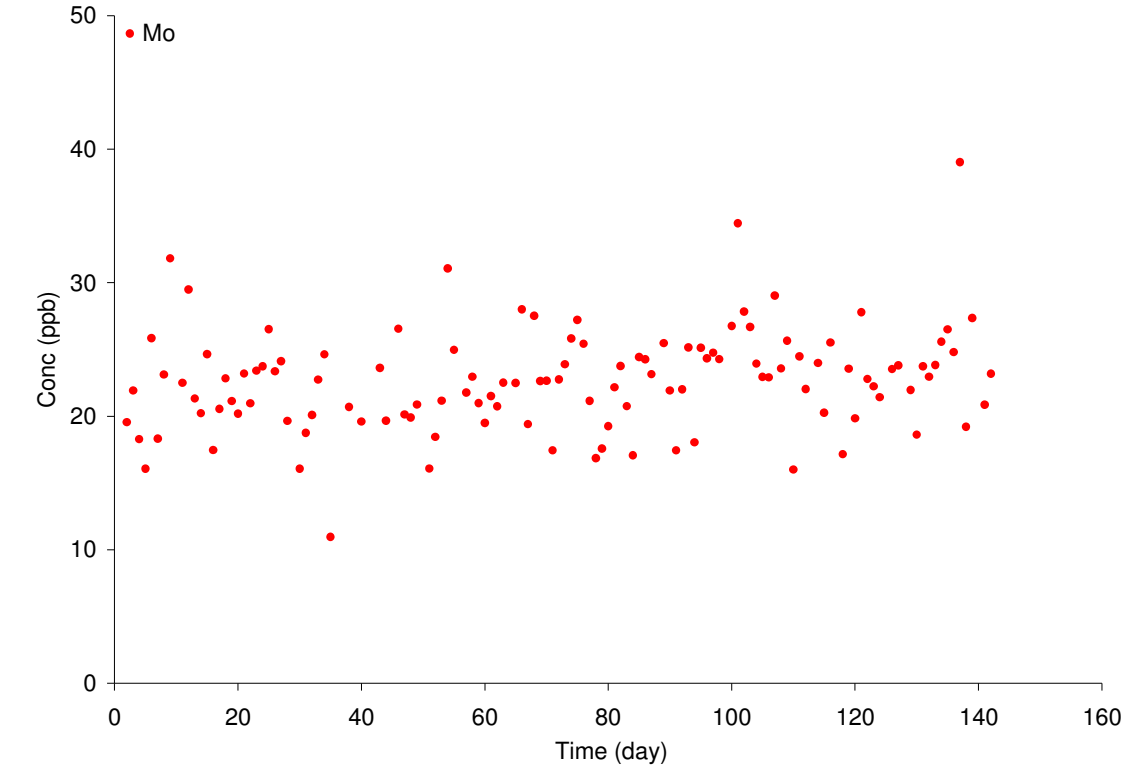
Figure A3-1: Analysis of elements at ppb level by TJA Iris ICP-OES (cont'd)

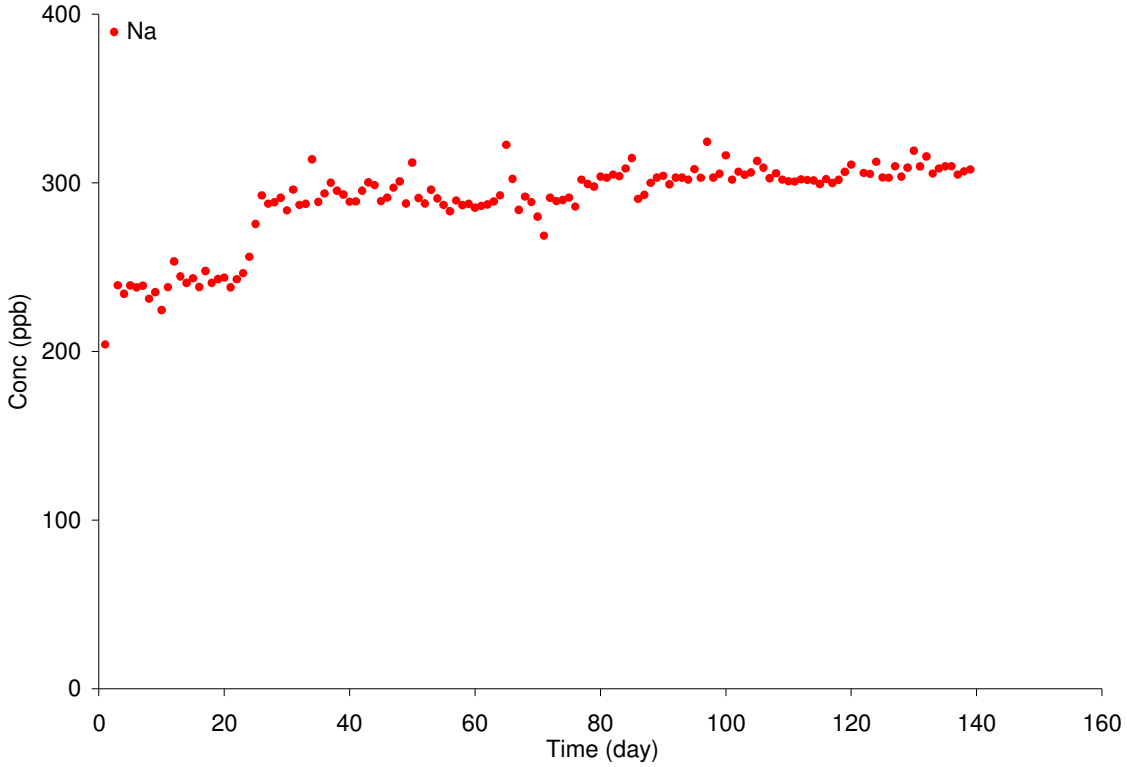




First day: 07/15/04. Day 25: Bottle switch. Day 94: Standard switch. Last day: 12/01/05.

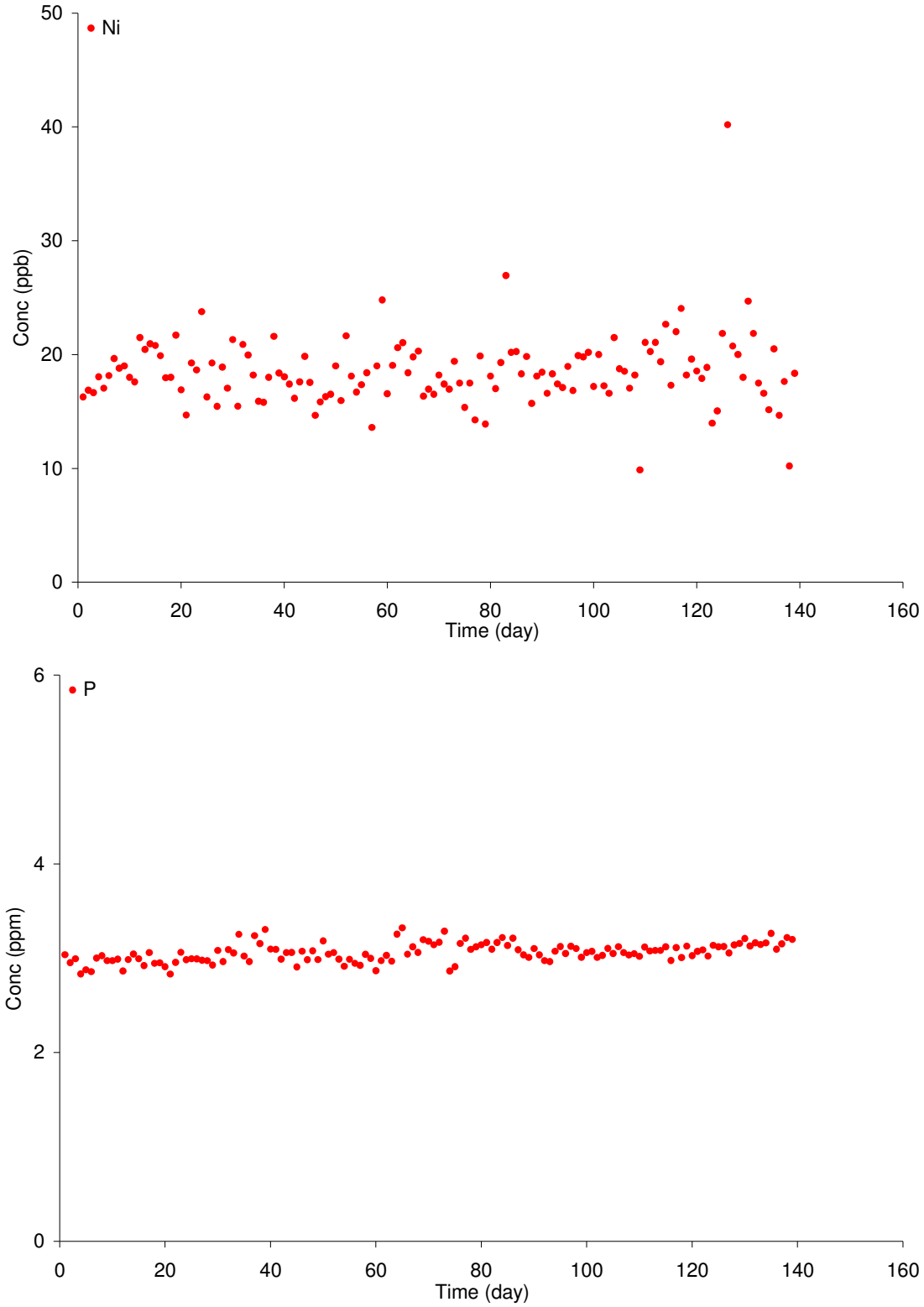
Figure A3-1: Analysis of elements at ppb level by TJA Iris ICP-OES (cont'd)





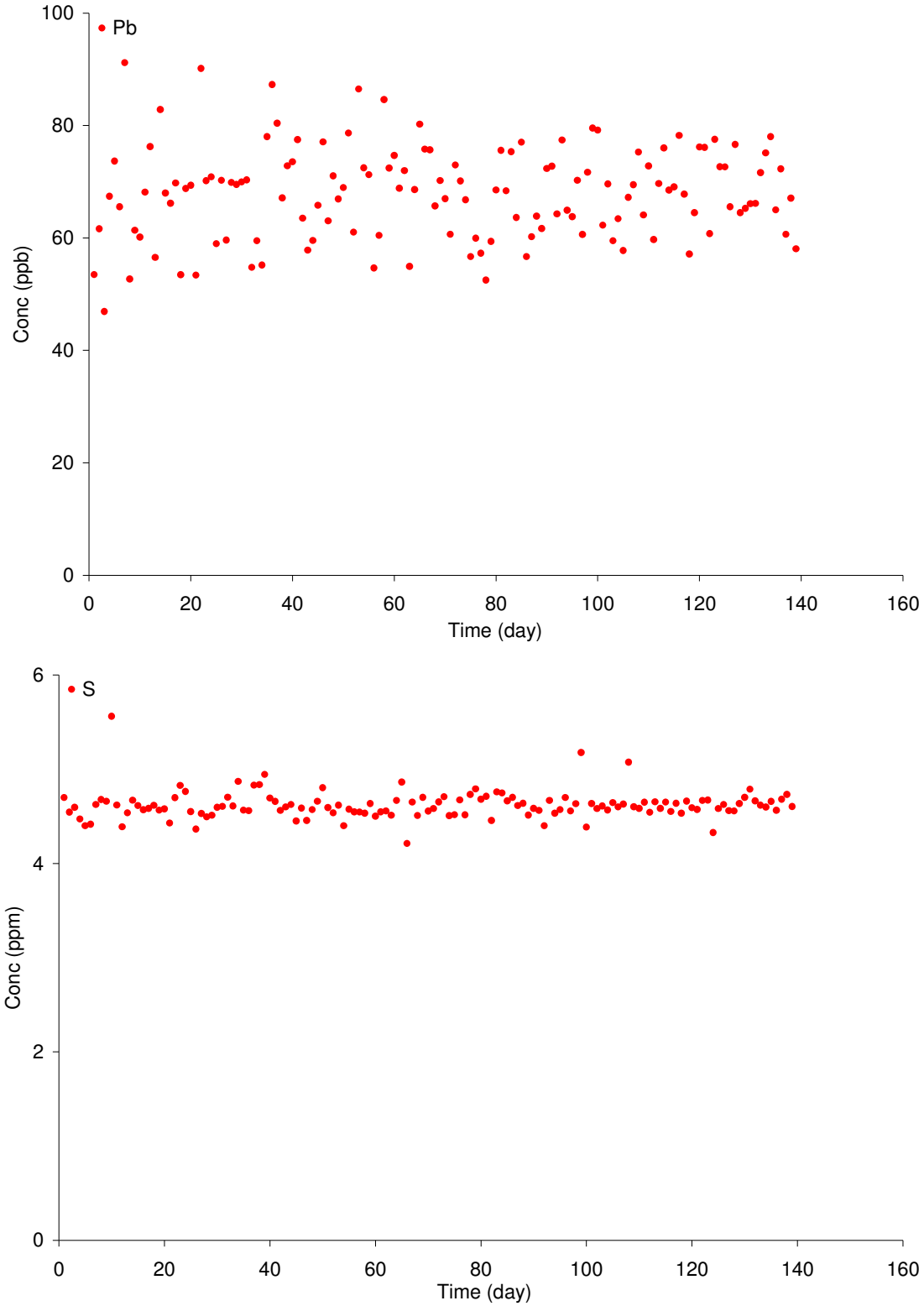
First day: 07/15/04. Day 25: Bottle switch. Day 94: Standard switch. Last day: 12/01/05.

Figure A3-1: Analysis of elements at ppb level by TJA Iris ICP-OES (cont'd)



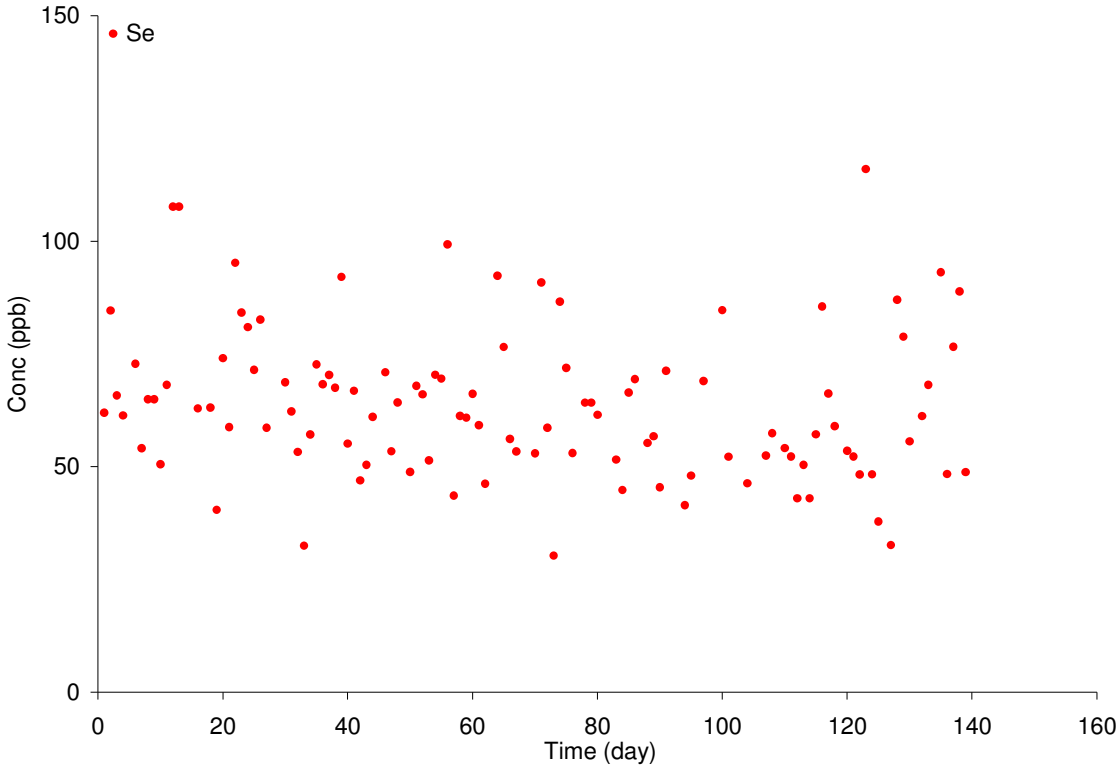
First day: 07/15/04. Day 25: Bottle switch. Day 94: Standard switch. Last day: 12/01/05.

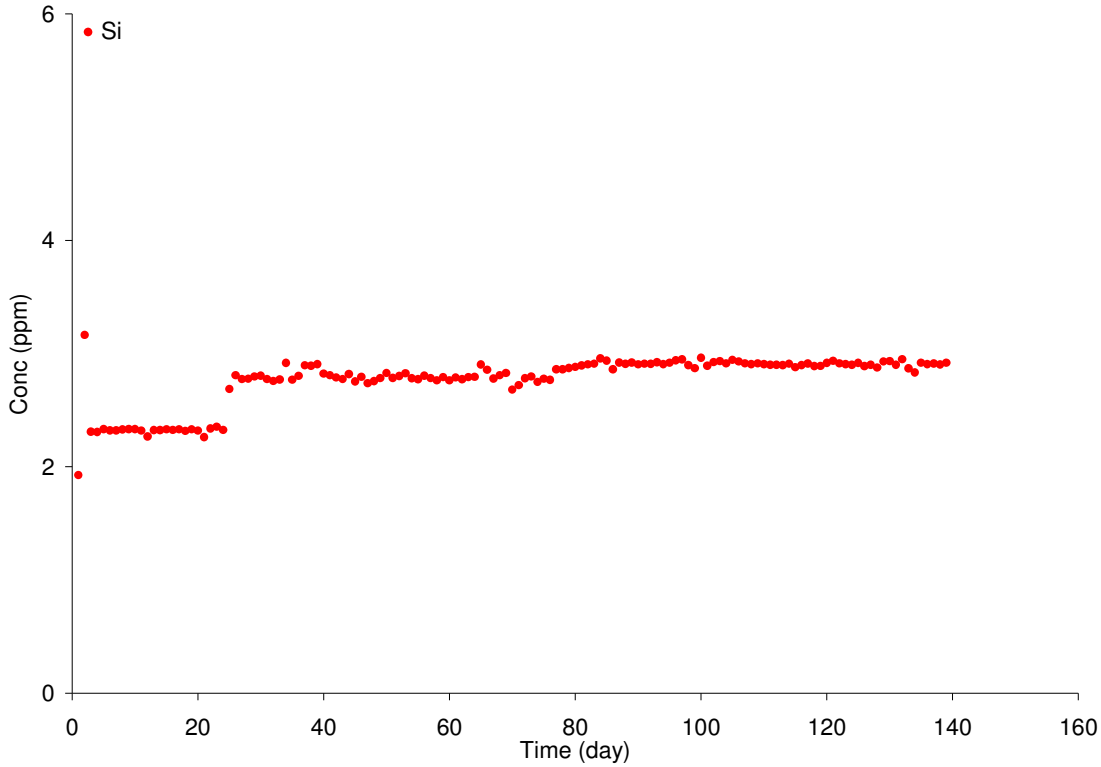
Figure A3-1: Analysis of elements at ppb level by TJA Iris ICP-OES (cont'd)



First day: 07/15/04. Day 25: Bottle switch. Day 94: Standard switch. Last day: 12/01/05.

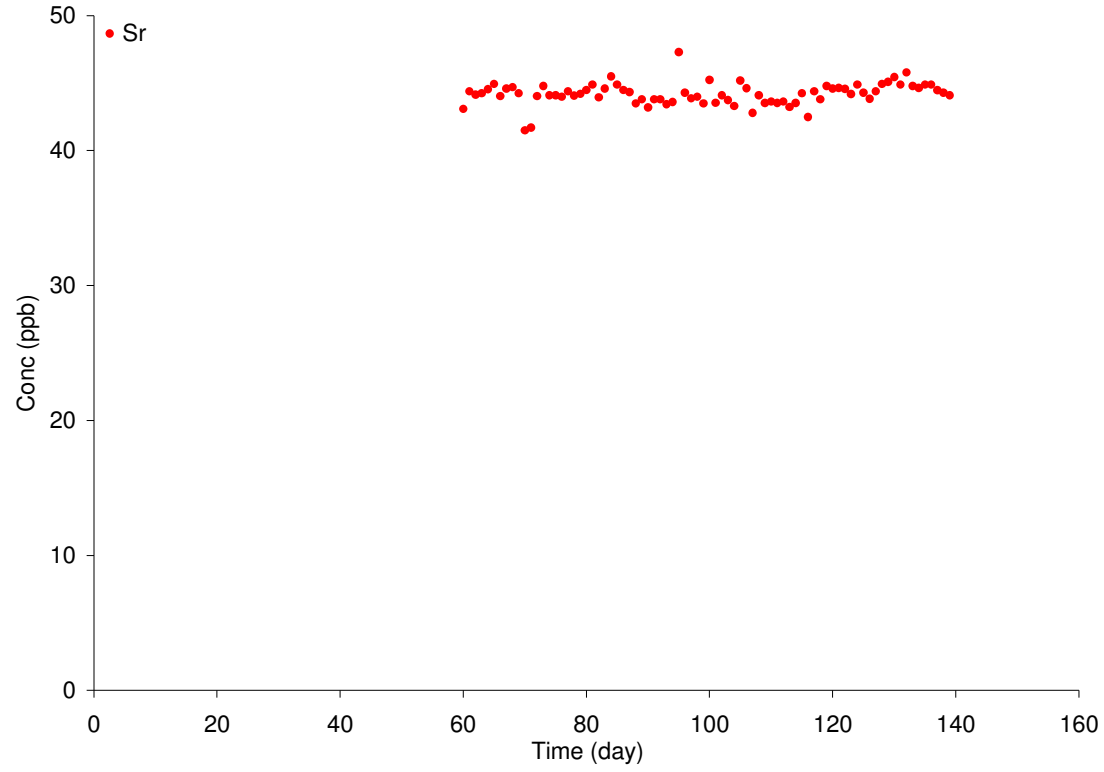
Figure A3-1: Analysis of elements at ppb level by TJA Iris ICP-OES (cont'd)

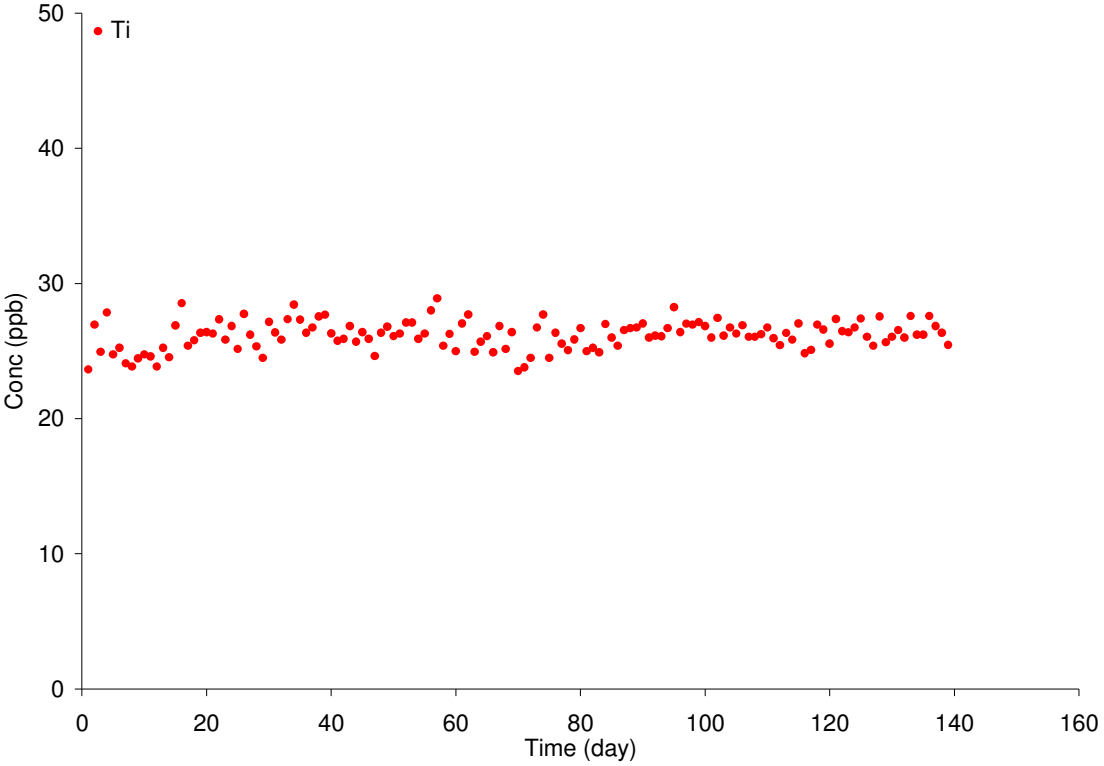




First day: 07/15/04. Day 25: Bottle switch. Day 94: Standard switch. Last day: 12/01/05.

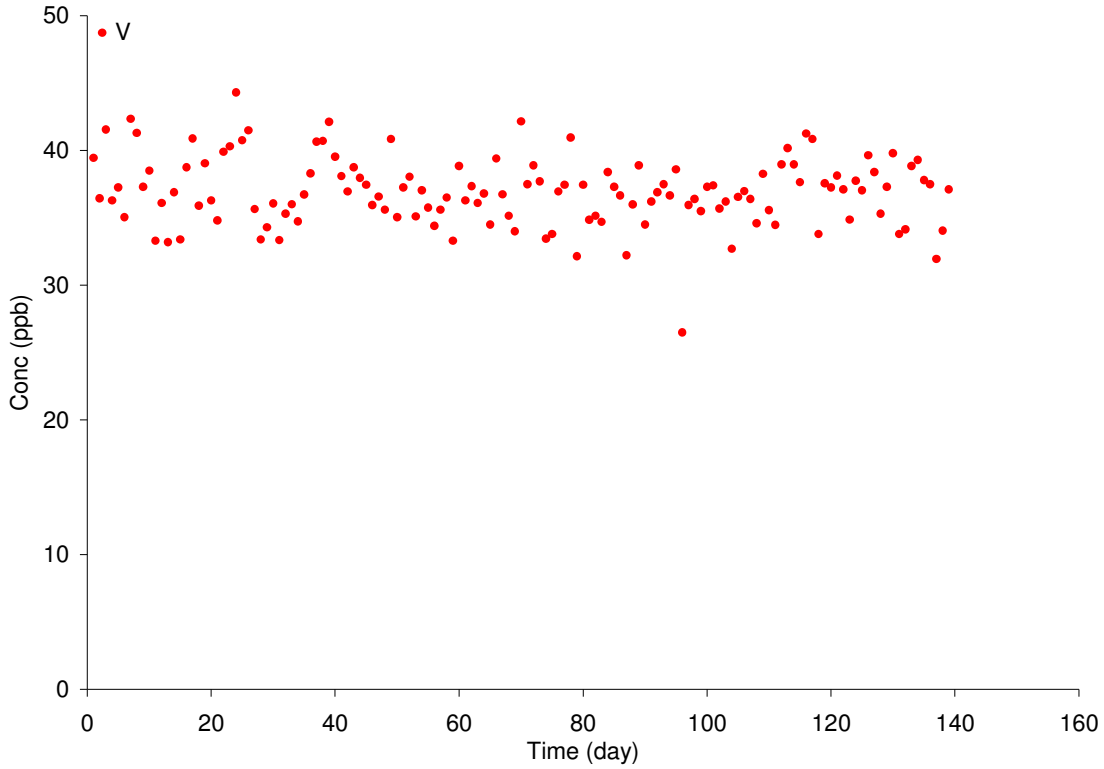
Figure A3-1: Analysis of elements at ppb level by TJA Iris ICP-OES (cont'd)

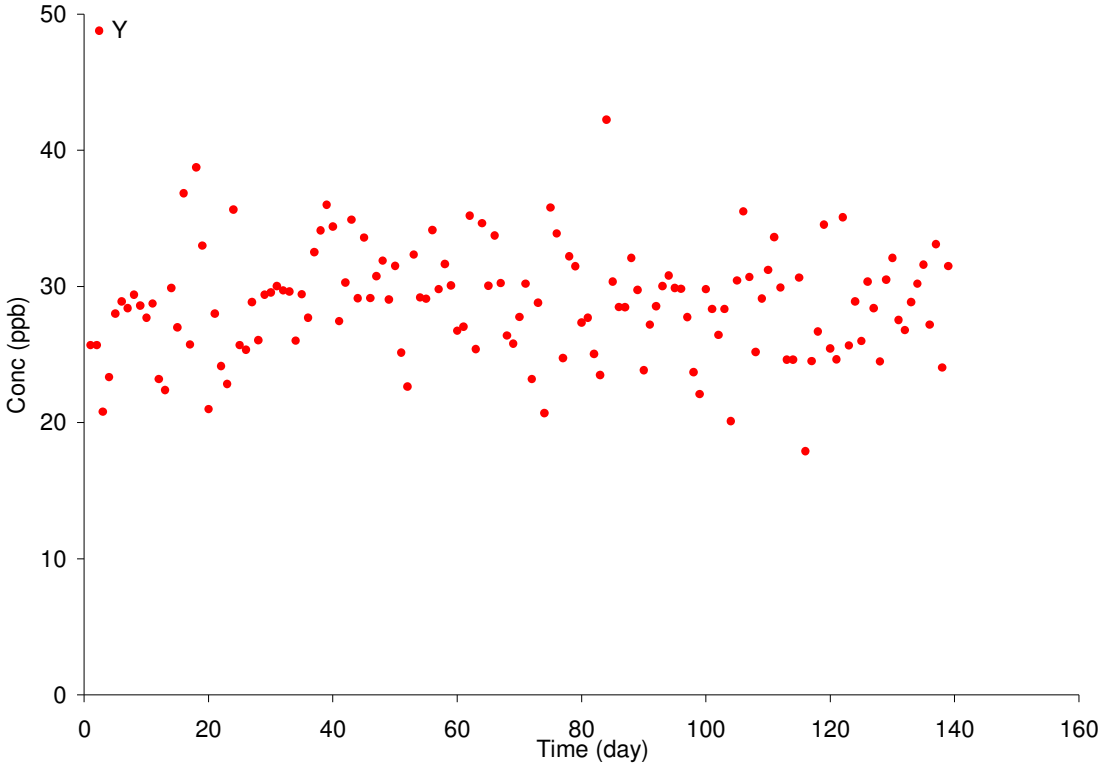




First day: 07/15/04. Day 25: Bottle switch. Day 94: Standard switch. Last day: 12/01/05.

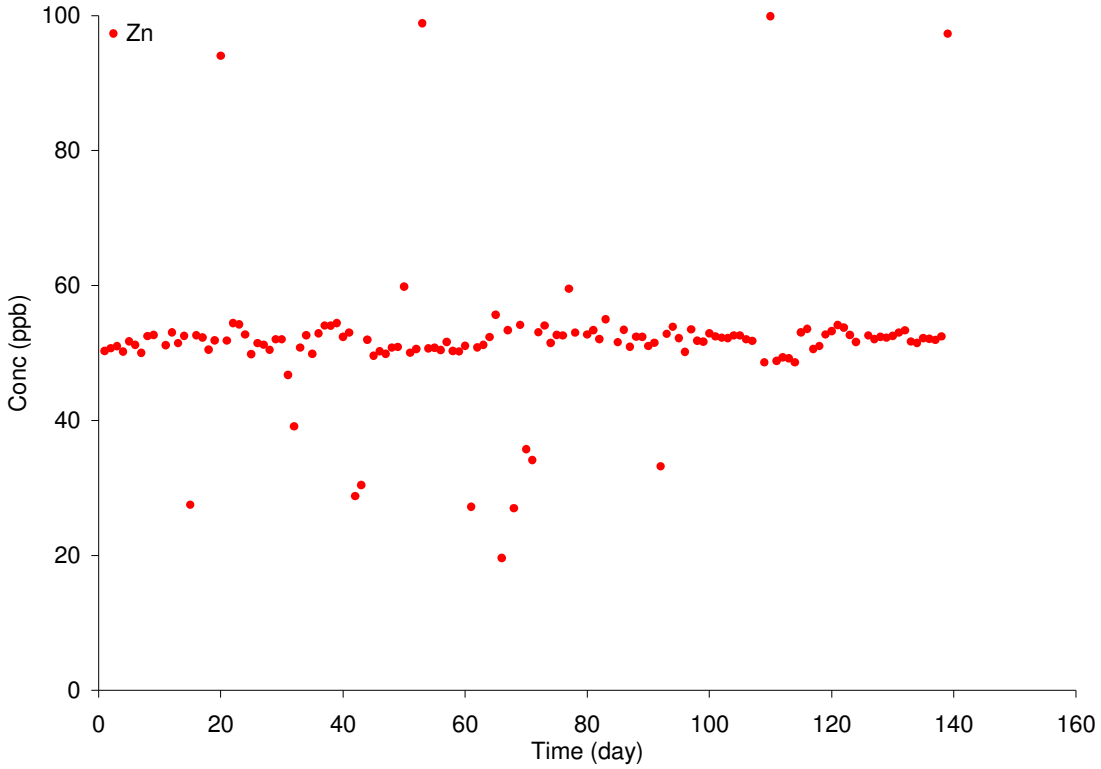
Figure A3-1: Analysis of elements at ppb level by TJA Iris ICP-OES (cont'd)





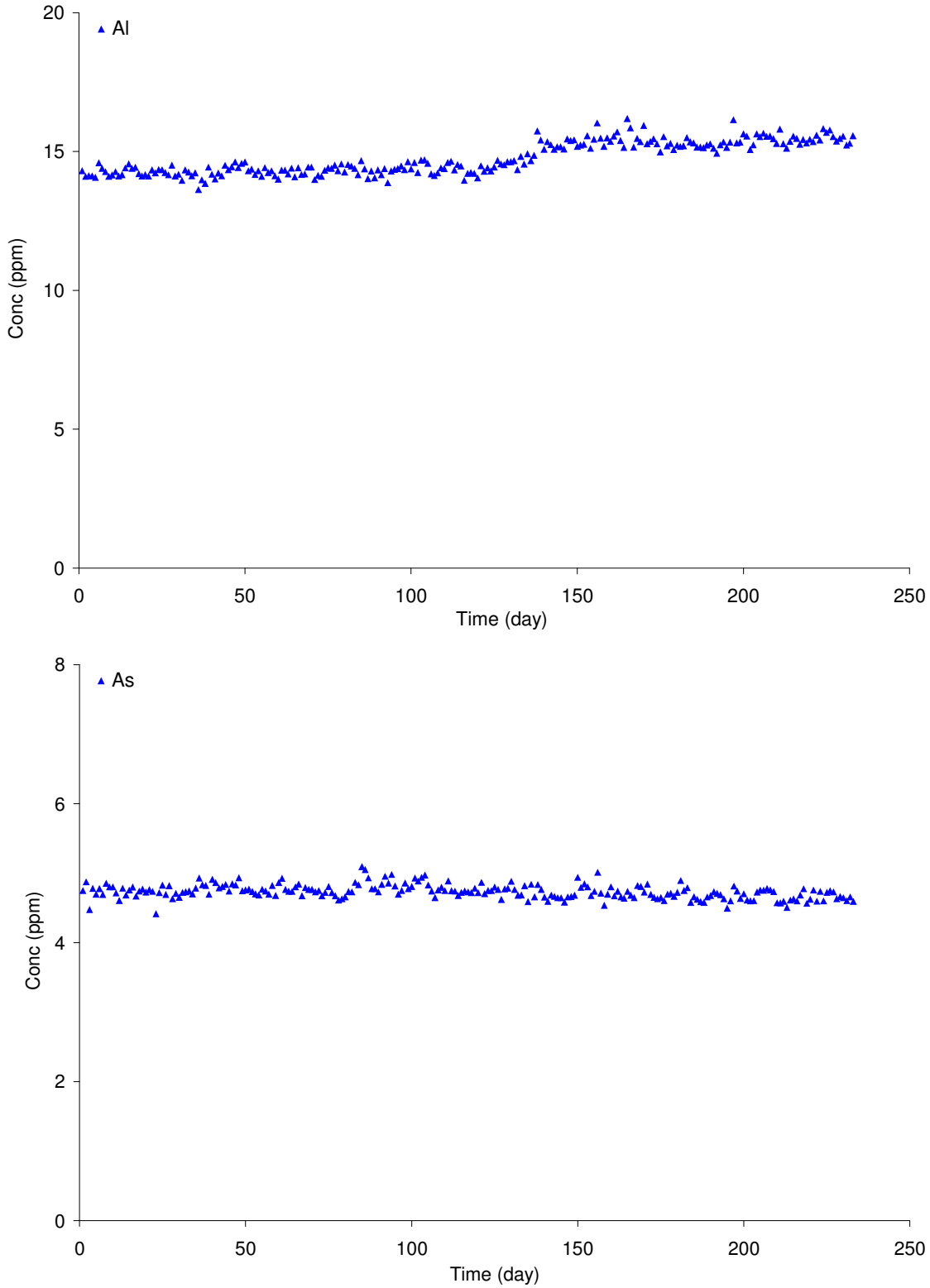
First day: 07/15/04. Day 25: Bottle switch. Day 94: Standard switch. Last day: 12/01/05.

Figure A3-1: Analysis of elements at ppb level by TJA Iris ICP-OES (cont'd)



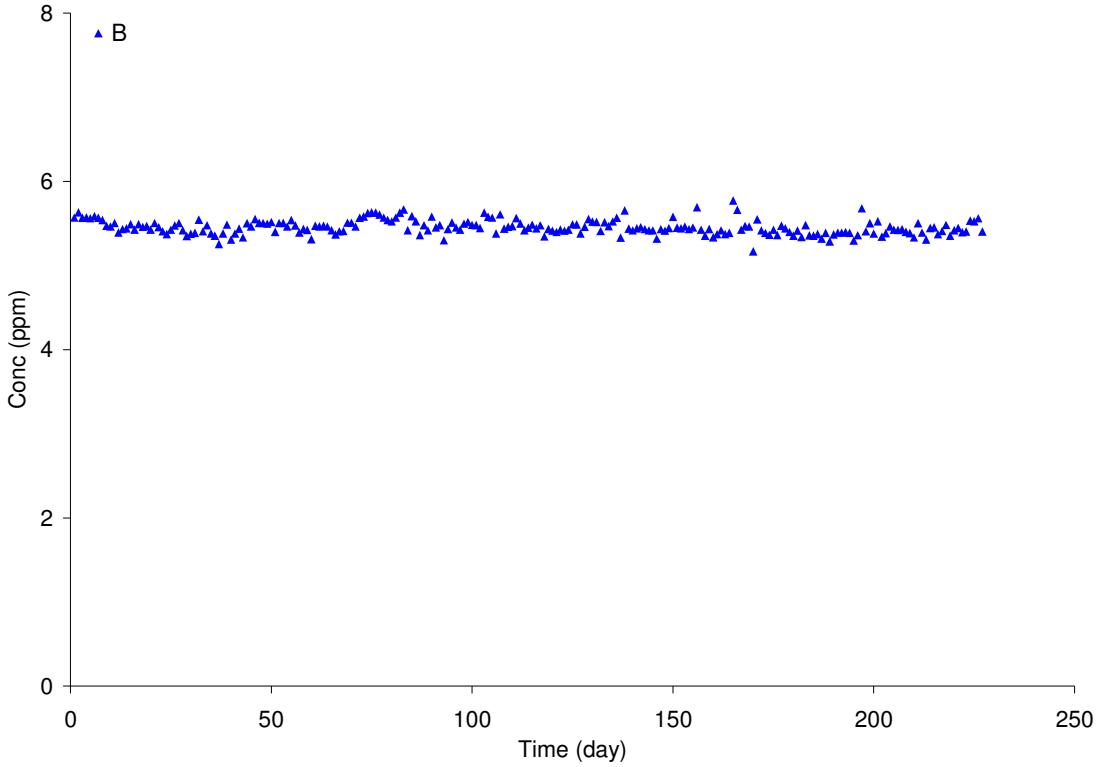
First day: 07/15/04. Day 25: Bottle switch. Day 94: Standard switch. Last day: 12/01/05.

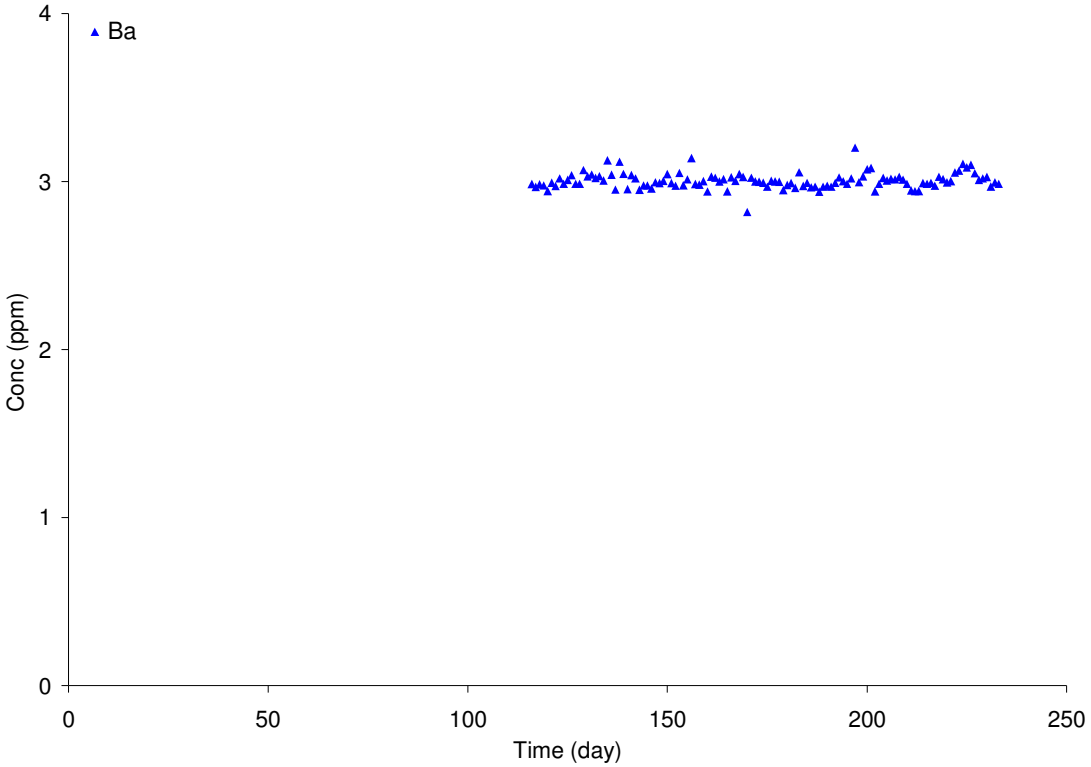
Figure A3-2: Analysis of elements at ppm level by TJA Iris ICP-OES



Day 1: 06/17/03. Day 6: new standard. Day 71: Lab moved. Day 102: new standard. Day 116: new bottle. Day 164: new bottle. Day 192: new standard. Day 233: 12/01/05.

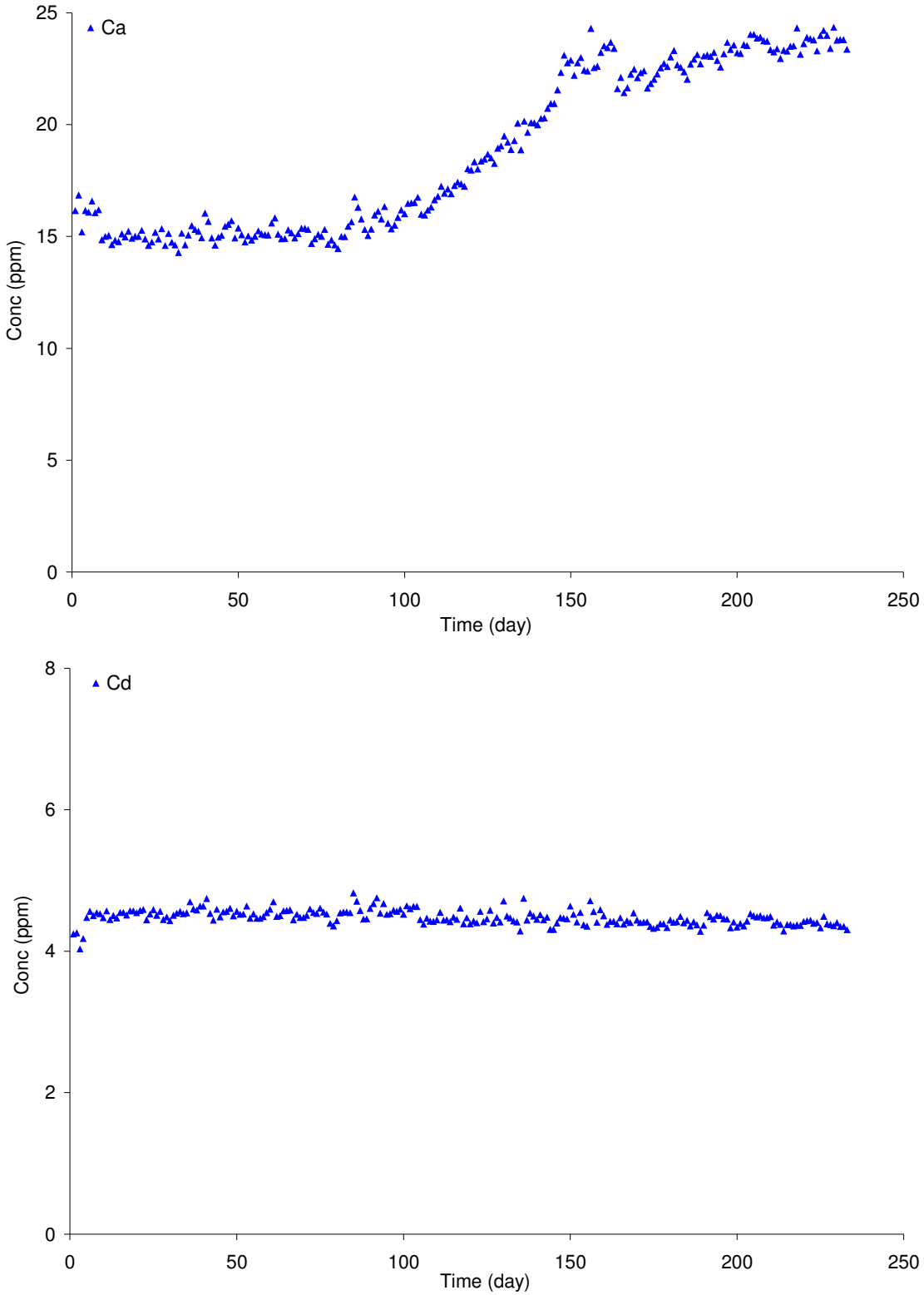
Figure A3-2: Analysis of elements at ppm level by TJA Iris ICP-OES (con'd)





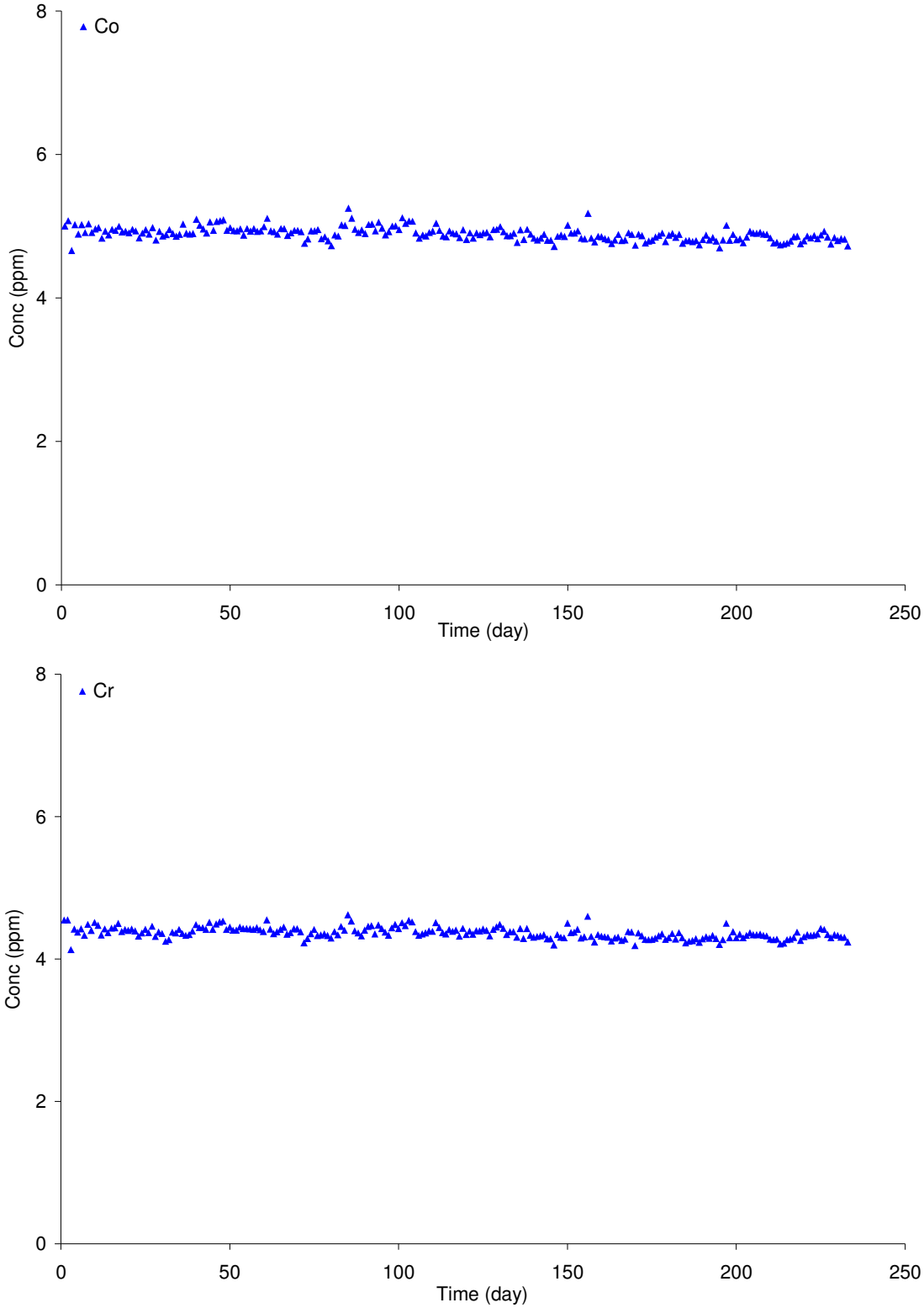
Day 1: 06/17/03. Day 6: new standard. Day 71: Lab moved. Day 102: new standard. Day 116: new bottle. Day 164: new bottle. Day 192: new standard. Day 233: 12/01/05.

Figure A3-2: Analysis of elements at ppm level by TJA Iris ICP-OES (con'd)



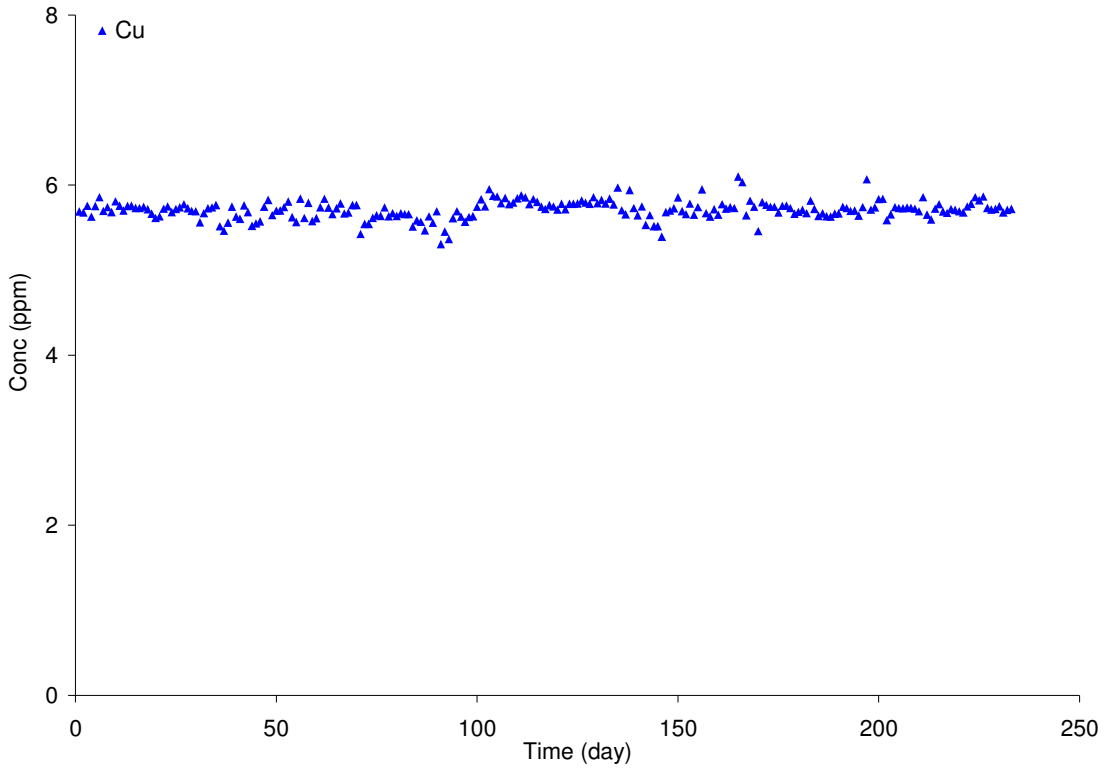
Day 1: 06/17/03. Day 6: new standard. Day 71: Lab moved. Day 102: new standard. Day 116: new bottle. Day 164: new bottle. Day 192: new standard. Day 233: 12/01/05.

Figure A3-2: Analysis of elements at ppm level by TJA Iris ICP-OES (con'd)



Day 1: 06/17/03. Day 6: new standard. Day 71: Lab moved. Day 102: new standard. Day 116: new bottle. Day 164: new bottle. Day 192: new standard. Day 233: 12/01/05.

Figure A3-2: Analysis of elements at ppm level by TJA Iris ICP-OES (con'd)



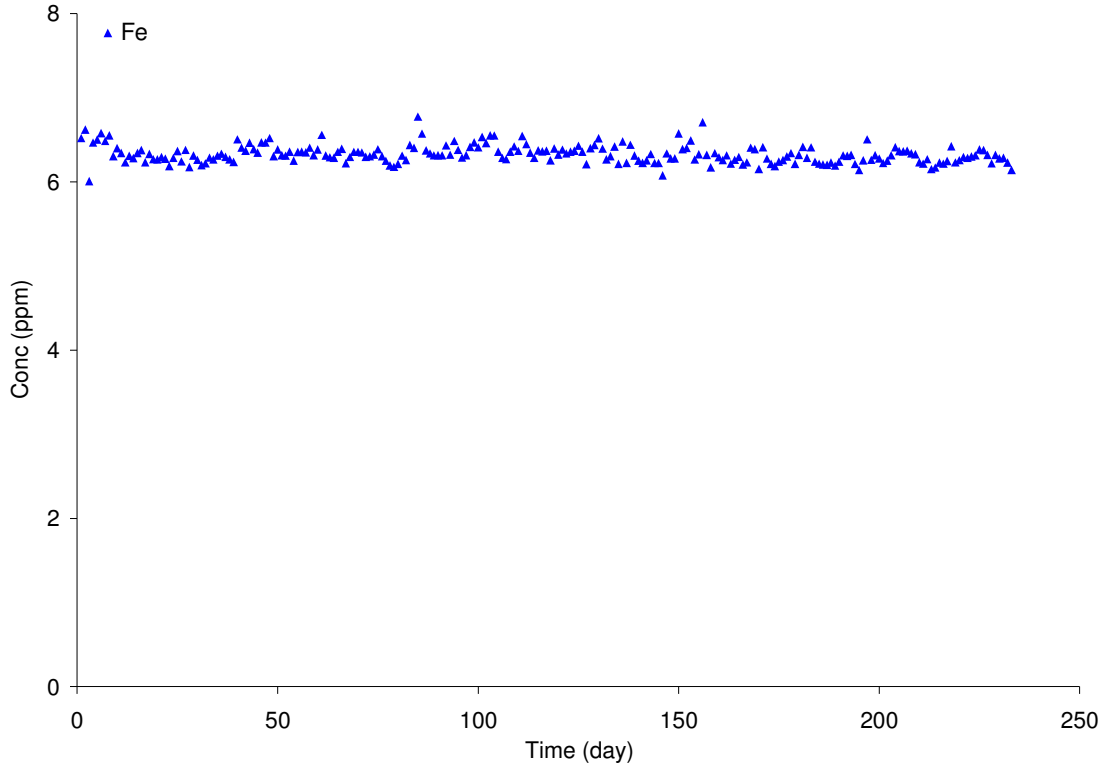


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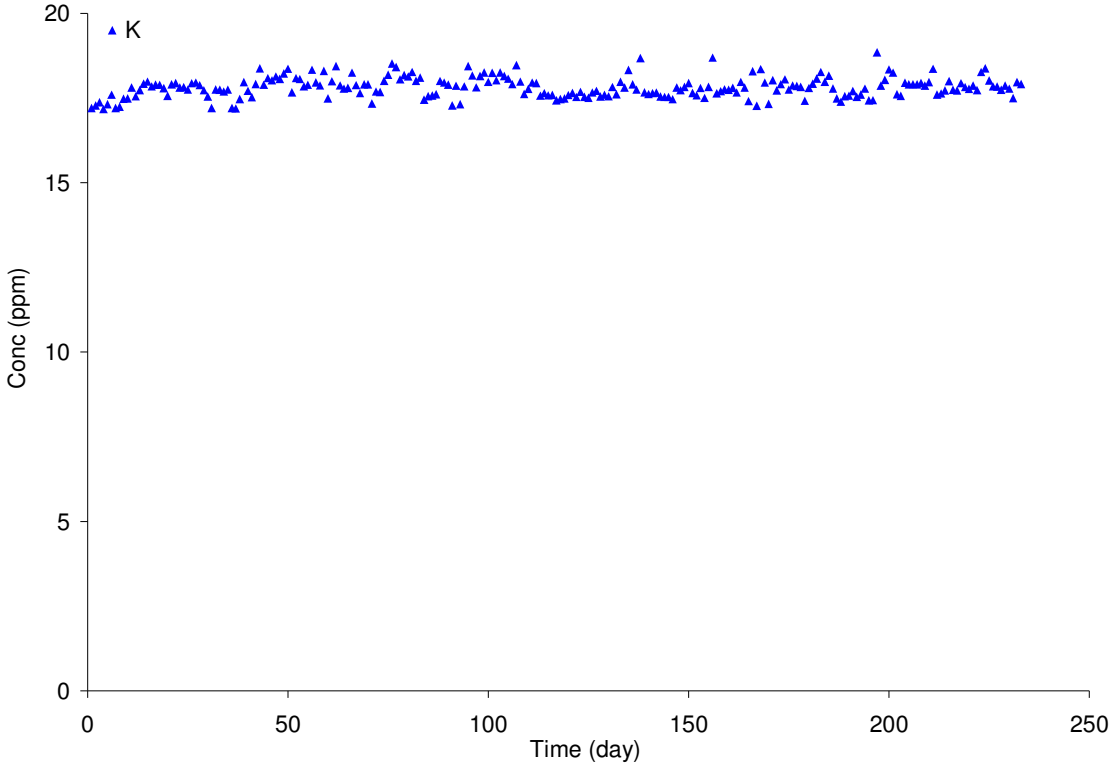
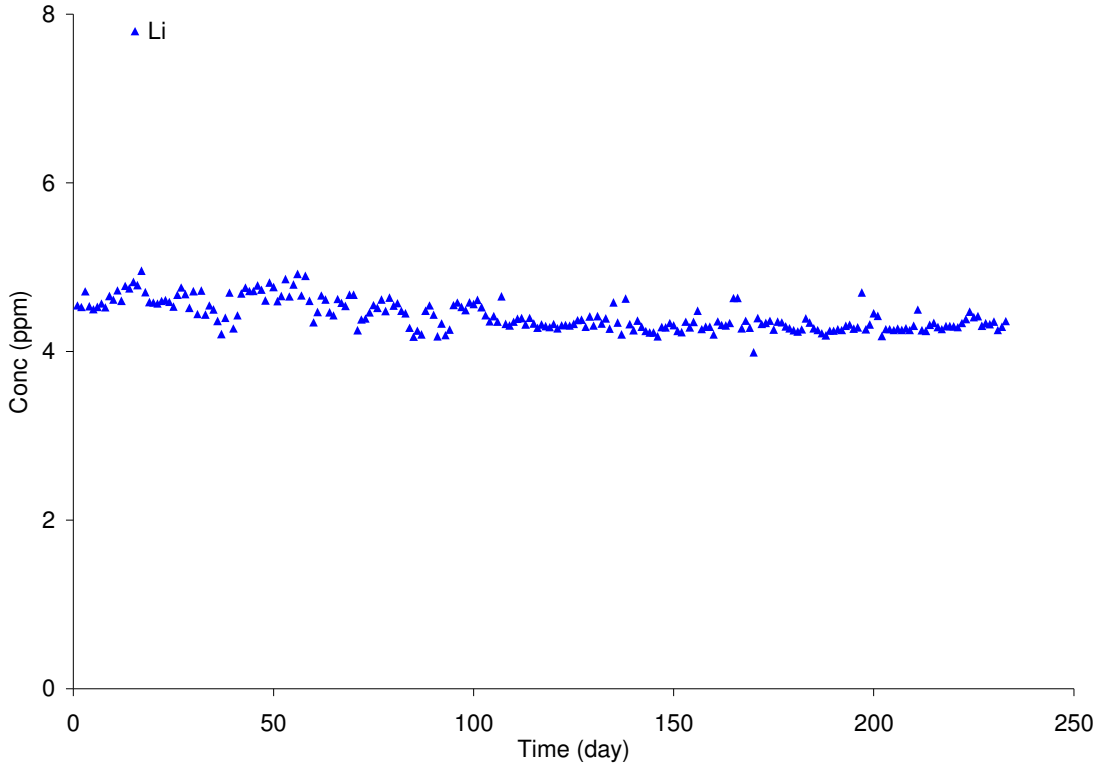
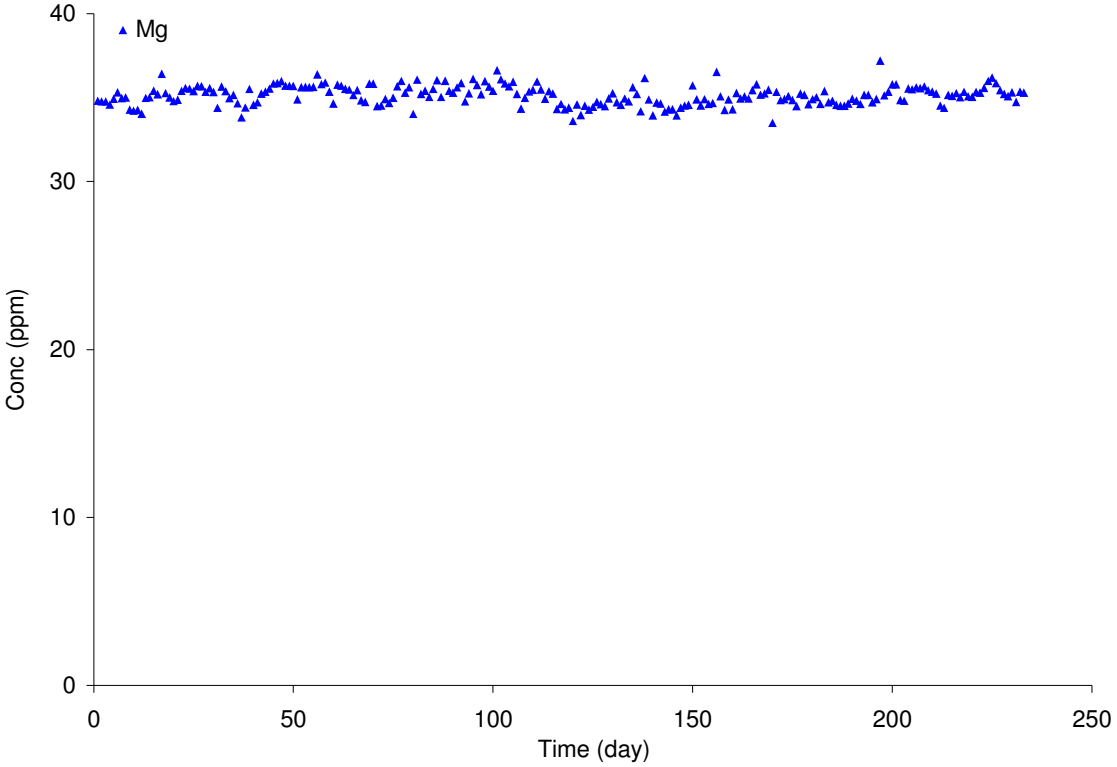
Figure A3-2: Analysis of elements at ppm level by TJA Iris ICP-OES (con'd)

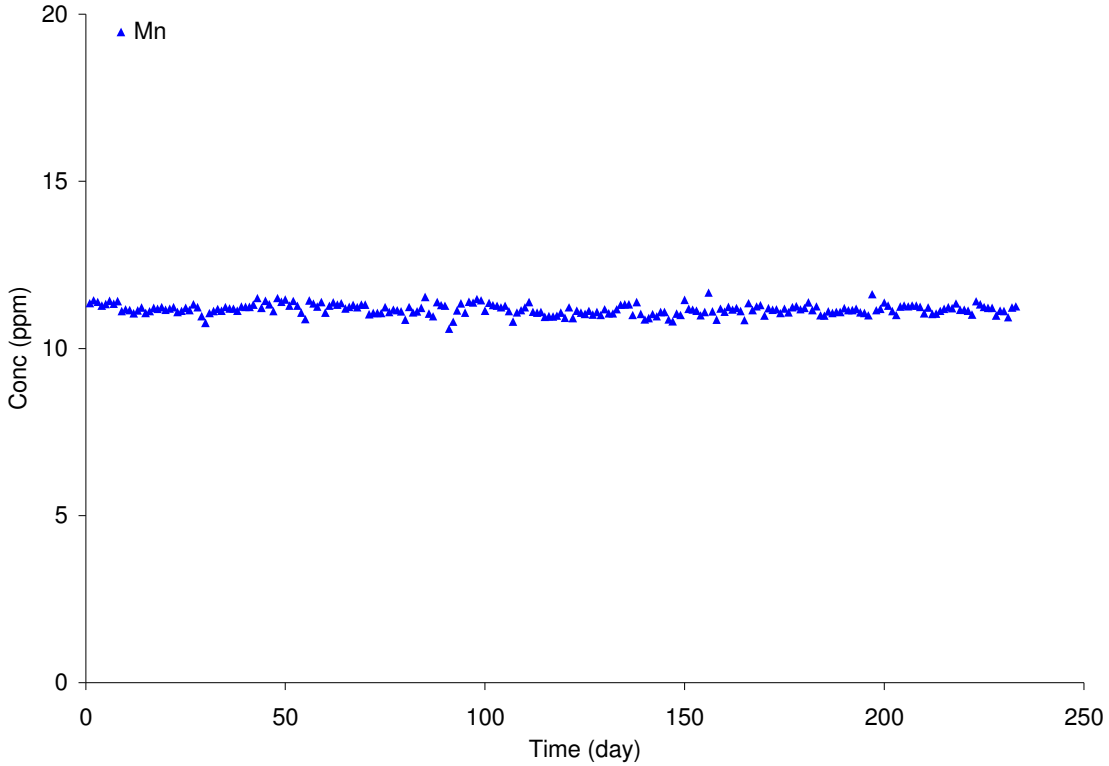




Day 1: 06/17/03. Day 6: new standard. Day 71: Lab moved. Day 102: new standard. Day 116: new bottle. Day 164: new bottle. Day 192: new standard. Day 233: 12/01/05.

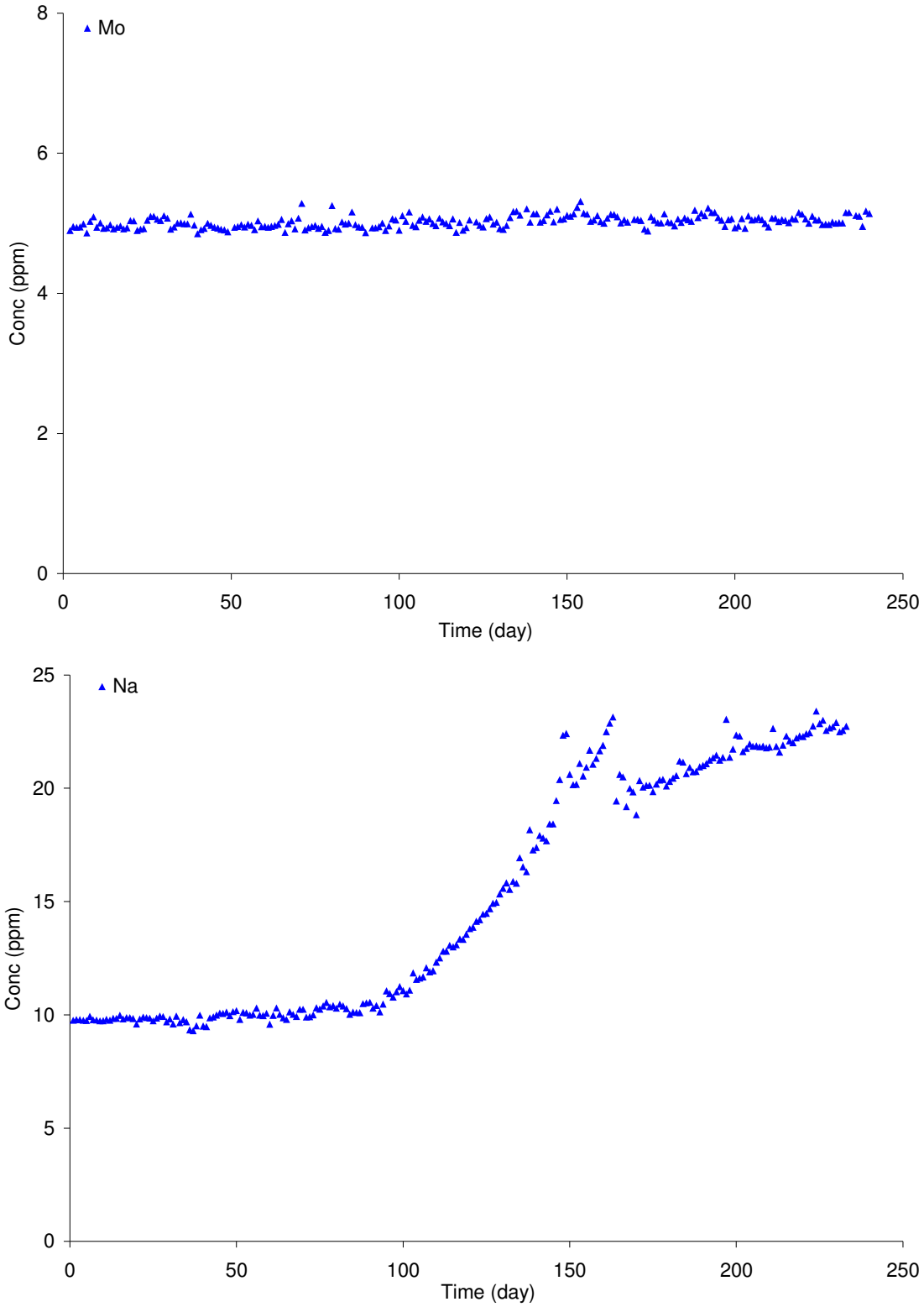
Figure A3-2: Analysis of elements at ppm level by TJA Iris ICP-OES (con'd)





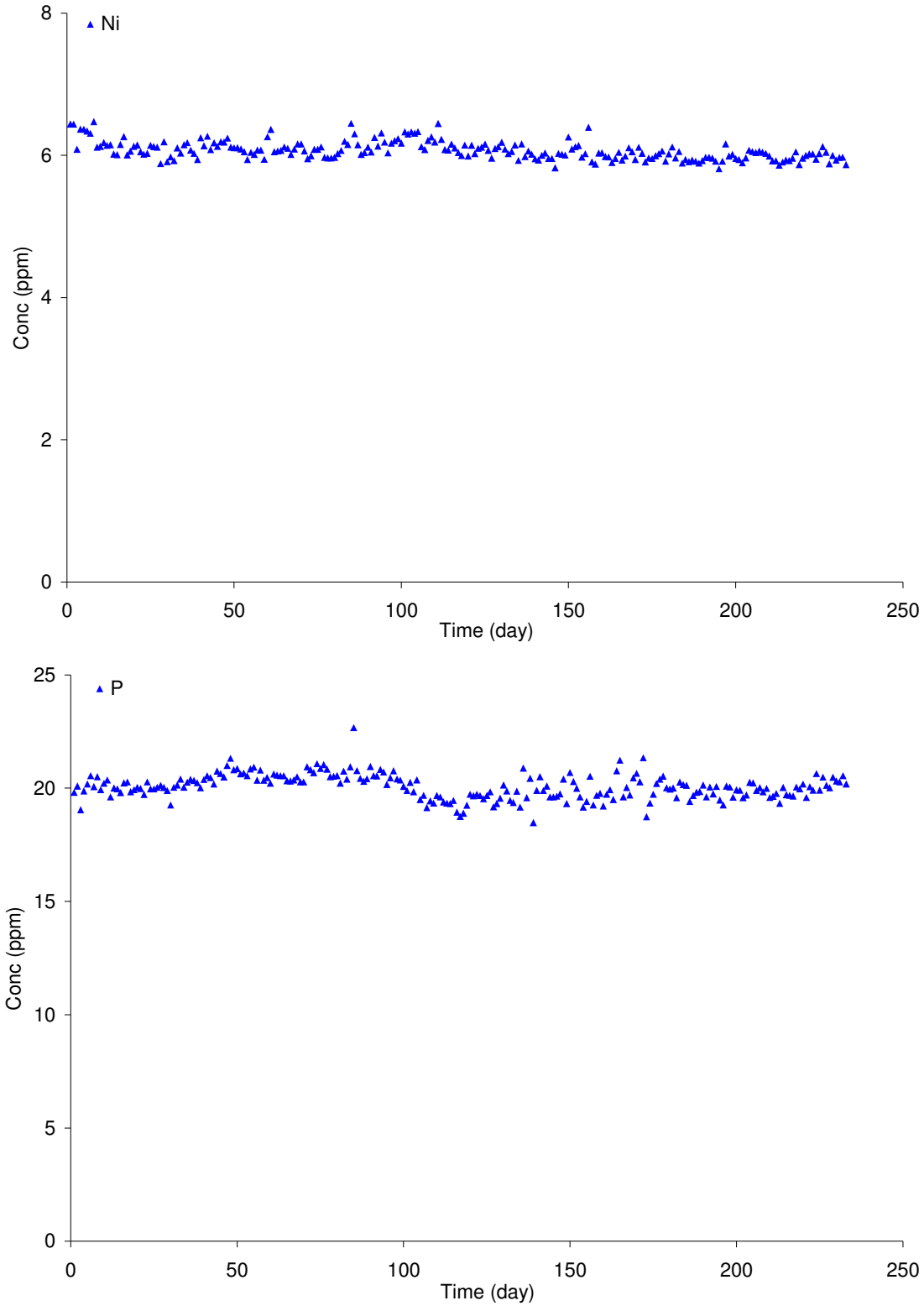
Day 1: 06/17/03. Day 6: new standard. Day 71: Lab moved. Day 102: new standard. Day 116: new bottle. Day 164: new bottle. Day 192: new standard. Day 233: 12/01/05.

Figure A3-2: Analysis of elements at ppm level by TJA Iris ICP-OES (con'd)



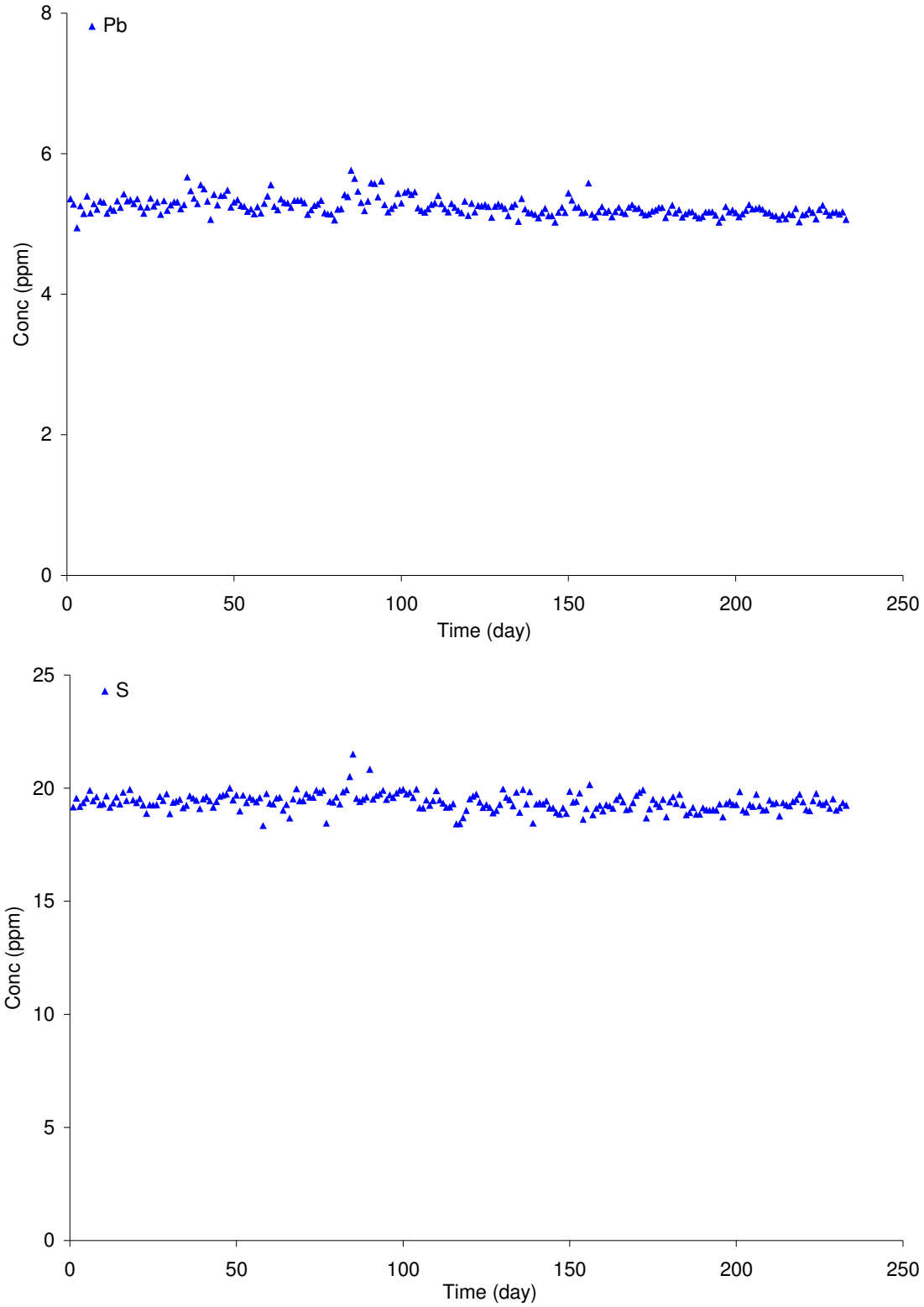
Day 1: 06/17/03. Day 6: new standard. Day 71: Lab moved. Day 102: new standard. Day 116: new bottle. Day 164: new bottle. Day 192: new standard. Day 233: 12/01/05.

Figure A3-2: Analysis of elements at ppm level by TJA Iris ICP-OES (con'd)



Day 1: 06/17/03. Day 6: new standard. Day 71: Lab moved. Day 102: new standard. Day 116: new bottle. Day 164: new bottle. Day 192: new standard. Day 233: 12/01/05.

Figure A3-2: Analysis of elements at ppm level by TJA Iris ICP-OES (con'd)



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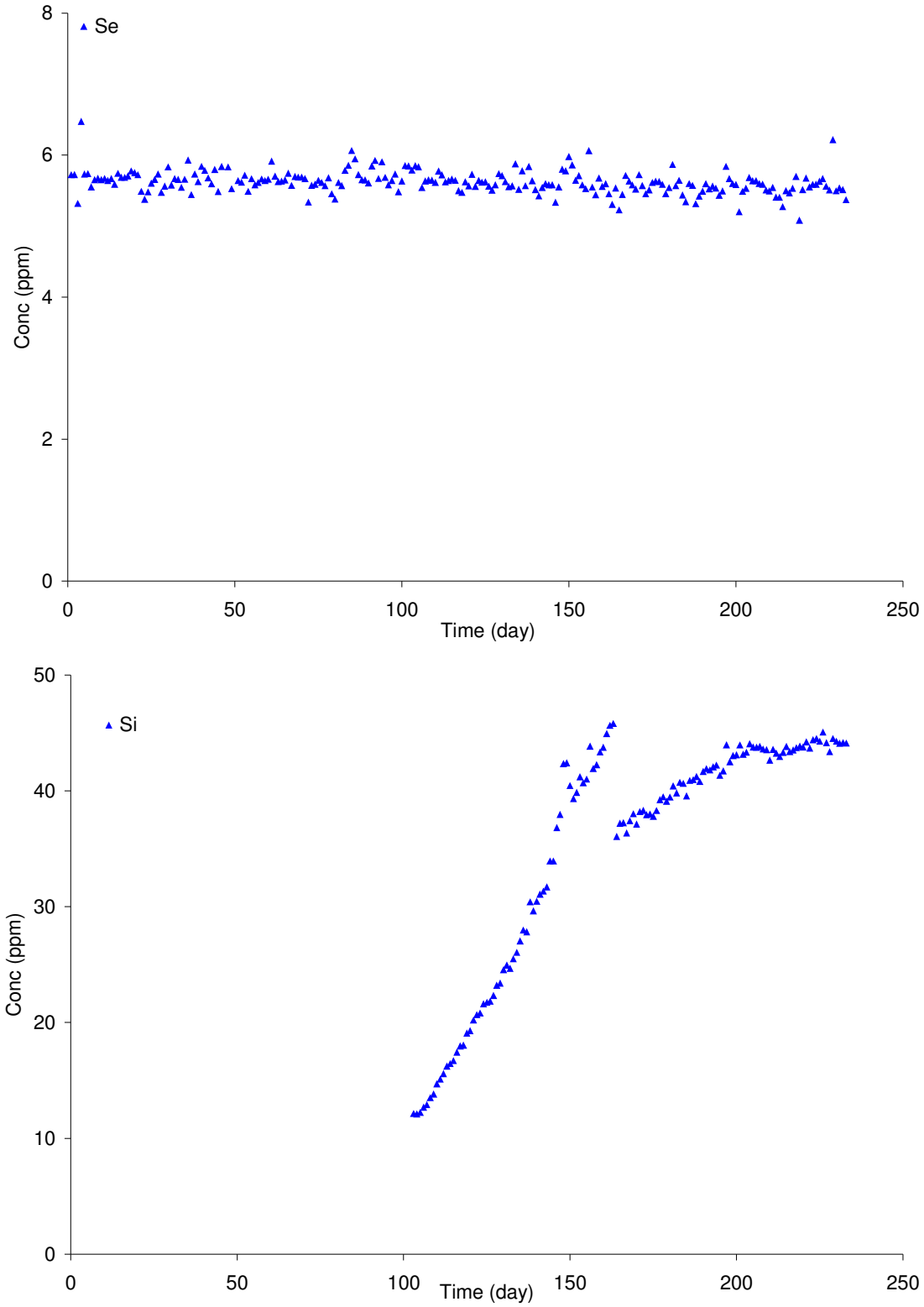
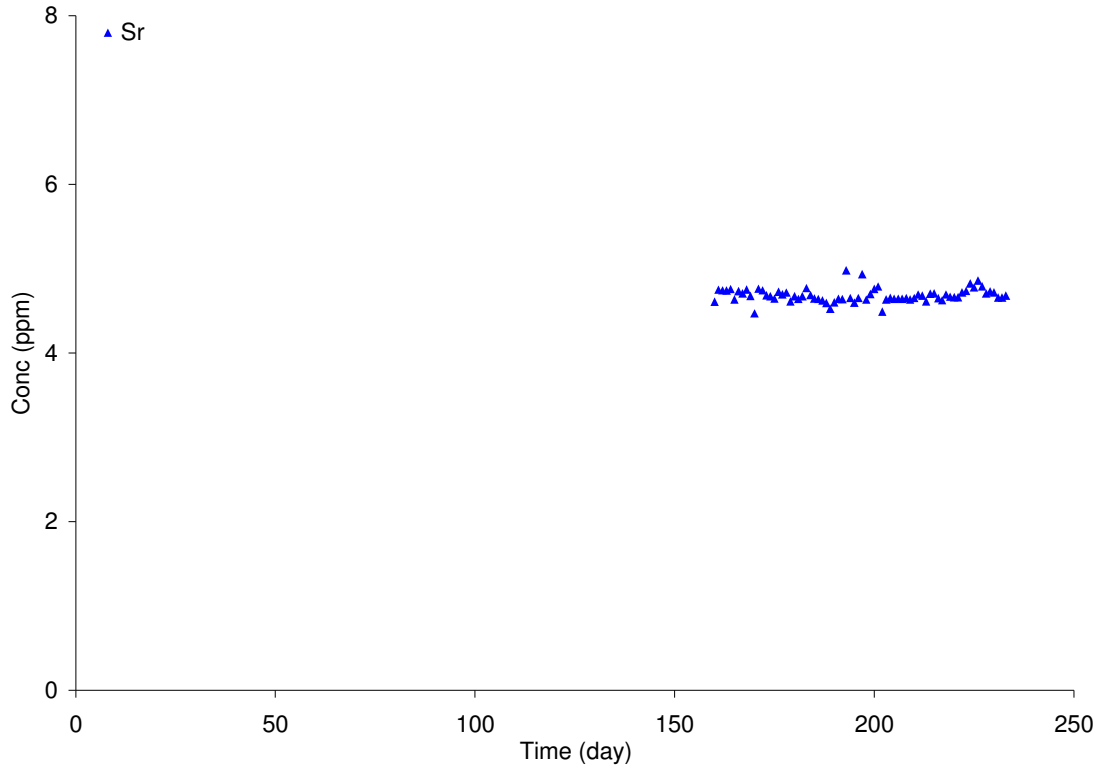
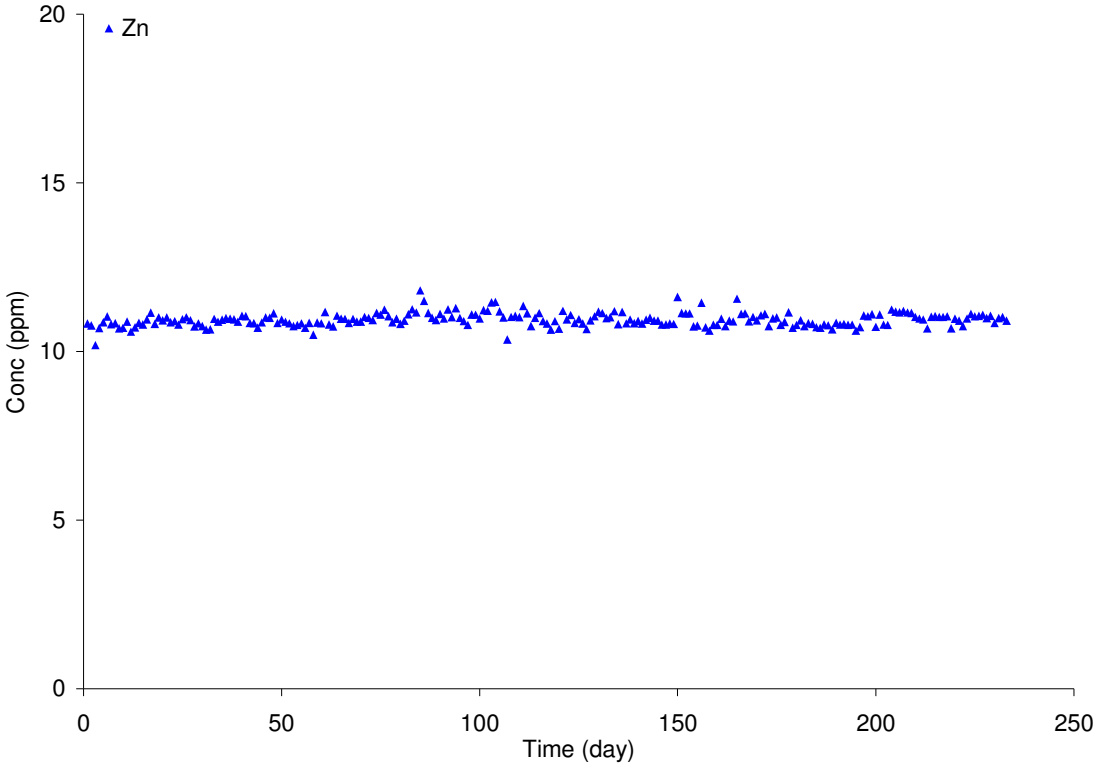


Day 1: 06/17/03. Day 6: new standard. Day 71: Lab moved. Day 102: new standard. Day 116: new bottle. Day 164: new bottle. Day 192: new standard. Day 233: 12/01/05.

Figure A3-2: Analysis of elements at ppm level by TJA Iris ICP-OES (con'd)





Day 1: 06/17/03. Day 6: new standard. Day 71: Lab moved. Day 102: new standard. Day 116: new bottle. Day 164: new bottle. Day 192: new standard. Day 233: 12/01/05.