Alkali element background reduction in laser ICP-MS

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Abstract

Alkali backgrounds in laser ablation ICP-MS analyses can be enhanced by electron-induced ionization of alkali contamination on the skimmer cone, reducing effective detection limits for these elements. Traditionally, this problem is addressed by isolating analyses of high alkali materials onto a designated cone set, or by operating the ICP-MS in a “soft extraction” mode, which reduces the energy of electrons repelled into the potentially contaminated sampling cone by the extraction field. Here we present a novel approach, where we replace the traditional alkali glass tuning standards with synthetic low-alkali glass reference materials. Using this vitreous tuning solution, we find that this approach reduces the amount of alkali contamination produced, halving backgrounds for the heavy alkali elements without any change to analytical procedures. Using segregated cones is still the most effective method for reducing lithium backgrounds, but since the procedures are complimentary both can easily be applied to the routine operations of an analytical lab.

1 Introduction

In solution ICP-MS, tuning and calibration are performed using carefully selected, high purity aqueous solutions. In contrast, laser ablation ICP-MS (LA-ICP-MS) tuning and calibration are often conducted using natural or multi-element glass reference materials such as the NIST 600-series glasses, which are generally not specifically chosen or synthesized for the purpose of tuning a plasma source mass spectrometer. This can create a host of contamination issues (Eggins and Shelley 2002).

The LA-ICP-MS Agilent 7500 lab in operation at the Research School of Earth Sciences (RSES), Australian National University (ANU) during 2006 was a general-purpose, multidisciplinary analytical facility. Samples analysed included zircon and other minerals for U-Pb geochronology; geological, synthetic, and biogenic carbonates for paleoclimatology; mantle minerals for diamond indicator studies; igneous, metamorphic, and synthetic minerals and silicate melts for the study of petrogenesis of various mantle and crustal rocks at a variety of pressures and temperatures; synthetic and natural sulfides for thermodynamic or ore-genesis research, and occasional solution (no laser ablation) ICP-MS analyses of platinum group elements. The extensive variety of analytical procedures performed led to a number of potential contamination and cross-contamination issues.

Of particular concern were the alkali elements. Once alkali elements are introduced to the skimmer and sampler cones, electron-induced secondary ionization can create large sample-independent backgrounds. Analytical protocols such as the soft extraction technique (Tye and Sakata 2000) will reduce these backgrounds, but at the expense of overall sensitivity, especially for low-mass ions.

Two experiments were performed in the LA- ICP-MS Agilent 7500 lab, in order to determine the ease and effectiveness of reducing alkali loads and backgrounds without changing analytical procedures. The first method involved segregating cones into high, low, and average expected alkali concentration. This is standard procedure in many labs, and served as a baseline for effectiveness, to which we could compare our new procedure. The second experiment replaced the NIST612 standard with a purpose-made alkali-free glass (Tune-1) with a composition especially chosen for tuning and evaluation of laser ablation and ICP-MS performance. This was, in effect, the vitreous equivalent of a tuning solution, with the tuning elements dissolved into a glass instead of dilute nitric acid. While this may seem to be an obvious approach, we do not know of any previous attempts to dissolve tuning species into a glass with a composition chosen to eliminate unwanted contaminants.

2 Methods

Cone segregation involved analysing samples with different expected alkali contents on different cones. A ‘dirty’ cone set (C-5) was assigned to use for lithium borates (Eggins 2003), stoichiometric sodium and potassium minerals, and doped or felsic glasses. Another cone set (E-1) was set aside for low level lithium, rubidium, and caesium work. The remaining cones were used for routine mineral analyses that did not fall into either of these two categories. The backgrounds of Li, Na, Rb, and Cs for the various cone sets were monitored during the daily tune-up from March-July 2006. Potassium was not recorded, as the backgrounds of both stable K isotopes are complicated by argon hydrides and the shoulder of the intense $^{40}Ar^+$ peak from the argon plasma. $^{40}K^+$ was completely obscured by $^{40}Ar^+$.

Tuning the instrument in the morning before the analysis can comprise 5-25% of the total daily plasma load, depending on the duration (2-12 hours) and type of analyses performed. The concentrations of Li, Na, and Rb in NIST 612 and 610 are significantly higher than MORB (Sun & McDonough 1989), while the Cs concentration in these synthetic glasses is many times higher than most natural samples (Table 1). A nominally alkali-free glass (Tune-1) was synthesized to replace the NIST 612 glass previously used in tuning. Tune-1 was used from August-December 2006, and backgrounds and machine performance were recorded in a similar fashion.

Tune-1 was designed to be an anorthite-wollastonite-diopside-quartz eutectic CMAS glass (Longhi, 1987). This composition was chosen for the low melting point (1129°C) and low silica content, which allows for more rapid diffusive homogenization of the dopants. The dopants were chosen according to the following criteria: 1) the element must be soluble in the glass. 2) The element must be refractory enough not to evaporate during fusion in the one atmosphere furnace. 3) To minimize interferences, elements with few isotopes were favoured over those with many. 4) A decent mass range was desired, with a dopant every 40 to 50 AMU. 5) Rare earth elements were avoided as it was unclear how well separated the available reagents were. 6) An element with an isotopic ratio greater than 10:1 but less than 20: 1 was desired for performing deadtime corrections to the electron multiplier ($^{138}Ba/^{135}Ba \sim 11$ was eventually chosen). 7) If possible, elements which ionized well in the ICP were selected. 8) The element had to be available on the shelf of the experimental petrology store, as this project was unfunded. 9) U and Th were both included as their relative behaviour was of interest to geochronologists at the time.

To satisfy these requirements as best as possible, Tune-1 was doped with 50 micromols/mol of Be, Mn, Nb, Ba, Ta, Th, and U. The glass was synthesized via the silica gel process (Hamilton and Henderson 1968), with the Ca, Mg, Al, Be, Mn, Ba, Th, and U dissolved as nitrates, and the Nb, Ta, and Si added as ethoxides. The Tune-1 measured composition is given in Table 2.

The major element (Ca, Si, Al, Mg) composition of the glass was determined using WD spectrometry on the Cameca SX100 electron microprobe at RSES. The beam conditions were 15kV and 10nA with the spot purposefully defocused to 5µm. The following synthetic standards were used for calibration: Ca and Si, wollastonite/$CaSiO_3$; Al, $CaAl_2O_4$; Mg, periclase/MgO. All standards were prepared at RSES from high purity powders (Bill Hibberson, pers. comm. 2006) and appropriate conditions of synthesis. Forty points across the sample were analysed and the results statistically collated to give the standard deviation reported.

The trace elemental composition of the glass was determined using laser ICP-MS. LA-ICP-MS analysis was performed at RSES using the Agilent 7500 series mass spectrometer. The Lambda Physik lpx 120i 193nm excimer laser laser supplied by Resonetics was attenuated by using a 25% reflectance mirror on the final bend of the custom-built laser flight tube, yielding a power output of approximately 2-3 J/cm^2. The custom-built two volume mixing cell is the forbearer to both the Laurin Technic RESOlution cell and the Helix cells sold commercially, with the details described in Eggins et al. (2003), and references therein. Ablation took place at 5 Hz.

The following analytical technique was used to determine the Rb and Cs content of Tune-1. Selected chalcophile elements were also measured for a different experiment, and those results are not reported here. Analysis time was 75 seconds, with 25 seconds of background collected before ablation commenced. A 187 micron spot was used. The following masses were measured: ^{9}Be, ^{29}Si, ^{43}Ca, ^{85}Rb, ^{107}Ag, ^{109}Ag, ^{111}Cd, ^{114}Cd, ^{118}Sn, ^{119}Sn, ^{121}Sb, ^{123}Sb, ^{133}Cs, ^{182}W, ^{183}W, ^{203}Tl, ^{205}Tl, ^{208}Pb, ^{209}Bi, ^{232}Th, ^{238}U. All isotopes were counted for 30 ms except for Si and Ca, which were measured for 5 ms. Including switching time, this cycle was repeated every 0.6222 seconds.

For the dopants, Na, and Li, a 54 um spot was used, with a laser rep rate of 4 Hz. Analysis time was 60 seconds, with 20 seconds of background collected before ablation commenced. The following masses were measured: ^{7}Li, ^{9}Be, ^{23}Na, ^{25}Mg, ^{27}Al, ^{29}Si, ^{31}P, ^{43}Ca, ^{47}Ti, ^{55}Mn, ^{57}Fe, ^{93}Nb, ^{137}Ba, ^{181}Ta, ^{232}Th, ^{238}U. All isotopes were counted for 30 ms except for Na, Mg, Ca and Fe, which were measured for 20 ms, and Si, which was measured for 10 ms.

Data was reduced via Excel spreadsheet in the manner of Longerich et al. (1996). ^{43}Ca was the internal standard, using the EPMA value of 28.46% CaO. Trace element abundances were standardized using the Pearce et al. (1997) values for NIST 612. The concentrations of dopants and alkali contaminants are listed in Table 2.

Each morning, following the daily instrumental tuning regime, alkali backgrounds were recorded as raw counts, and converted to µg/g equivalent using a daily cps/ µg/g calibration factor. The counts per µg/g in routine analysis can vary by a factor of two due to the condition of the cones, the laser and optics, the electrostatic lenses, and other unknown factors. This is why µg/g equivalent is reported instead of raw counts.

Once Tune-1 was in use, freshly cleaned cones were installed on those days when low level analyses of alkali elements were to be performed. This subset of the tune glass backgrounds are representative of the backgrounds that were present during alkali analysis. Low level alkali analyses were generally standardized against natural basalt BCR-2G, which has lower alkali concentrations than NIST 612 or 610 (Table 1).

3 Results

The cone segregation experiment, using NIST 612 as a tuning glass, was performed from March to July 2006. In early August, the custom-made glass Tune-1 replaced NIST 612 as the glass used for tuning. Cone segregation of the high alkali cone set (C-5) was continued, and data were collected through December 2006.

The mean µg/g equivalent backgrounds for Li, Na, Rb, and Cs are reported in table 3, and the daily values are in table 4. The High alkali cone set (C-5) has significantly higher backgrounds for Li than all other cone sets, but the low alkali cone set (E-1) is similar to the other cones (sample cones D, J, A, K; skimmer cones 6,2,4,9,7), for all elements except lithium. Cone segregation was quite effective at reducing Li backgrounds on the low Li cone set (Figure 1, Table 3). The use of low concentration cones dropped the Cs background by about a factor of two. However, cone segregation had no appreciable impact on Na or Rb background levels.

The adoption of Tune-1 approximately halved the backgrounds for Li, Rb, and Cs compared to the backgrounds associated with tuning on NIST 612. Na was reduced by 25%. However, the background produced by a newly cleaned set of cones (tuned using Tune-1) is 2-3 times lower still (Figure 1, table 3), showing that backgrounds can be dropped for those days when low level alkali elements are to be analysed.

4 Discussion

The analysis of the tune glass reveals a few errors in synthesis. Excess Be is caused by an aborted attempt to dissolve Be metal in concentrated nitric acid before adding Be as a nitrate solution. The Si deficit is probably a result of incomplete hydration of the tetra ethyl orthosilicate, and explains the slightly high trace elemental compositions. The glass appears to be homogenous despite these minor problems. The alkali content, while detectable, is orders of magnitude lower than the NIST 612 glass.

Day to day background levels in alkali elements were highly variable throughout the study. Two instances where a lithium borate was run on a coneset other than the designated one are clearly visible in the data (Figure 1a). Many, but not all, of the other variations can be explained by use of NIST 612 or 610 as a reference material under various spot sizes and ablation times. Cleaning cones generally dropped the backgrounds of all elements except lithium. However, despite the day to day noise, some systematic trends were noticed.

Segregating lithium borate flux experiments onto a dedicated cone set produced an order of magnitude decrease in Li backgrounds for non-Li cones, as expected. Replacing the NIST glass used for tuning with a custom-made glass reduced most alkali backgrounds by about a factor of 2. The changes only involved machine setup, tuning and performance verification, and did not require any changes to methods or standardization for analysing unknowns. Judging by the alkali levels found on clean cones, a further factor of 2-3 reduction is possible for days when alkali need to be measured at the lowest levels. We note, however, that the lithium backgrounds are lowest for the low-alkali cones tuning with NIST 612. The reason these are higher when the tune glass is used is not clear, but it is possible that the spike in Li backgrounds on the low level cones at the end of the NIST run was a contamination event that was never properly cleaned, and persisted into the Tune-1 experiments.

5 Conclusions

When tuning LA-ICP-MS we have observed that use of the low alkali glass, Tune-1, is an effective means of reducing alkali backgrounds and improving analytical precision and lowering limits of detection. For the heavy alkali in particular, it is more effective than simply segregating cones based on expected target composition.

This reduction in alkali contamination does not preclude use of instrumental methods such as soft extraction (Tye & Sakata 2000) to further depress the alkali background. Rather, it reduces the build-up of unwanted alkali elements in parts of the instrument where secondary ionization can reintroduce them into subsequent samples as contamination. As this is only a change to the instrument setup procedure, it does not require a change the protocols used by analysts. The lower backgrounds that result from this study have enabled the determination of the alkali content of olivine (Mallmann et al., 2009), feldspar lamellae (Parsons et al., 2009), ultramafic melt inclusions (Kallio and Ireland 2006), and Martian meteorites (Stopar et al. 2007). Although only a dozen glass beads were cast, limited supplies are available from the authors on request.

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Table 1. Alkali contents of popular natural and synthetic ICPMS reference materials. Li, Rb, Cs in ppm (mg/kg). Na is weight percent oxide. Values from Govindaraju 1994, Eggins et al. 1997, Norman et al. 1998, Hinton 1999, and Gao et al. 2002. LiBO flux Li content is an estimate; exact content depends on tetraborate/metaborate ratio, and rock type fluxed.

Element	LiBO flux	610	612	BCR	BHVO	Tune-1
Li	~83,000	484	41	9.6	4.9	0.184
Na_2O	variable	13.76%	14%	3.15%	2.26%	0.0021%
Rb	variable	431	32	49	9.5	0.012
Cs	variable	360	41	1.1	0.1	0.01

Table 2. Major and trace elemental composition of glass Tune-1. Errors are 1 sigma. Major elements from EPMA, minor elements from ICPMS.

Element	% g/g	
CaO	28.5% ±0.1%	
MgO	2.16% ±0.04%	
Al_2O_3	13.1% ±0.1%	
SiO_2	56.5% ±0.2%	
Dopant	µg/g	µmol/mol
Be	42.1±0.2	80.1±0.3
Mn	186.3±0.9	58.1±0.3
Nb	314.1±0.8	57.9±0.2
Ba	429.9±1.2	53.7±0.1
Ta	612.8±2.7	58.0±0.3
Th	704.1±2.5	52.0±0.2
U	723.7±14.6	52.1±1.0
Contaminant		
Li	0.17±0.02	0.43±0.04
Na	14.8±1.3	11.0±0.9
Rb	0.012±0.002	0.0025±0.0004
Cs	0.010±0.001	0.0013±0.0001

Table 3. Mean daily backgrounds in ppm equivalent. Low conc refers to cone set E-5, which was reserved for low alkali samples. Li free refers to all cones except the dedicated high alkali set. Clean cones is the background on freshly cleaned cones after tuning on the Tune-1 glass, before any analyses are performed.

	Li	Na	Rb	Cs
all 612	86.6	623	0.090	0.037
Li free 612	4.20	642	0.094	0.039
low conc 612	0.29	705	0.090	0.020
Li free Tune	1.83	474	0.044	0.015
low conc tune	0.37	499	0.054	0.016
clean cones	0.54	161	0.022	0.005

Table 4a: Mean daily backgrounds in µg/g equivalent from tuning using the NIST 612 glass.

Date	*skimmer cone*	*sampler cone*	*Li bkg*	*Na bkg*	*Rb bkg*	*Cs bkg*
10/03/2006	j	2	0.13	860.74	0.081	0.028
13/03/2006	j	2	0.22	783.27	0.093	0.035
14/03/2006	j	2	0.20	350.45	0.026	0.009
15/03/2006	j	2	0.16	683.83	0.039	0.016
16/03/2006	j	2	7.31	384.08	0.032	0.011
17/03/2006	j	2	7.85	490.26	0.040	0.016
21/03/2006	j	2	6.63	449.75	0.051	0.021
22/03/2006	c	5	280.58	258.70	0.018	0.011
23/03/2006	c	5	712.95	275.27	0.018	0.008
24/03/2006	j	2	4.97	363.73	0.013	0.004
27/03/2006	j	2	1.14	109.62	0.013	0.005
29/03/2006	k	4	1.10	3425.75	0.230	0.115
31/03/2006	k	4	0.52	1037.87	0.042	0.015
3/04/2006	k	4	0.40	1208.37	0.223	0.087
4/04/2006	k	4	0.34	1261.59	0.143	0.049
5/04/2006	k	4	0.39	1068.95	0.095	0.039
6/04/2006	k	4	0.28	1119.94	0.182	0.071
7/04/2006	d	9	0.38	824.22	0.092	0.039
10/04/2006	d	9	0.18	721.55	0.077	0.031
11/04/2006	d	9	0.16	756.37	0.068	0.029
13/04/2006			0.15	608.52	0.228	0.100
18/04/2006			0.22	363.35	0.138	0.069
19/04/2006			0.11	362.53	0.094	0.059
20/04/2006			0.19	469.20	0.137	0.077
21/04/2006			0.17	275.83	0.116	0.057
26/04/2006	e	1	0.28	772.24	0.029	0.011

Date	*skimmer cone*	*sampler cone*	*Li bkg*	*Na bkg*	*Rb bkg*	*Cs bkg*
27/04/2006			0.43	695.87	0.071	0.030
1/05/2006	c	5	0.03	234.94	0.020	0.006
2/05/2006	c	5	2.85	625.57	0.167	0.092
3/05/2006	c	5	1.06	409.54	0.131	0.036
4/05/2006	c	5	0.89	315.58	0.083	0.025
5/05/2006	c	5	0.81	330.10	0.061	0.016
8/05/2006	c	5	0.43	276.55	0.113	0.034
9/05/2006	j	2	1.03	972.29	0.090	0.035
10/05/2006			0.31	361.38	0.040	0.023
11/05/2006			0.14	180.90	0.053	0.030
15/05/2006			45.66	797.04	0.148	0.049
16/05/2006			59.58	542.41	0.076	0.029
17/05/2006			89.88	620.02	0.136	0.063
19/05/2006			0.19	263.64	0.038	0.019
22/05/2006			0.14	386.39	0.078	0.033
23/05/2006			0.10	287.61	0.041	0.014
24/05/2006			0.08	420.53	0.065	0.033
29/05/2006	e	1	0.03	185.05	0.097	0.004
31/05/2006	j	2	0.23	540.93	0.102	0.074
1/06/2006	e	1	0.03	117.14	0.231	0.017
1/06/2006	j	2	0.06	338.97	0.057	0.026
5/06/2006			0.10	219.85	0.068	0.038
6/06/2006			0.21	352.27	0.057	0.034
7/06/2006			0.24	281.16	0.071	0.044
8/06/2006			0.21	266.03	0.164	0.081
9/06/2006			0.19	306.67	0.084	0.047
13/06/2006	j	2	0.26	366.77	0.067	0.033

Date	*skimmer cone*	*sampler cone*	*Li bkg*	*Na bkg*	*Rb bkg*	*Cs bkg*
14/06/2006	c	5	54.31	290.85	0.138	0.065
15/06/2006	c	5	245.09	158.64	0.052	0.023
16/06/2006	c	5	263.34	94.82	0.064	0.019
19/06/2006	c	5	3.80	1369.72	0.070	0.032
21/06/2006	c	5	3.16	1182.13	0.037	0.014
22/06/2006	c	5	1.68	977.39	0.073	0.030
23/06/2006	c	5	0.61	819.26	0.090	0.027
26/06/2006	c	5	76.51	764.24	0.135	0.052
27/06/2006	c	5	3279.83	657.11	0.085	0.018
28/06/2006	j	2	0.66	470.63	0.137	0.074
4/07/2006	d	4	0.94	748.62	0.104	0.043
5/07/2006	d	4	1.04	780.64	0.219	0.098
6/07/2006	c	5	0.23	443.88	0.059	0.020
7/07/2006	d	4	0.70	843.98	0.236	0.101
12/07/2006	d	4	0.48	486.56	0.091	0.044
13/07/2006	e	1	0.76	971.26	0.060	0.022
14/07/2006	e	1	0.14	774.74	0.059	0.020
18/07/2006	e	1	0.10	585.21	0.047	0.016
20/07/2006	e	1	0.19	787.62	0.144	0.019
21/07/2006	e	1	0.32	630.06	0.040	0.012
25/07/2006	e	1	0.57	1354.36	0.100	0.032
27/07/2006	e	1	0.34	878.88	0.117	0.040
3/08/2006	c	5	1575.30	1280.07	0.099	0.048
4/08/2006	a	4	6.87	723.24	0.025	0.011
7/08/2006	a	4	1.99	567.16	0.025	0.010

Table 4b: Mean daily backgrounds in µg/g equivalent from tuning using the Tune-1 glass.

Date	*skimmer cone*	*sampler cone*	*Li bkg*	*Na bkg*	*Rb bkg*	*Cs bkg*
9/08/2006	a	4	2.00	514.40	0.016	0.006
10/08/2006	a	4	1.09	1439.83	0.043	0.013
11/08/2006	a	4	0.77	902.18	0.055	0.018
14/08/2006	a	4	1.37	452.61	0.024	0.008
15/08/2006	a	4	1.08	796.94	0.034	0.010
16/08/2006	a	4	1.48	439.43	0.018	0.006
17/08/2006	a	4	0.21	883.06	0.032	0.009
18/08/2006	a	4	0.53	1400.18	0.083	0.017
20/08/2006	a	4	0.68	772.84	0.024	0.005
21/08/2006	a	4	0.90	368.04	0.011	0.003
21/08/2006	c	5	167.29	1046.24	0.613	0.170
22/08/2006	c	5	218.54	759.97	0.488	0.191
23/08/2006	c	5	365.30	664.10	0.434	0.198
4/09/2006	d	9	0.16	142.18	0.014	0.006
5/09/2006	d	9	0.34	112.77	0.009	0.003
6/09/2006	d	9	0.29	220.22	0.011	0.004
7/09/2006	d	9	0.29	257.43	0.014	0.005
8/09/2006	d	9	0.30	220.43	0.124	0.065
12/09/2006	d	9	0.18	664.68	0.149	0.069
13/09/2006	c	5	12.94	76.32	0.014	0.004
14/09/2006	c	5	21.09	105.01	0.020	0.006
15/09/2006	c	5	17.92	61.70	0.010	0.004
18/09/2006	e	1	0.30	699.00	0.181	0.046
18/09/2006	e	9	1.07	7.57	0.014	0.010
18/09/2006	c	5	4.18	260.06	0.040	0.022
19/09/2006	d	9	0.22	60.86	0.011	0.006

Date	*skimmer cone*	*sampler cone*	*Li bkg*	*Na bkg*	*Rb bkg*	*Cs bkg*
21/09/2006	d	9	0.09	106.44	0.052	0.011
22/09/2006	d	9	0.10	317.45	0.071	0.016
26/09/2006	c	5	10.09	226.23	0.024	0.011
27/09/2006	c	5	283.63	337.15	0.042	0.016
28/09/2006	c	5	326.27	367.70	0.046	0.019
29/09/2006	c	5	826.78	511.94	0.144	0.055
29/09/2006	e	1	0.64	34.97	0.007	0.003
29/09/2006	d	9	0.37	466.57	0.085	0.032
10/10/2006	d	9	0.61	438.80	0.203	0.089
10/10/2006	j	2	0.73	59.32	0.009	0.005
11/10/2006	j	2	2.75	152.15	0.007	0.003
12/10/2006	j	2	1.51	152.68	0.014	0.004
17/10/2006	j	2	0.95	598.86	0.028	0.011
18/10/2006	j	2	0.69	507.74	0.016	0.006
19/10/2006	j	2	0.56	354.14	0.019	0.008
20/10/2006	j	2	0.68	536.71	0.017	0.006
23/10/2006	j	2	0.86	280.69	0.019	0.007
24/10/2006	j	2	19.11	694.11	0.060	0.026
25/10/2006	j	2	12.66	771.84	0.055	0.022
27/10/2006	e	1	0.09	52.90	0.011	0.002
31/10/2006	c	5	6.94	22.20	0.008	0.002
1/11/2006	c	5	11.89	147.23	0.006	0.002
2/11/2006	c	5	324.38	128.81	0.008	0.002
3/11/2006	c	5	178.84	300.52	0.017	0.003
7/11/2006	j	2	9.82	683.59	0.031	0.009
8/11/2006	j	2	16.83	725.89	0.033	0.011
9/11/2006	j	2	8.60	288.02	0.025	0.008

Date	*skimmer cone*	*sampler cone*	*Li bkg*	*Na bkg*	*Rb bkg*	*Cs bkg*
10/11/2006	c	5	217.02	432.29	0.034	0.008
13/11/2006	j	2	4.21	237.98	0.023	0.007
13/11/2006	e	1	0.08	97.03	0.110	0.006
14/11/2006	e	1	0.14	112.57	0.010	0.003
15/11/2006	j	2	3.35	121.40	0.026	0.010
16/11/2006	j	2	0.67	329.30	0.033	0.013
17/11/2006	d	9	0.30	42.56	0.004	0.002
20/11/2006	c	5	317.87	314.98	0.020	0.007
22/11/2006	c	5	101.05	62.41	0.037	0.006
24/11/2006	c	5	83.24	320.34	0.042	0.010
27/11/2006	e	1	0.15	596.33	0.025	0.006
29/11/2006	e	1	0.19	638.18	0.025	0.007
30/11/2006	c	5	73.62	217.96	0.014	0.004
1/12/2006	c	5	86.85	413.92	0.027	0.007
2/12/2006	e	1	0.22	598.30	0.057	0.009
4/12/2006	e	1	0.19	634.70	0.045	0.009
5/12/2006	c	5	155.70	563.94	0.034	0.010
6/12/2006	e	1	0.33	741.09	0.036	0.008
7/12/2006	e	1	0.30	724.49	0.035	0.009
8/12/2006	e	1	0.16	524.38	0.024	0.006
11/12/2006	e	1	0.80	596.19	0.062	0.023
12/12/2006	e	1	0.77	559.75	0.068	0.026
13/12/2006	e	1	0.39	605.62	0.075	0.031
14/12/2006	e	1	0.51	659.52	0.085	0.037
15/12/2006	e	1	0.40	889.42	0.089	0.040
19/12/2006	e	1	0.33	712.80	0.068	0.027

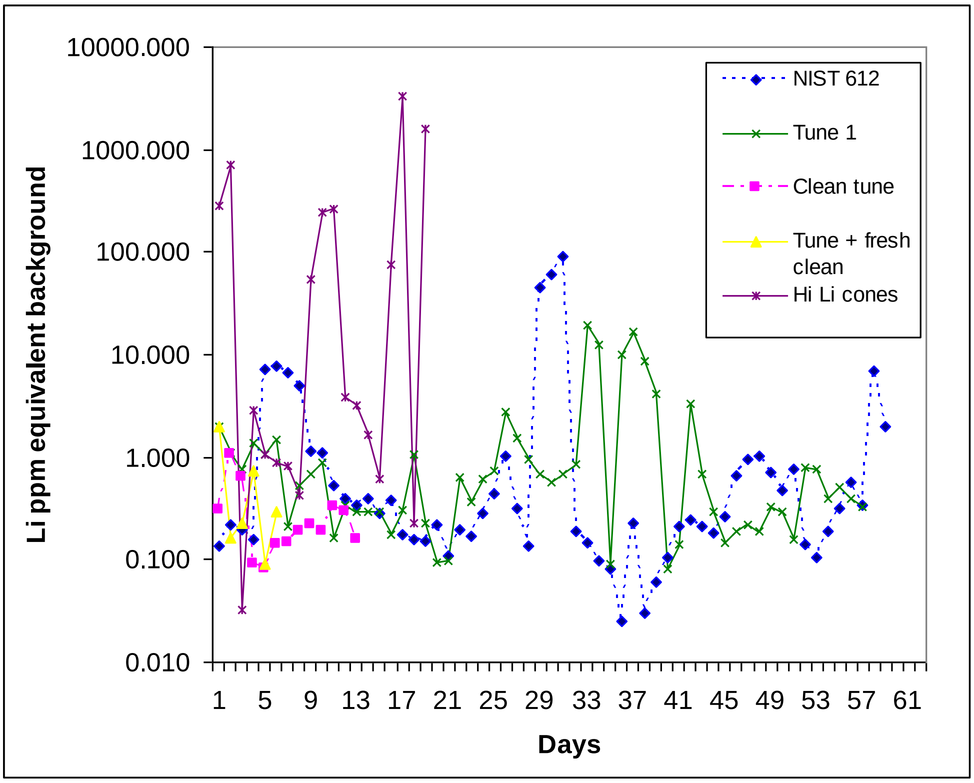

Figure 1a. Daily Li backgrounds as µg/g equivalent for high Li cones, standard cones tuned with NIST612, standard cones tuned with Tune-1, low level cones tuned with Tune-1, and freshly cleaned cones tuned with Tune-1.

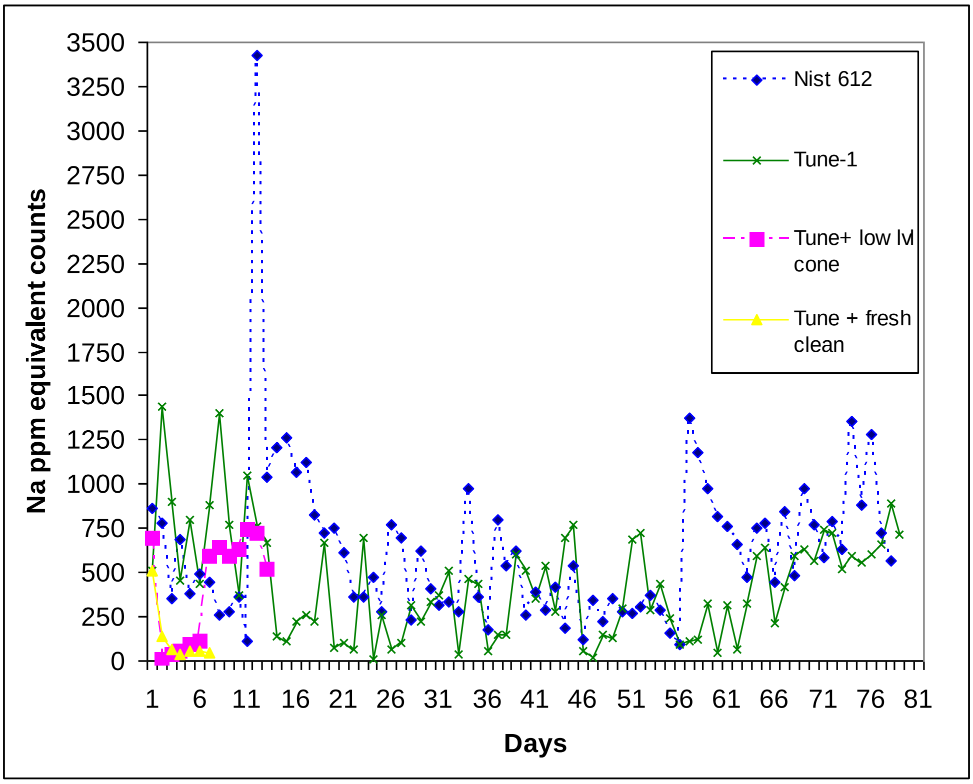

Figure 1b. Daily Na backgrounds as µg/g equivalent for tuning done with NIST 612, Tune-1, and Tune-1 with low level and freshly cleaned sets of cones for low level alkali work.

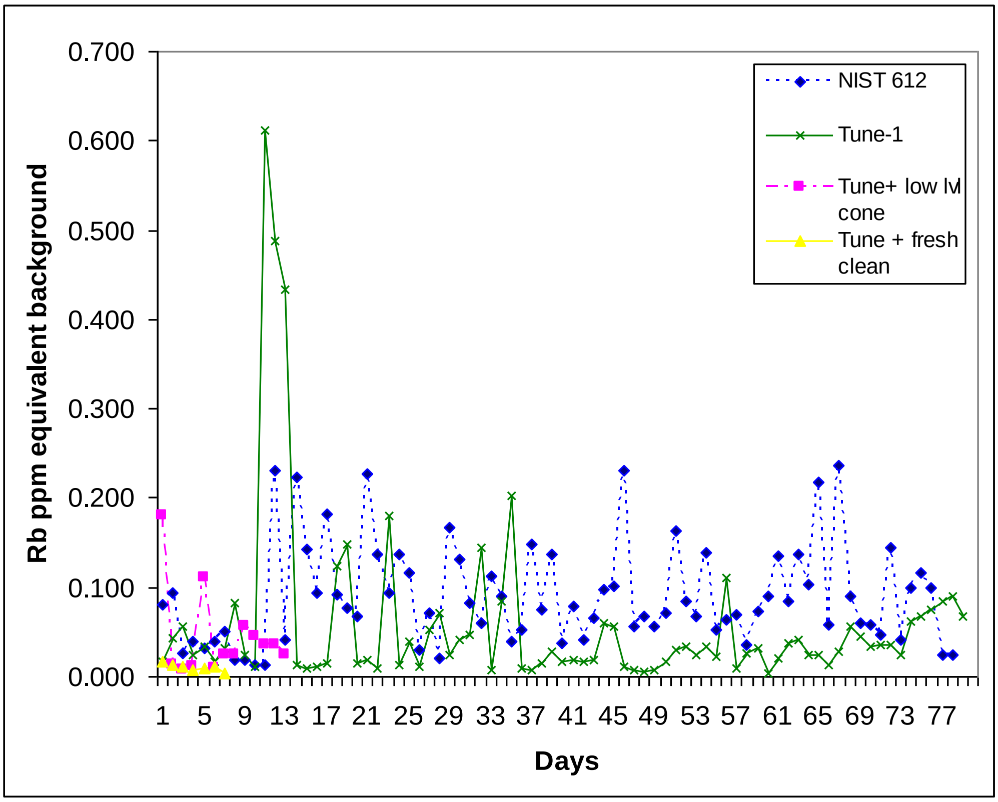

Figure 1c. Daily Rb backgrounds as µg/g equivalent for tuning done with NIST 612, Tune-1, and Tune-1 with low level and freshly cleaned sets of cones for low level alkali work.

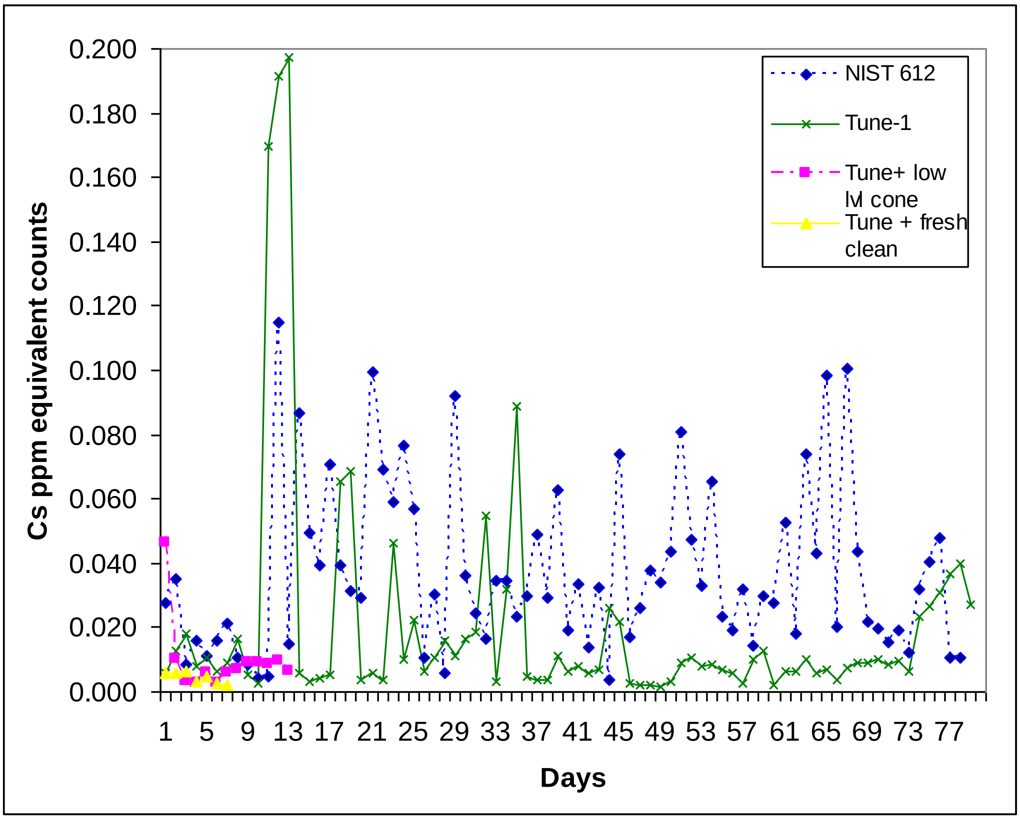

Figure 1d. Daily Cs backgrounds as µg/g equivalent for tuning done with NIST 612, Tune-1, and Tune-1 with low level and freshly cleaned sets of cones for low level alkali work.