

Data report for elemental analysis of IMPROVE samples collected during
October, November, December 2007
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SUMMARY

This report summarizes the quality assurance performed during elemental analysis of the IMPROVE samples collected in October, November and December of 2007. The elemental analyses include the determination of most elements with atomic numbers from 11 to 26 (Na-Fe) by energy dispersive X-ray fluorescence (XRF) with a Cu-anode system, most elements from 27 to 40 (Ni-Zr) and 82 (Pb) by XRF with a Mo-anode system, and hydrogen by Proton Elastic Scattering Analysis (PESA) with the Crocker cyclotron. The following data assessments and quality controls are obtained for all analyses:

- Concentration calibration and verification (calibration check)
- Energy calibration
- Laboratory replicates (reanalysis)
- Systems comparison
- Field blanks

Analysis details and key events are summarized below.

Oct 2007 samples were analyzed on Cu-Vac2 and Nov and Dec 2007 samples were analyzed on Cu-Vac1. All calibration checks performed on the Cu-Vac1, Cu-Vac2 and Mo systems during the analyses of the Oct-Dec 2007 samples met criteria.

Section 1. Overview of Elemental Analysis Systems

The elements Na and Mg (considered qualitative only) and Al to Fe are reported from two XRF systems with a Cu-anode grounded X-ray tube, Cu-Vac1 and Cu-Vac2. Both systems operate under vacuum. Default settings for sample analysis (20 kV, 10 mA for 1000sec/sample) were used for each system.

The elements Ni to Zr and Pb are reported from a similar system with a Mo-anode grounded X-ray tube operating in air. Samples were analyzed for 1000 seconds at 23 mA and 35 kV (default settings for sample analysis).

The PESA system operates under vacuum and uses a proton beam (4.5 MeV H⁺) from the Crocker cyclotron to quantify the concentration of hydrogen (H). Samples were analyzed for 15 seconds, with an average current value of approximately 50 nA collected on a Faraday cup.

Section 2. General Statistics of October, November and December 2007 data

XRF and PESA analyses were carried out on 1629 samples collected in Oct 2007, 1657 samples collected in Nov 2007 and 1602 samples collected in Dec 2007. All samples were analyzed between 1 February 2008 and 11 April 2008 on the Mo-anode XRF system, between 1 May 2008 and 24 May 2008 on Cu-Vac2, between 30 April 2008 and 11 July 2008 on Cu-Vac1, and on 6/6/08, 6/23-24/08 (Oct, Nov 2007 samples), and 7/1-2/08 (Dec 2007 samples) on the PESA system.

Table 1 summarizes the fourth quarter 2007 detection rates on the three systems, with rates for Sep 2007 included for comparison.

PESA					
Z	element	10-2007	11-2007	12-2007	9-2007
1	H	100%	100%	99%	100%

Cu-anode XRF					
Z	element	10-2007	11-2007	12-2007	9-2007
11	Na	65%	35%	32%	57%
12	Mg	50%	22%	16%	19%
13	Al	70%	76%	60%	26%
14	Si	99%	95%	86%	97%
15	P	6%	4%	3%	0%
16	S	100%	100%	100%	100%
17	Cl	24%	19%	23%	14%
19	K	100%	100%	100%	100%
20	Ca	100%	100%	100%	100%
22	Ti	100%	97%	89%	99%
23	V	88%	89%	67%	88%
24	Cr	52%	59%	48%	25%
25	Mn	97%	97%	90%	97%
26	Fe	100%	100%	100%	100%

Mo-anode XRF					
Z	element	10-2007	11-2007	12-2007	9-2007
28	Ni	55%	43%	54%	56%
29	Cu	94%	96%	89%	94%
30	Zn	100%	100%	100%	100%
33	As	41%	43%	35%	66%
34	Se	87%	85%	80%	90%
35	Br	100%	100%	100%	100%
37	Rb	75%	75%	68%	85%
38	Sr	93%	90%	87%	95%
40	Zr	44%	32%	27%	33%
82	Pb	98%	100%	96%	96%

Table 1. Percentage of cases in which the element was detected on each system. September 2007 data included for reference.

Section 3. **Quality Control**

3.1 Concentration calibration and verification (calibration checks)

Both XRF systems are calibrated with thin (6.3um) film foil standards produced by Micromatter. The standards used for samples from the second quarter of 2007 are listed below in Table 2. Because their concentrations are relatively high, standards are analyzed at reduced X-ray tube current (2.6 mA on XRF-Cu systems and 10mA on XRF-Mo system) to maintain counting live times comparable with those of actual IMPROVE samples.

Standard	Certified Elemental Concentrations +/- 5% ($\mu\text{g}/\text{cm}^2$)	Serial #
NaCl	Na: 19.1, Cl: 29.4	16518
MgF ₂	Mg: 20.6	16519
Al	Al: 40.7	16520
SiO	Si: 23.9	16521
GaP*	P: 4.5	16500
CuS _x	S: 12.9 Cu: 37.6	16523
KCl	Cl: 22.5 K: 24.9	16296
CaF ₂	Ca: 24.9	16525
Ti	Ti: 13.7	16504
V	V: 12.2	16505
Cr	Cr: 15.8	16507
Mn	Mn: 14.6	16506
Fe	Fe: 14.7	16508
Ni	Ni: 10.5	16509
Cu	Cu: 12.4	16510
ZnTe*	Zn: 5.2	16511
GaAs*	Ga: 8 As: 8.7	16512
Se	Se: 12.9	16513
CsBr	Br: 5.1	16514
RbI	Rb: 5.7	16515
SrF ₂	Sr: 10.9	16516
Pb	Pb La: 16 Pb Lb: 16	16517

Table 2. Micromatter standard foils used for all analyses. .Standards (*) with variable stoichiometry.

Spectra from the foil standards are processed and analyzed by the same software used for samples. The performance of all systems (shown in Figures 1-3) is monitored approximately weekly by monitoring the ratios of the system response at each calibration check to the response observed at the last calibration (based on the curve fit). If the ratios lie within the acceptance limits 0.9 – 1.1 for all quantitative elements, then the system is considered stable and the existing calibration factors continue to be used. Deviations beyond 10% trigger an investigation of the problem and possible system recalibration. After a recalibration, all samples analyzed since the last successful calibration verification are reanalyzed with the new calibration factors.

The analysis dates for each sample month are listed in the legends of Figures 1-3. September 2007 samples analysis dates are included for reference.

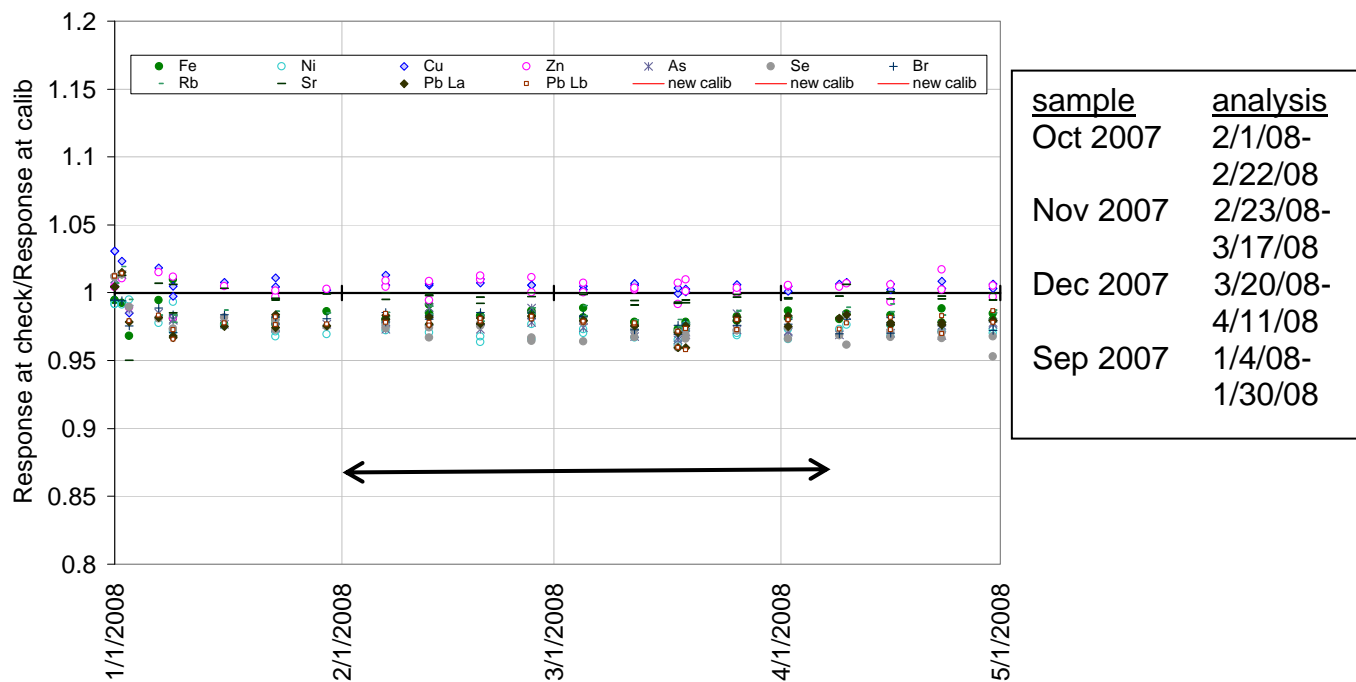


Figure 1. Mo XRF system performance chart based on standards

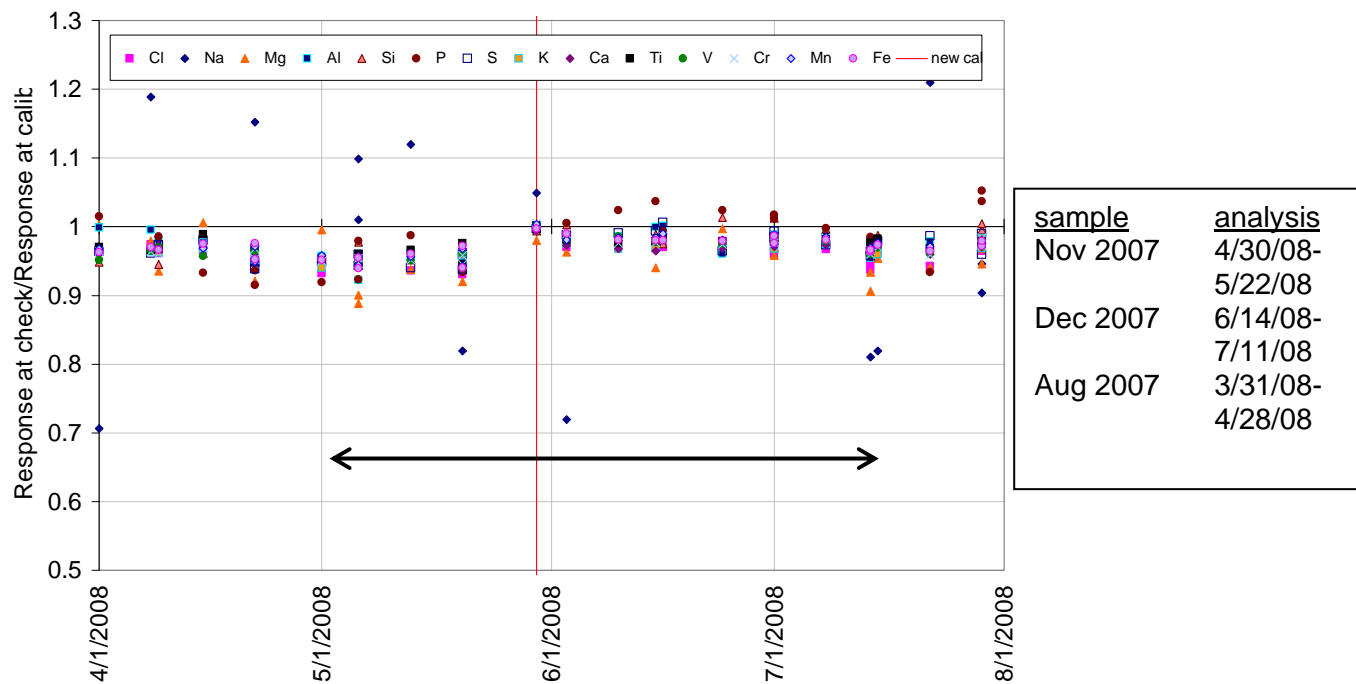


Figure 2. Cu-Vac1 XRF system performance chart based on standards.

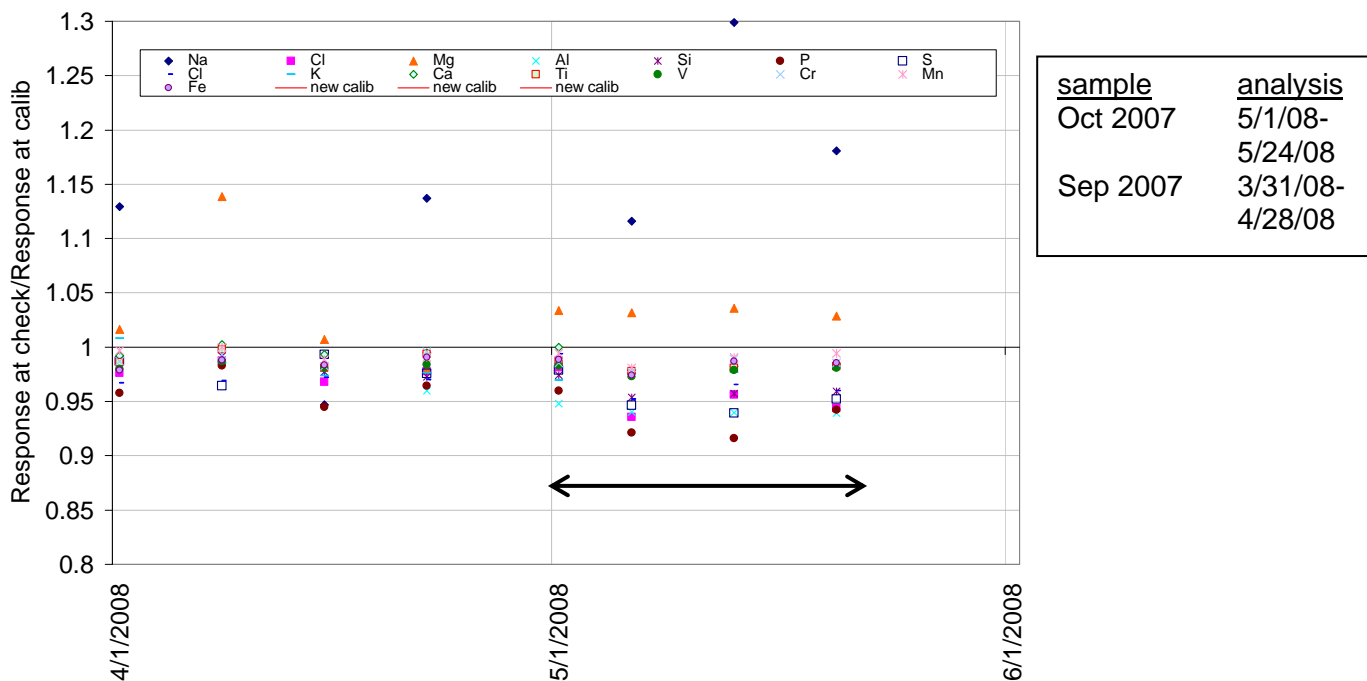


Figure 3. XRF Cu-Vac2 system performance chart based on standards.

None of the standards ratios exceeded acceptance limits during the analysis of the October-December 2007 samples on the Mo system. All calibration checks were within criteria.

The November and December 2007 samples were analyzed on the XRF Cu-Vac1 system and the October 2007 samples on the XRF Cu-Vac2 system. All weekly calibration checks for quantitative elements on the Cu-Vac1 and Cu-Vac2 systems were within criteria.

Eight Mylar foils were used for calibrations and calibration checks of the PESA system. Over the time the foil may become damaged and is replaced with a new one. The change is recorded and the calculated H concentration for each of the PESA standards is entered in the table. The current H concentrations are listed below:

PESA Standard	1	2	3	4	5	6	7	8
Calculated H amount (ug/cm ²)	20.61	20.61	14.45	14.45	20.28	20.28	34.58	34.58

As with XRF, the calibration factor is based on the average ratio of observed counts for the eight PESA standards to their calculated H concentration.

The PESA system is recalibrated at the beginning of every analytical session and re-tuned during sample analysis, because of variations in the ion source production, amplitude harmonics, and optics. The eight Mylar blanks used as calibration standards are reanalyzed approximately every 100-200 samples to verify the calibration throughout the session. If the ratio of reported to calculated concentrations for these standards drifts outside 5% range during an analysis run., the cyclotron is re-tuned, the system is recalibrated, and the samples are reanalyzed. Figure 4 shows calibration verifications and calibrations during the analysis of the Oct-Dec 2007 samples.

Mylar PESA standards
 October, November, December 2007 samples

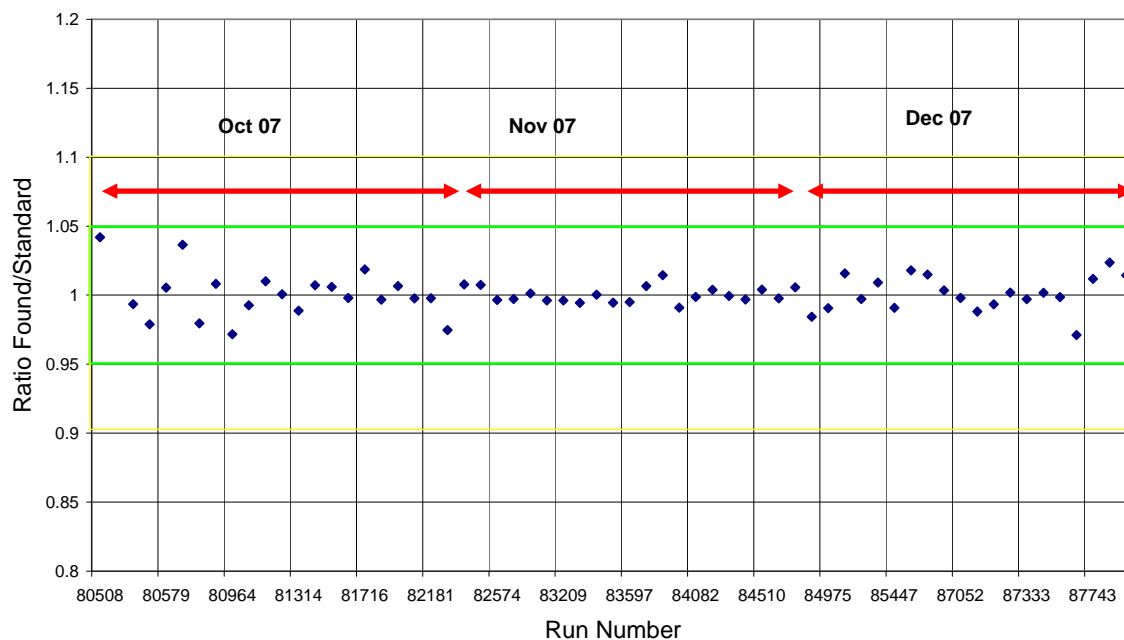


Figure 4. PESA standards for Oct-Dec 2007 samples

3.2 X-ray energy calibration

In addition to the peak counts associated with a known concentration (concentration calibration), the energy channel associated with a known fluorescence line must also be determined; this is the energy calibration. Energy calibrations were performed for the analyses of each sample month on Mo system and whenever determined necessary for Cu systems. The established relationships have a form

$$energy = intercept + slope * channel$$

The following energy calibration equations (in energy units of KeV) were used for the analysis:

	XRF-Cu1				change	XRF-Cu2				change	XRF-Mo				change
	intercept	slope	full scale	from Jun05		intercept	slope	full scale	from Oct05		intercept	slope	full scale	from Jun07	
Oct-07															
Nov-07	-3.80E-02	1.67E-02	8.493	0.03%											
Dec-07	-3.80E-02	1.67E-02	8.493	0.03%											

3.3 Reanalysis

The reproducibility of XRF and PESA data is tracked over time by reanalyzing selected sample filters. Different reanalysis protocols are used for the XRF and PESA reanalyses, reflecting the different impacts of their exciting beams on the Teflon filter substrate, as explained in previous reports.

Filters to be reanalyzed by PESA are selected from the previous quarter's X-module (collocated A-module) samples. During the analysis of Oct 2007 samples, 30 MEVEX, OLYMX, PMRFX filters from May 2007 were reanalyzed multiple times. For Nov 2007 samples, 28 SAFOX, SAMAX, TRCRX from June 2007 were reanalyzed, and multiple reanalyses for Dec 2007 samples were performed on 30 MEVEX, OLYMX, PMRFX filters from Jul 2007. Figure 5 compares the original and repeat analyses.

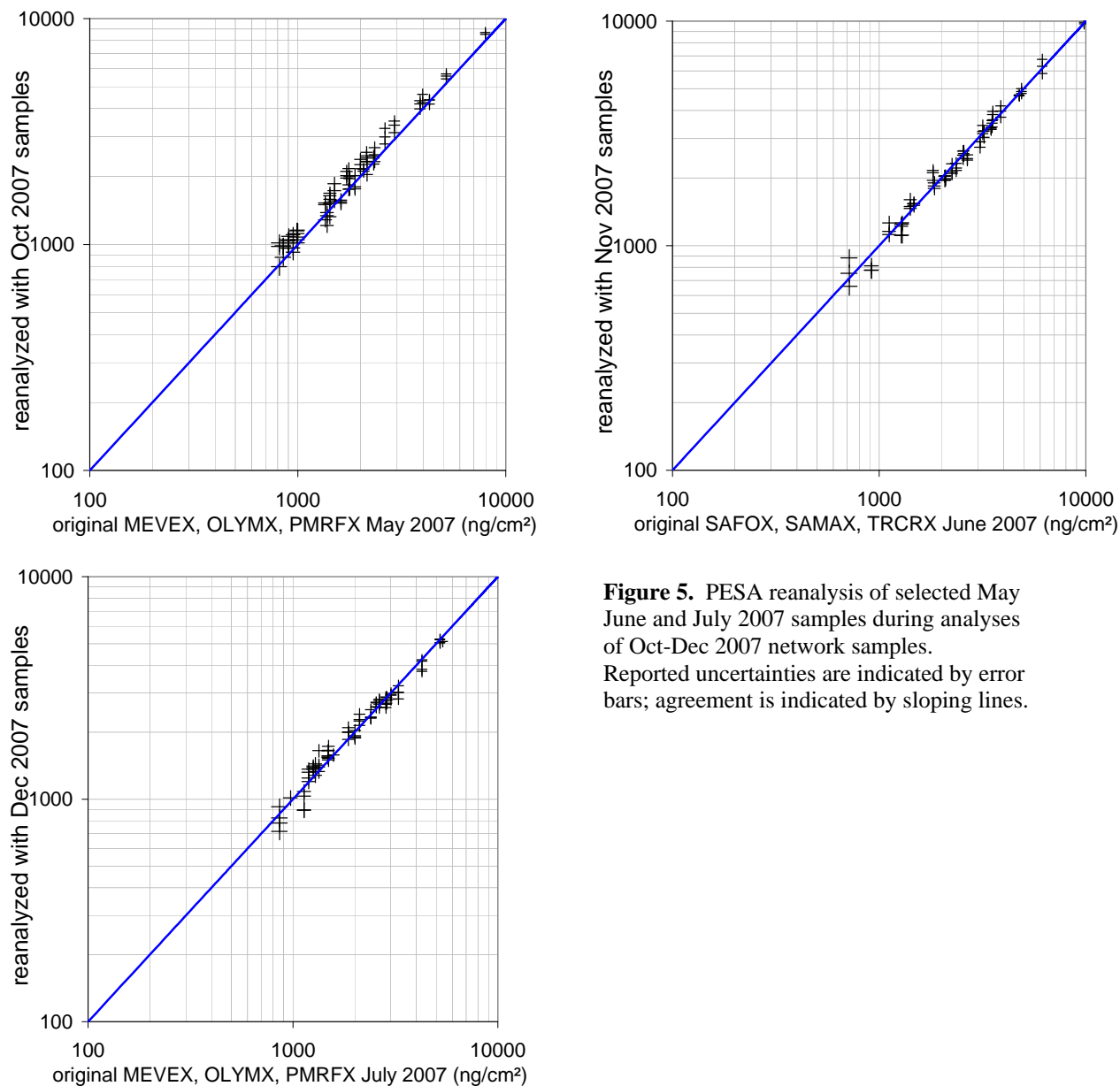


Figure 5. PESA reanalysis of selected May June and July 2007 samples during analyses of Oct-Dec 2007 network samples. Reported uncertainties are indicated by error bars; agreement is indicated by sloping lines.

XRF reanalyses are conducted repeatedly on a fixed collection of sample filters referred to as REANAL1 and REANAL2 and described in previous reports. The trays were reanalyzed approximately monthly on the systems during 2007 analyses of Oct-Dec 2007 samples. All results are summarized in the figures 6-8 below.

For all systems the mean loadings calculated based on approximately 12 consecutive runs (about a year of data during which calibrations have been based on a fixed collection of standard reference foils) are used as a benchmark for comparison. As described in previous reports, the average ratio of observed deviations from all samples (from the mean) to reported measured uncertainties for each of four selected elements (for Mo: Fe, Cu,

Zn and Br and for Cu: Si, S, Ca and Fe) is calculated and shown on vertical axis. Horizontal continuous and dotted red lines serve as proposed action and warning limits.

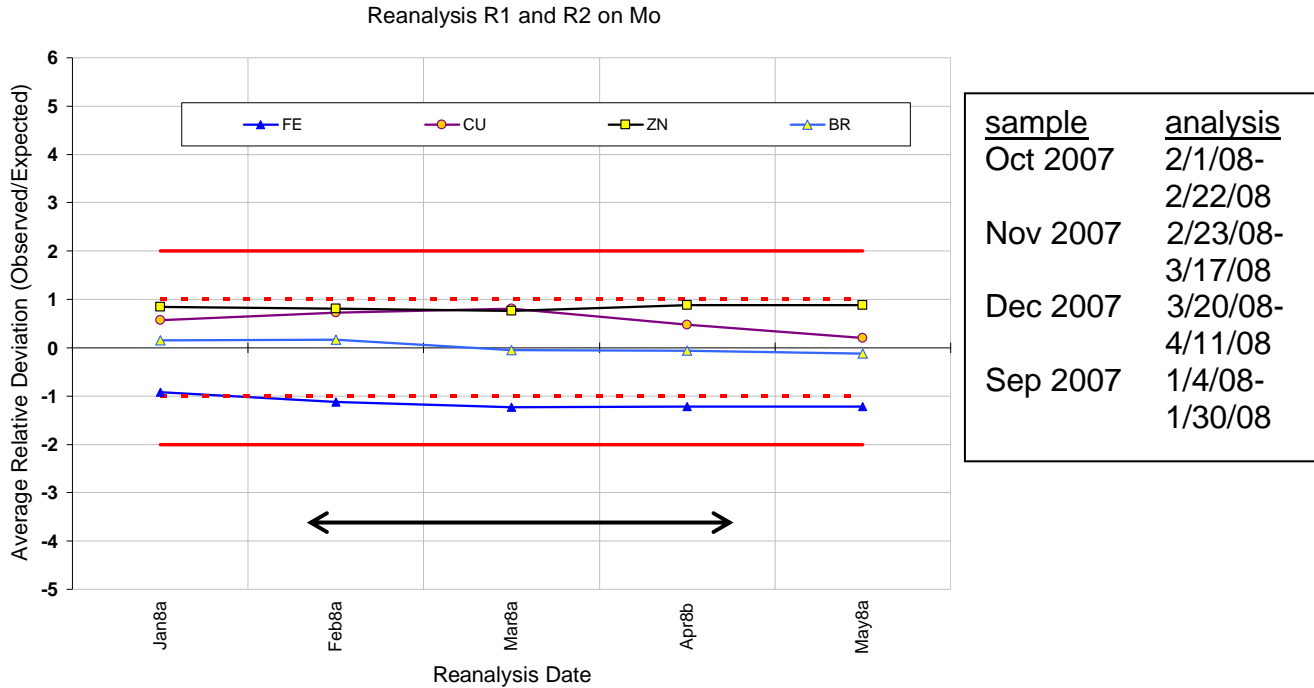


Figure 6. Reanalyses of REANAL1 and REANAL2 samples on XRF-Mo system. Horizontal arrow indicates when Oct-Dec 2007 network samples were analyzed.

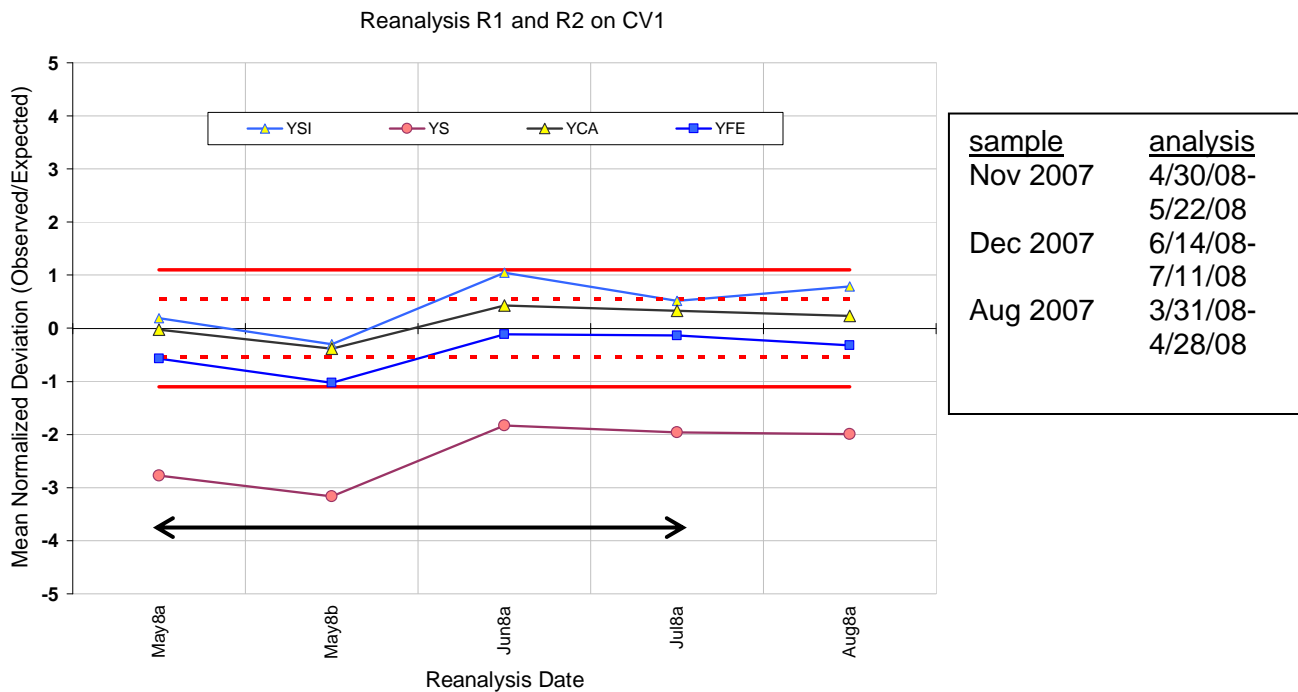


Figure 7. Reanalyses of REANAL1 and REANAL2 samples on XRF-Cu1 system. Horizontal arrow indicates when Nov, Dec 2007 network samples were analyzed.

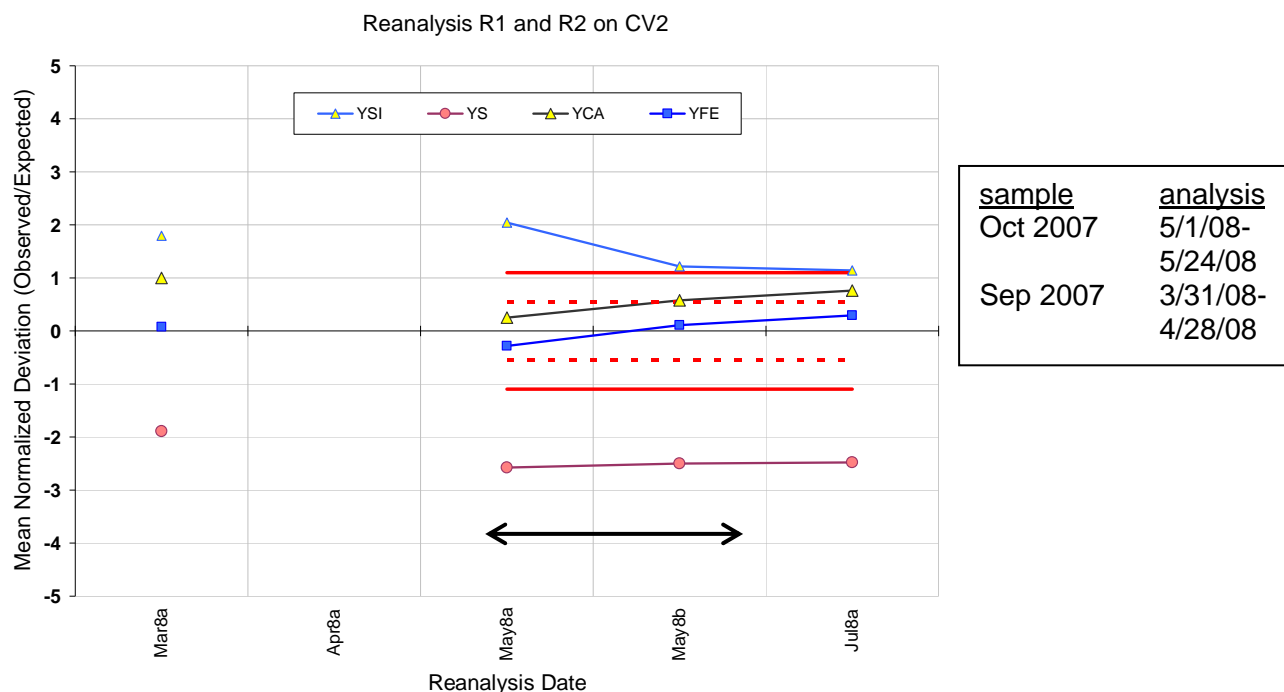


Figure 8. Reanalyses of REANAL1 and REANAL2 samples on XRF-Cu2 system. Horizontal arrow indicates when Oct 2007 network samples were analyzed.

3.4 Systems comparison

Additional comparison between selected elements measured independently by the Cu and Mo systems is performed for each data set. The elements Calcium and Iron are reported from the Cu system (Cu-Vac1 or Cu-Vac2) but are also quantified by the Mo system. Figures 9 and 10 compare the two measurements of these two elements for the samples from Oct-Dec 2007. Reported uncertainties are shown as bars for each sample, and reported MDL's are indicated by green and pink points for both systems. The increase in analytical uncertainty closer to the MDL's can be observed for all cases.

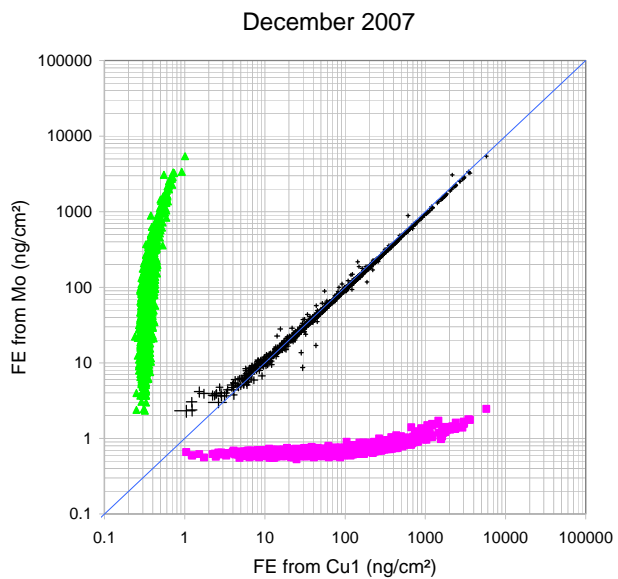
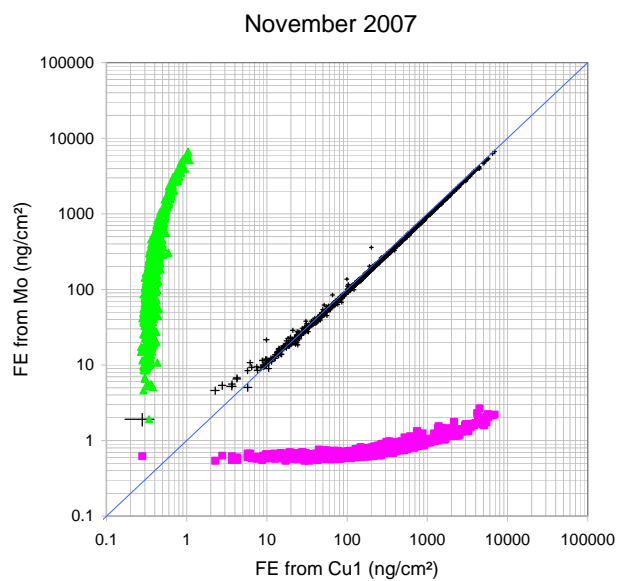
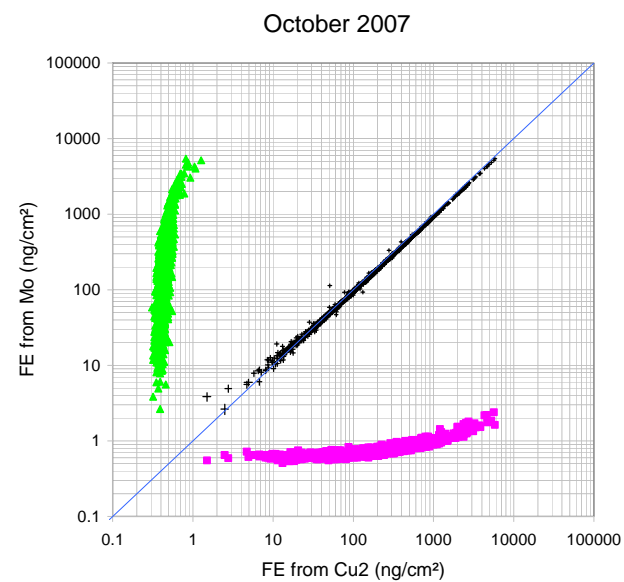


Figure 9. Comparison of Iron data obtained independently from Cu (x-axis) and Mo (y-axis) systems. Cu1 refers to Cu-Vac1 and Cu2 to Cu-Vac2.

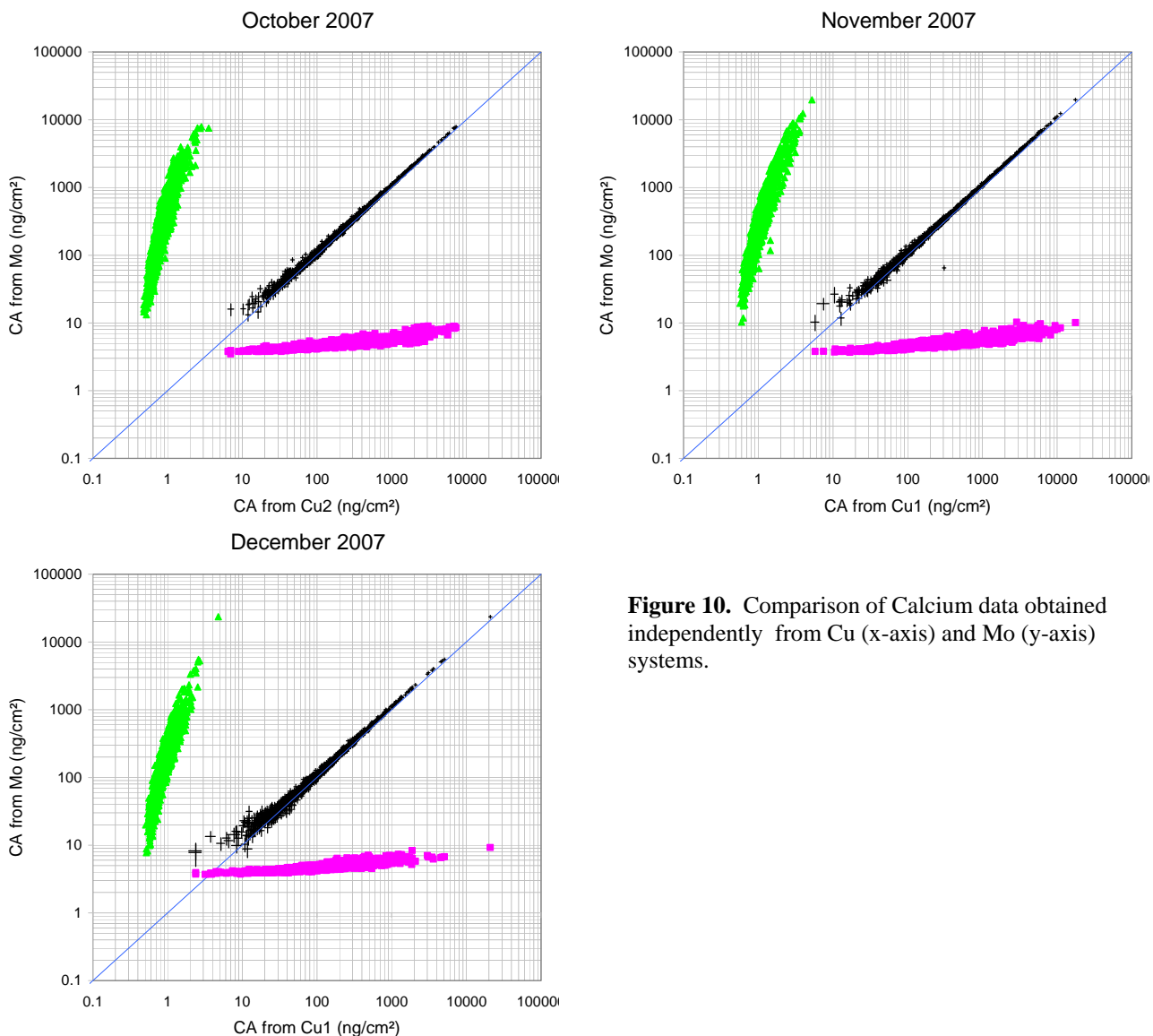


Figure 10. Comparison of Calcium data obtained independently from Cu (x-axis) and Mo (y-axis) systems.

Calcium and iron determinations by the Mo system contain more uncertainty than those from the Cu systems, and are accordingly not used to report concentrations. Their value in these system comparisons is the additional qualitative check they provide on both systems' performance.

3.5 Field blanks

Eleven field blanks for October 2007, 32 field blanks for November 2007 and 17 field blanks for December 2007 samples were exposed at selected sites on selected sampling events. The field blanks were analyzed on both, XRF-Mo and Cu-Vac1 or Cu-Vac2 systems. The Cu-anode system used for analysis of the field blanks was the same system used for the corresponding samples.

As in previous reports, 95th, 90th and 75th percentile field blank loadings are shown for each system in the tables below. They are given as percentiles of well measured network sample loadings during October, November and December 2007. Loadings are considered well measured when their uncertainties are less than 10%. Thus, the 95th percentile field blank loading for Fe (Oct 2007 samples) was at or above about 3.1% of all well measured sample loadings on Cu system (5.4% on Mo system).

Cu anode

Oct 2007	Na	Mg	Al	Si	P	S	Cl	K	Ca	Ti	V	Cr	Mn	Fe
95 %ile	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	2.0%	0.0%	0.0%	0.0%	0.1%	3.1%
90 %ile	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	1.8%	0.0%	0.0%	0.0%	0.0%	2.7%
75 %ile	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.9%	0.0%	0.0%	0.0%	0.0%	0.9%
Nov 2007	Na	Mg	Al	Si	P	S	Cl	K	Ca	Ti	V	Cr	Mn	Fe
95 %ile	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.2%	0.0%	0.0%	0.0%	0.0%	4.3%
90 %ile	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.2%	0.0%	0.0%	0.0%	0.0%	0.4%
75 %ile	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.2%
Dec 2007	Na	Mg	Al	Si	P	S	Cl	K	Ca	Ti	V	Cr	Mn	Fe
95 %ile	0.0%	0.0%	0.0%	0.1%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	4.3%
90 %ile	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	1.3%
75 %ile	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.2%

Mo anode

Oct 2007	Fe	Ni	Cu	Zn	As	Pb	Se	Br	Rb	Sr	Zr
95 %ile	5.4%	0.0%	0.1%	3.2%	0.0%	0.6%	0.0%	0.0%	0.0%	0.0%	0.0%
90 %ile	5.2%	0.0%	0.0%	0.1%	0.0%	0.1%	0.0%	0.0%	0.0%	0.0%	0.0%
75 %ile	0.9%	0.0%	0.0%	0.0%	0.0%	0.1%	0.0%	0.0%	0.0%	0.0%	0.0%
Nov 2007	Fe	Ni	Cu	Zn	As	Pb	Se	Br	Rb	Sr	Zr
95 %ile	10.3%	0.0%	0.0%	32.0%	0.0%	1.2%	0.0%	0.0%	0.0%	0.0%	0.0%
90 %ile	1.0%	0.0%	0.0%	19.0%	0.0%	0.8%	0.0%	0.0%	0.0%	0.0%	0.0%
75 %ile	0.3%	0.0%	0.0%	7.9%	0.0%	0.5%	0.0%	0.0%	0.0%	0.0%	0.0%
Dec 2007	Fe	Ni	Cu	Zn	As	Pb	Se	Br	Rb	Sr	Zr
95 %ile	5.4%	0.0%	0.0%	40.5%	0.0%	1.7%	0.0%	0.0%	0.0%	0.0%	0.0%
90 %ile	2.7%	0.0%	0.0%	20.6%	0.0%	1.2%	0.0%	0.0%	0.0%	0.0%	0.0%
75 %ile	0.1%	0.0%	0.0%	3.8%	0.0%	0.4%	0.0%	0.0%	0.0%	0.0%	0.0%

Field blank loadings are negligible compared to samples for all elements except for Zn (Nov and Dec 2007), as observed previously.