Data report for elemental analysis of IMPROVE samples collected during January, February, March 2009
UC Davis – Submitted June 18, 2010

SUMMARY

This report summarizes the quality assurance performed during elemental analysis of the IMPROVE samples collected in January, February and March of 2009. 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.

In this report, new control charts are introduced for monitoring the performance and long-term stability of the systems independently of calibrations.

January, February and March 2009 samples were analyzed on Cu-Vac2. All calibration checks performed on the Cu-Vac2 and Mo systems during the analyses of Jan-Mar 2009 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 January, February and March 2009 data

XRF and PESA analyses were carried out on 1821 samples collected in January 2009, 1516 samples collected in February 2009 and 1711 samples collected in March 2009. All samples were analyzed between 15 May 2009 and 30 July 2009 on the Mo-anode XRF system, between 23 April 2009 and 16 July 2009 on Cu-Vac2, and on 6/10-12/09 (January 2009 samples), 6/30/09-7/2/09 (February 2009 samples), and 9/10-11/09 to 9/24-25/09 (March 2009 samples) on the PESA system.

Table 1 summarizes the first quarter 2009 detection rates on the three systems, with rates for December 2008 included for comparison.

PESA					
Z	element	1-2009	2-2009	3-2009	12-2008
1	H	99%	100%	100%	100%

Cu-anode XRF					
Z	element	1-2009	2-2009	3-2009	12-2008
11	Na	57%	70%	75%	67%
12	Mg	38%	35%	59%	44%
13	Al	74%	76%	88%	71%
14	Si	98%	99%	100%	98%
15	P	2%	3%	1%	2%
16	S	100%	100%	100%	100%
17	Cl	30%	32%	31%	40%
19	K	100%	100%	100%	100%
20	Ca	100%	100%	100%	100%
22	Ti	98%	99%	99%	98%
23	V	81%	86%	91%	80%
24	Cr	62%	68%	64%	49%
25	Mn	93%	97%	98%	94%
26	Fe	100%	100%	100%	100%

Mo-anode XRF					
Z	element	1-2009	2-2009	3-2009	12-2008
28	Ni	41%	46%	40%	58%
29	Cu	88%	83%	80%	88%
30	Zn	98%	99%	98%	100%
33	As	59%	64%	60%	30%
34	Se	85%	76%	79%	77%
35	Br	99%	100%	100%	100%
37	Rb	59%	78%	78%	70%
38	Sr	82%	89%	98%	91%
40	Zr	29%	35%	46%	36%
82	Pb	89%	83%	97%	98%

Table 1. Percentage of cases in which the element was detected on each system.
December 2008 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 first quarter of 2009 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. Due to some damage, the NaCl 16518 and CuSx 16523 standards were replaced on June 9, 2009 (Cu) and June 10, 2009 (Mo) with NaCl 17982 and CuSx 17977.

Standard	Certified Elemental Concentrations +/- 5% ($\mu g/cm^2$)	Serial #
NaCl	Na:19.1, Cl:29.4 Na:18, Cl:27.7	16518/17982
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 S:12.5 Cu:44.1	16523/17977
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 1a and 2a) was monitored approximately weekly by monitoring the ratios of the system response at each calibration check to the response observed at the last calibration. 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.

In addition, to highlight the performance and long-term stability of the physical system independent of calibration, the performance of all systems monitored by weekly checks with reference foils is tracked over time with normalized counts. A normalized count reading is the count rate (RACE counts per live time) per charge rate (charge per real time) obtained for any given foil. New control charts generated by the calibration checks show the series of weekly normalized counts on a logarithmic scale for all elements for both systems (Figures 1b and 2b). Different elements generally require separate charts with different count-scales to provide adequate visual resolution. Therefore, the control charts of selected elements, Fe, Cu, Zn and Pb for the Mo system and Si, S, Ca and Fe for the Cu system, with bands assigned to +/-3% (dotted lines) and +/-5% (solid lines) are presented as well (Fig 1c and Fig 2c).

The analysis dates for each sample month are listed in the legends of Figures 1-2. December 2008 samples analysis dates are included for reference.

A series of "improvements" and regular maintenance was performed on the Mo system starting in April 2009. That included refurbishing the detector, cleaning the detector window and, at the beginning of May 2009, installing additional Mo and Delrin shielding to the upper portion of the x-ray tube to reduce coherent scattering from fluorescence of metals in the tube's exterior.
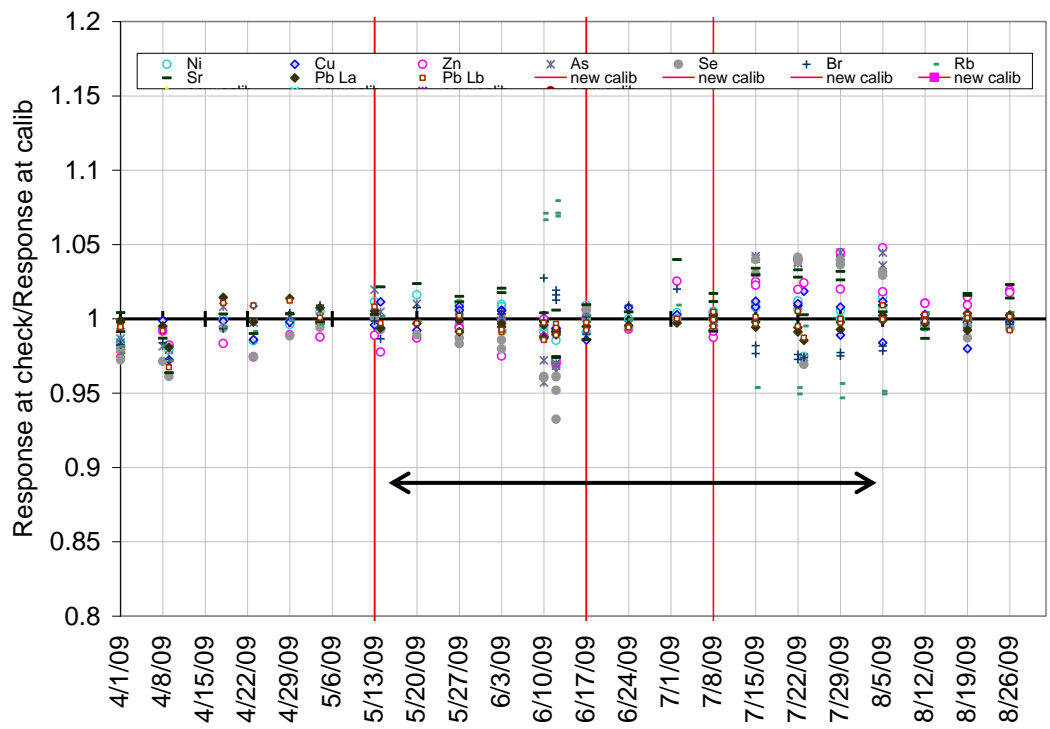
sample	analysis
Jan 2009	5/15/09-6/8/09
Feb 2009	6/11/09-7/1/09
Mar 2009	7/3/09-7/30/09
Dec 2008	4/10/09-5/3/09

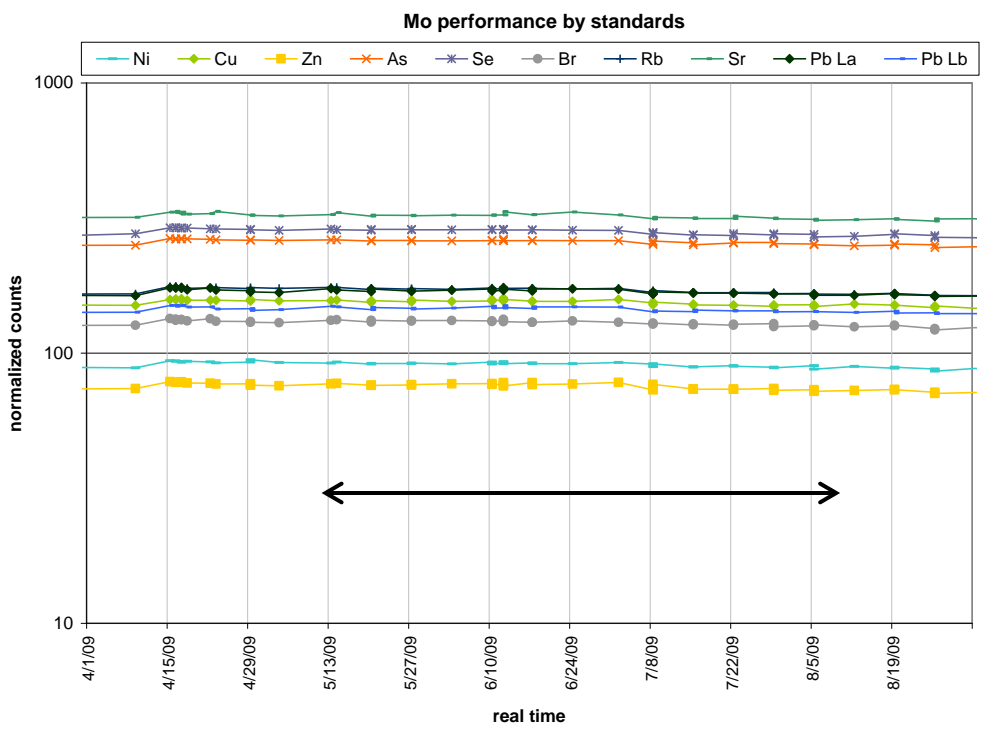**Figure 1A.** Mo XRF system performance chart referenced to last calibration.

Figure 1B. Mo XRF system performance chart based on normalized counts.
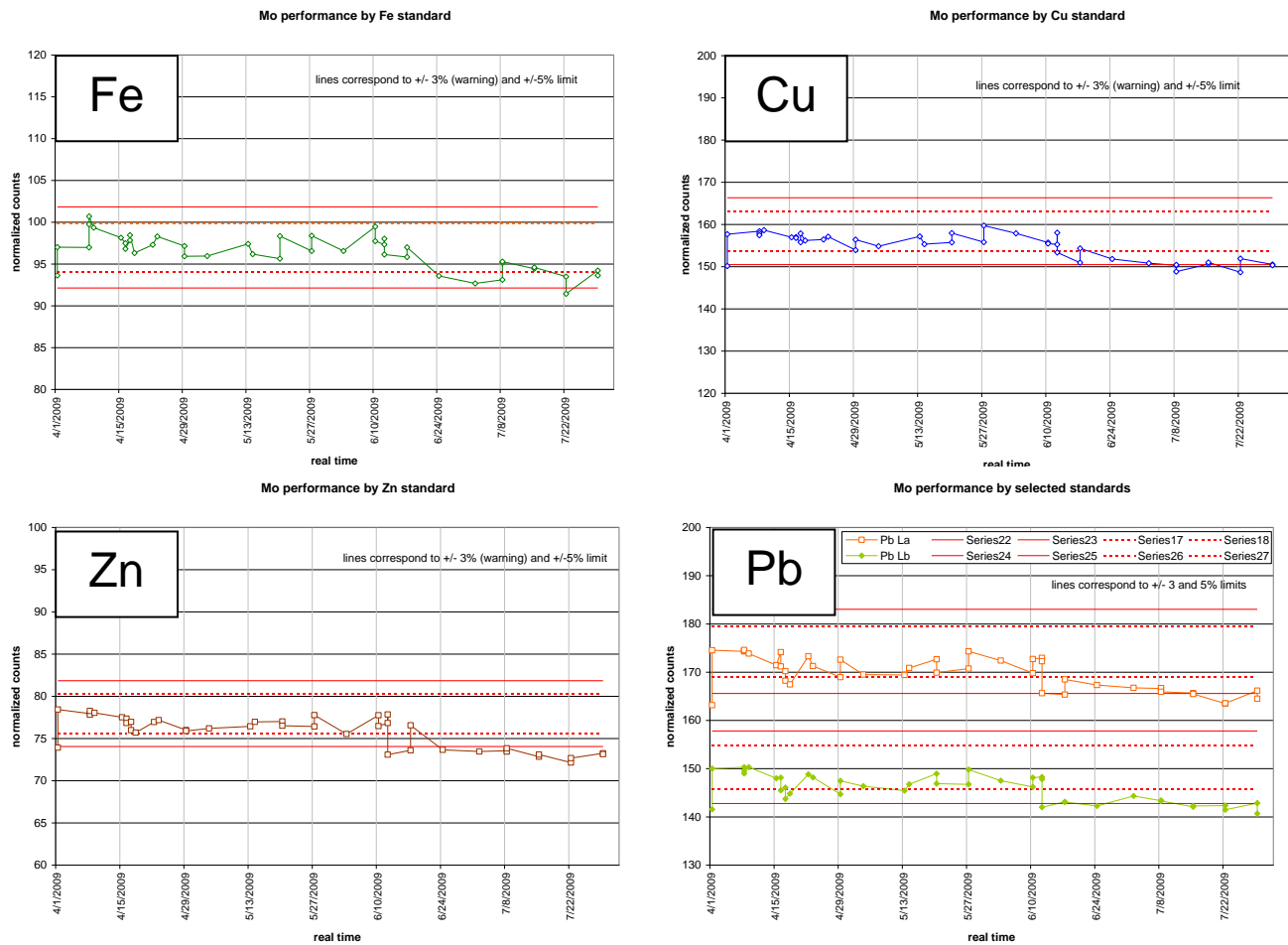
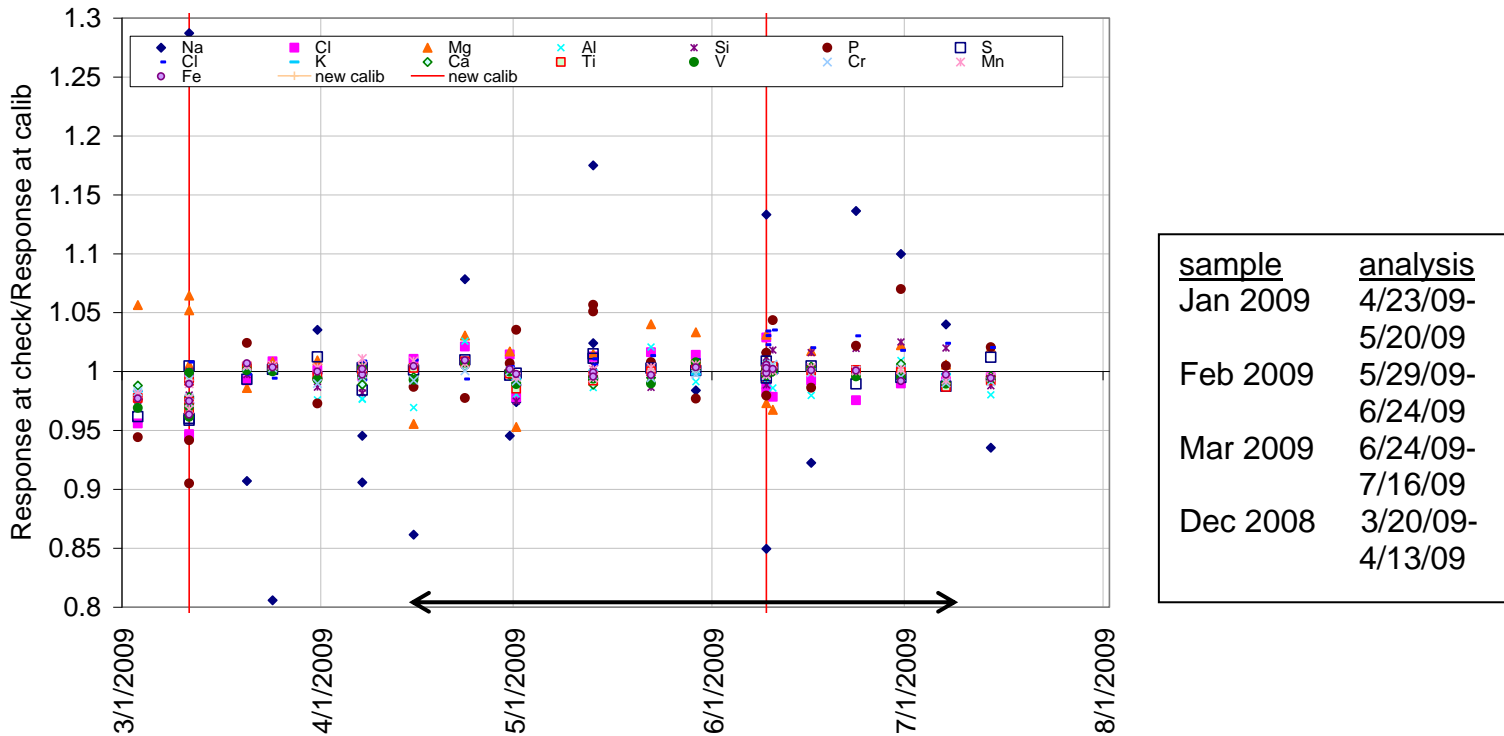**Figure 1C.**   Mo XRF system performance charts based on normalized count for selected elements, Fe, Cu, Zn and Pb.

Figure 2A. Cu-Vac2 XRF system performance chart referenced to last calibration. Vertical red lines indicate system recalibration.
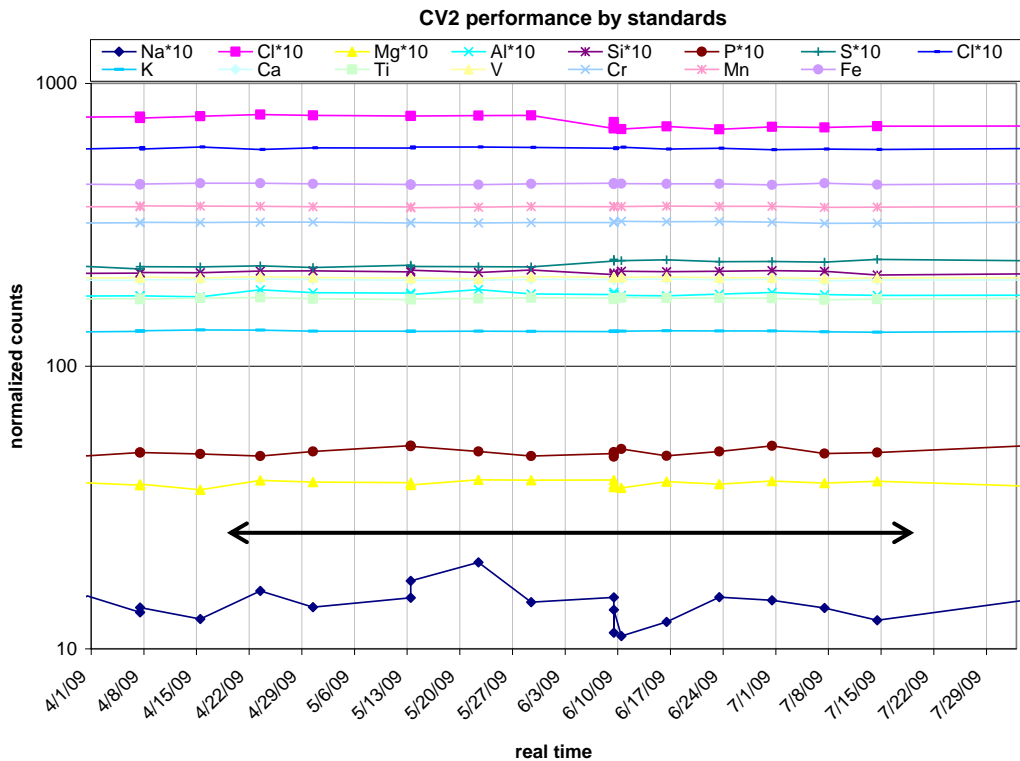
CV2 performance by standards

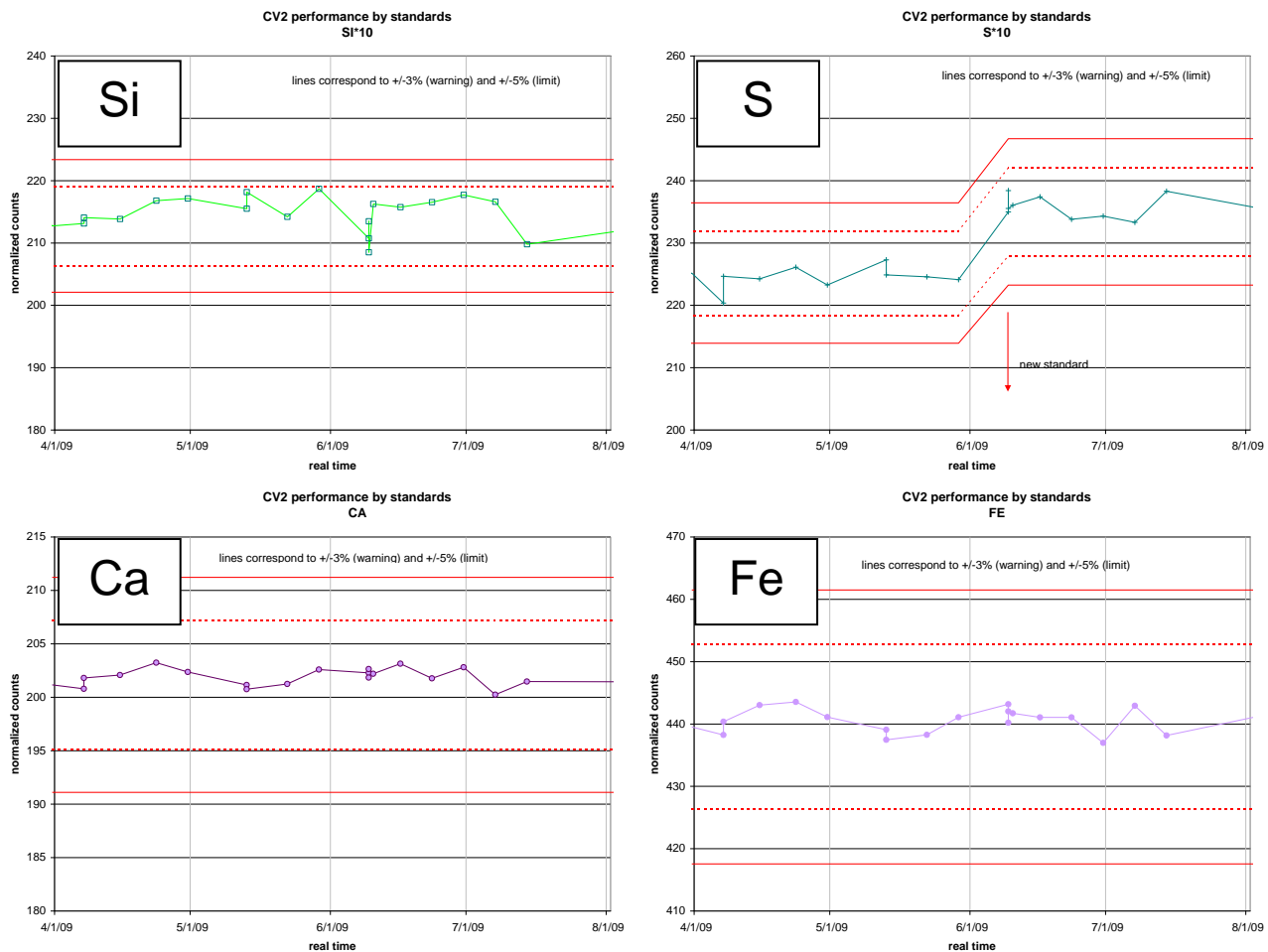**Figure 2B.** Cu Vac2 system performance chart based on normalized counts.

Figure 2C. Cu Vac2 system performance charts based on normalized count for selected elements: Si, S, Ca and Fe.

None of the standards ratios exceeded 0.9-1.1 acceptance limits during the analysis of Jan-Mar 2009 samples on Mo and Cu-Vac2 systems. Nevertheless, there were 3 recalibrations of the Mo system, in May 2009 due to detector cleaning and installation of the shielding, in June 2009 due to replacement of the selected standards and in July 2009 due to adjustments done to detector collimator. The June calibration was applied to the January and February samples and June and first July reanalyses (May reanalysis used May calibration), and the July calibration was applied to the March samples and second July reanalyses. Also, there were two recalibrations of the CuVac2 system performed in March 2009 and June 2009, due to cleaning of the detector window and the replacement of the selected standards (NaCl and CuSx), respectively. The March calibration was applied to the January samples and May reanalyses, and the June calibration was applied to the February-March samples and July-August reanalyses.

Eight Mylar foils were used for calibrations and calibration checks of the PESA system. Over the time the foil may become damaged and 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/cm2)	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 3 shows calibration verifications and calibrations during the analysis of the Jan-Mar 2009 samples.
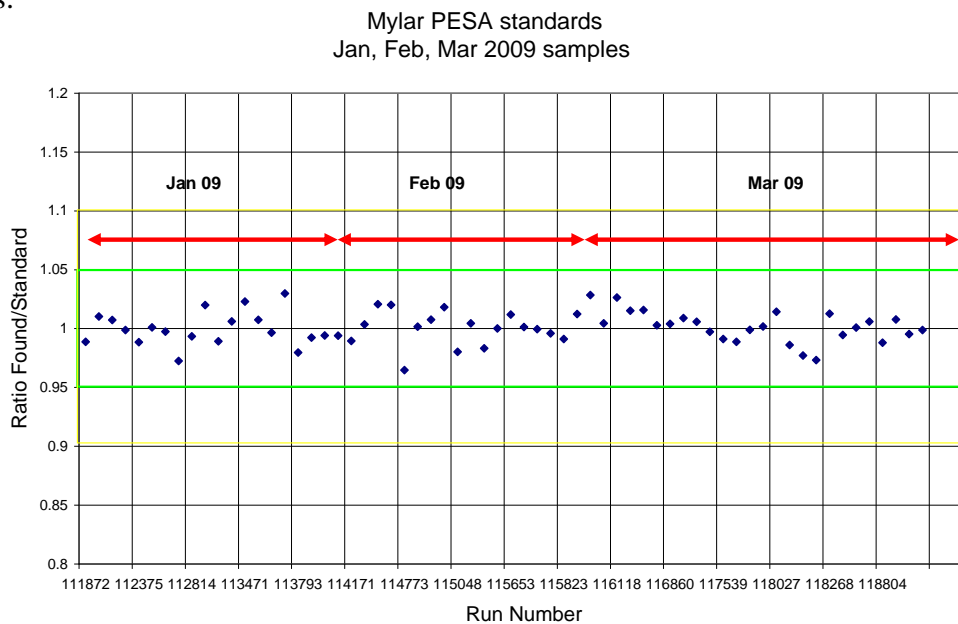

Figure 3. PESA standards for Jan-Mar 2009 samples

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*
Jan-09					-4.01E-02	1.71E-02	8.739	*-0.13%*	-6.68E-02	3.69E-02	18.816	*0.04%*
Feb-09					-4.01E-02	1.71E-02	8.739	*-0.13%*	-6.84E-02	3.69E-02	18.816	*0.04%*
Mar-09					-4.01E-02	1.71E-02	8.739	*-0.13%*	-5.81E-02	3.69E-02	18.835	*0.14%*

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 Jan 2009 samples, SAFOX, SAMAX and TRCRX filters from Aug 2008 were reanalyzed multiple times. For Feb 2009 samples, MEVEX, SAFOX and PMRFX filters from Sep 2008 were reanalyzed, and multiple reanalyses for Mar 2009 samples were performed on MEVEX, SAFOX and PMRFX filters from Oct 2008. Figure 4 compares the original and repeat analyses.
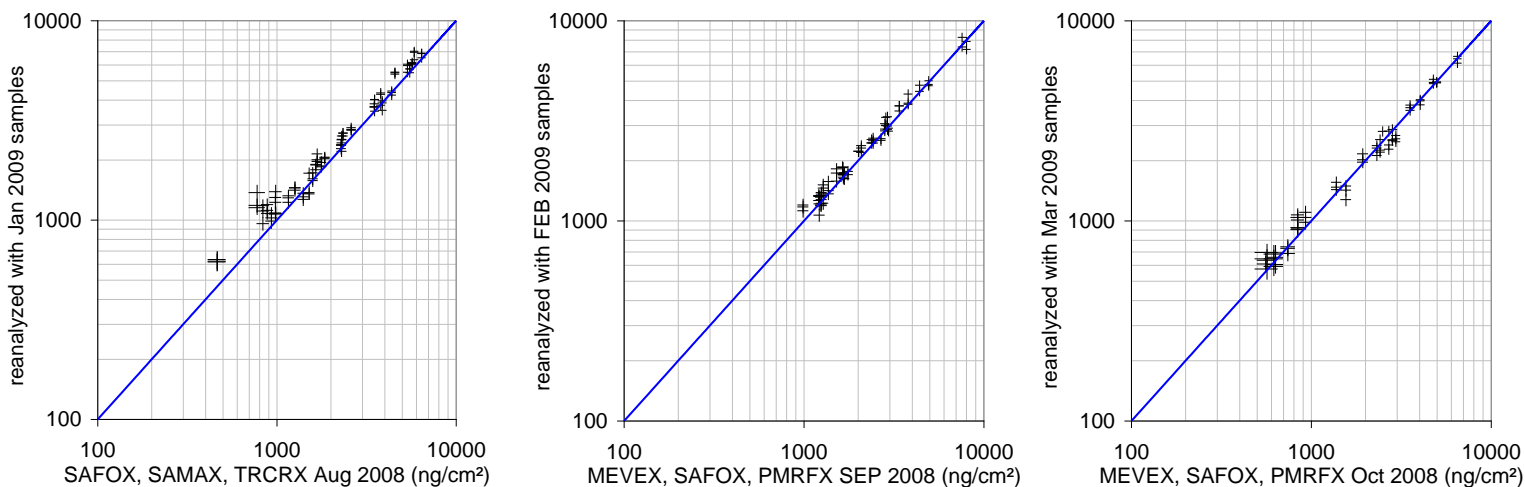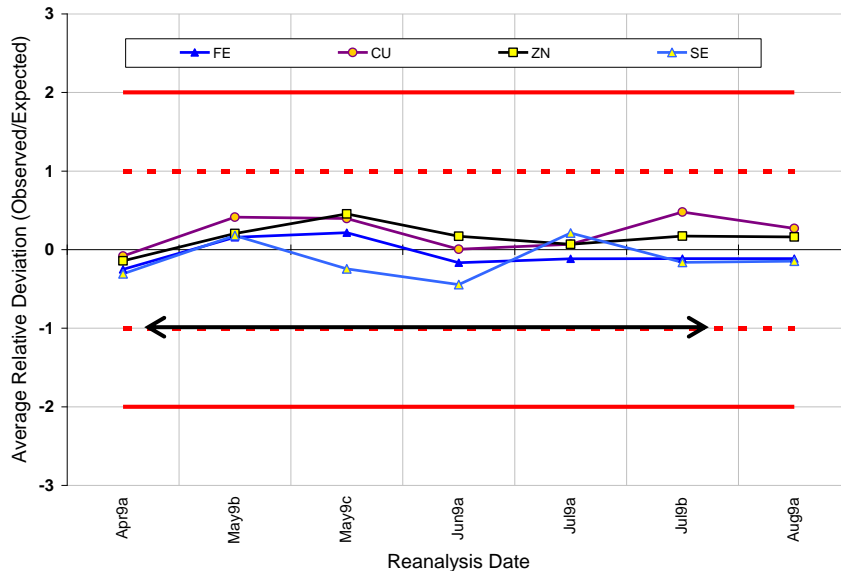

Figure 4. PESA reanalysis of selected Aug, Sep, Oct 2008 samples during analyses of Jan-Mar 2009 network samples.

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 Mo, and Cu-Vac2 systems during analyses of the Jan-Mar 2009 samples. All results are summarized in the Figures 5 and 6 below.

For all the systems, the mean loadings calculated based on approximately 12 consecutive runs (about a year of data during which calibrations have been based on a curve fit approach) are used as a benchmark for comparison. The average ratio of observed deviations from all samples (from the mean) to reported measured uncertainties for each element is calculated and shown on the y-axis. Figures 5-6 highlight the reanalysis results for four elements selected for each system, Fe, Cu, Zn and Se (descending trends in Br shown previously suggest volatility) for Mo and Si, S, Ca and Fe for Cu. These major elements serve here as general indicators of system performance and the horizontal continuous and dotted red lines shown are intended to provide proposed action and warning limits, respectively. They are based on historical systems' performance only and may need to be reevaluated if any operational conditions change. The horizontal black arrows indicate the periods of analysis of the first quarter 2009 samples.
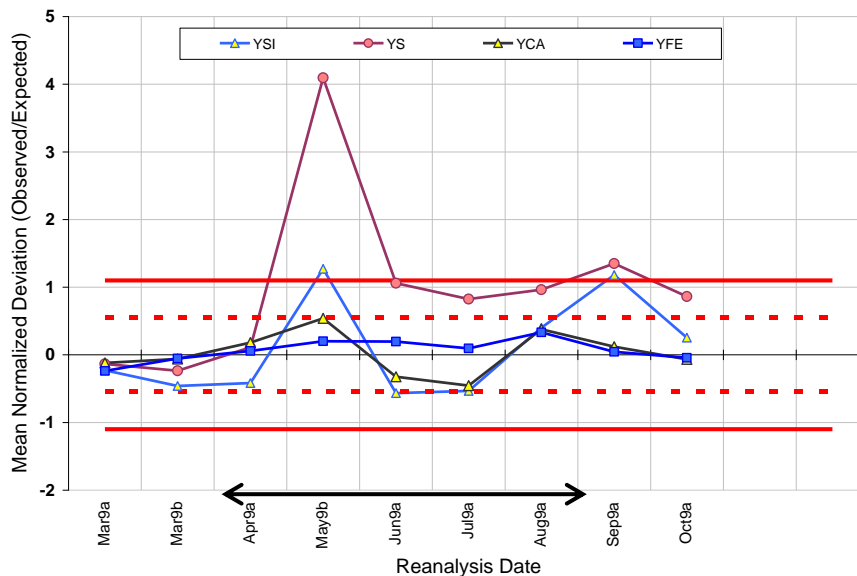

Figure 5. Reanalyses of REANAL1 and REANAL2 samples on XRF-Mo system. Horizontal arrow indicates when Jan-Mar 2009 network samples were analyzed.

Figure 6. Reanalyses of REANAL1 and REANAL2 samples on XRF-Cu2 system. . Horizontal arrow indicates when Jan-Mar 2009 network samples were analyzed.

The high deviation observed in Figure 6 for S in May 2009 is wholly due to the different calibration used only in that month. January 2009 samples are also reported with this calibration. The same curve fitting protocol was used for each calibration performed throughout the period depicted in Figure 6, but the curves associated with

individual calibrations can vary. The elevated reanalysis values are consistent with the 14% difference between calibration coefficients for S applied to the April and May 2009 reanalysis. The medians of $3S/SO_4$ ratios (Figure 7) also show elevated values for corresponding January 2009 samples, about 14% compared to Dec 2008 samples.
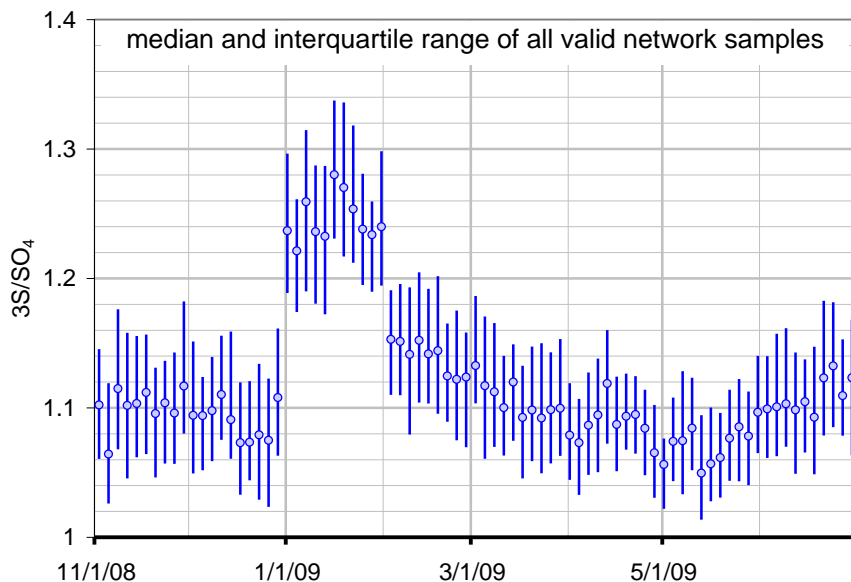

Figure 7. Median ratio of $3S/SO_4$ in network for each sample day

The implementation of new CuSx standard yield higher Cu system response for Sulfur and the new calibration followed (February and March 2009 samples). The Sulfur deviations observed in Figure 6 from June 2009 (when the calibration was applied) are consistently about 5-7% higher. Again, this seems to follow the differences in applied calibration tables, for Sulfur about 5-6%.

The necessary steps are being taken to assure that new calibrations are performed only when absolutely necessary (current, more formal, criteria) and that the calibration tables are developed in the timely matter to assure the processing of the reanalysis samples in "real time".

System 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 8 and 9 compare the two measurements of these two elements for the samples from Jan-Mar 2009. 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.
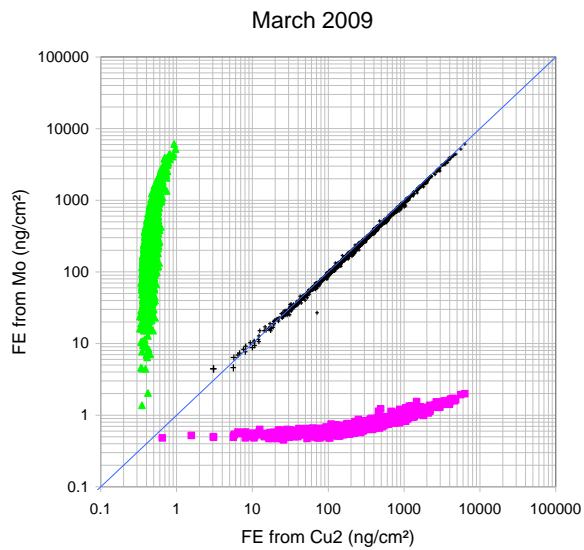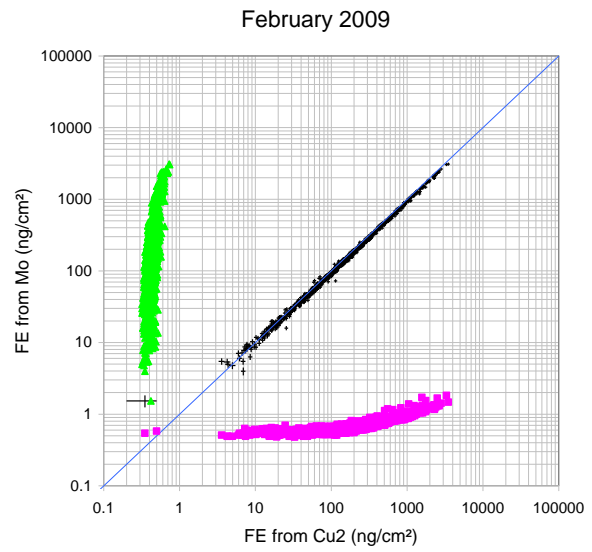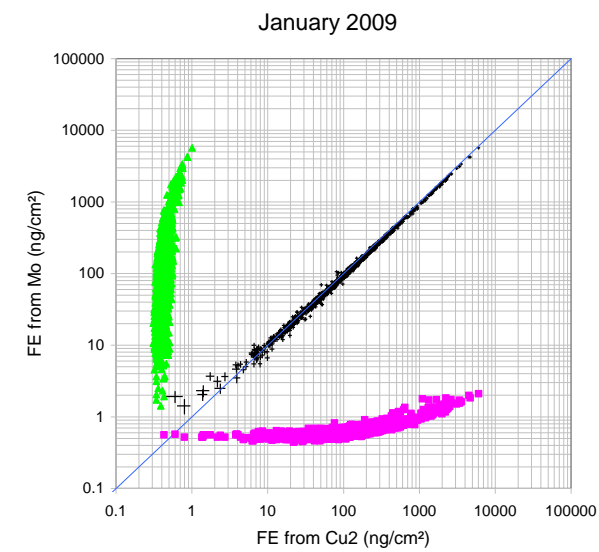
January 2009

February 2009

March 2009

Figure 8. Comparison of Iron data obtained independently from Cu (x-axis) and Mo (y-axis) systems.
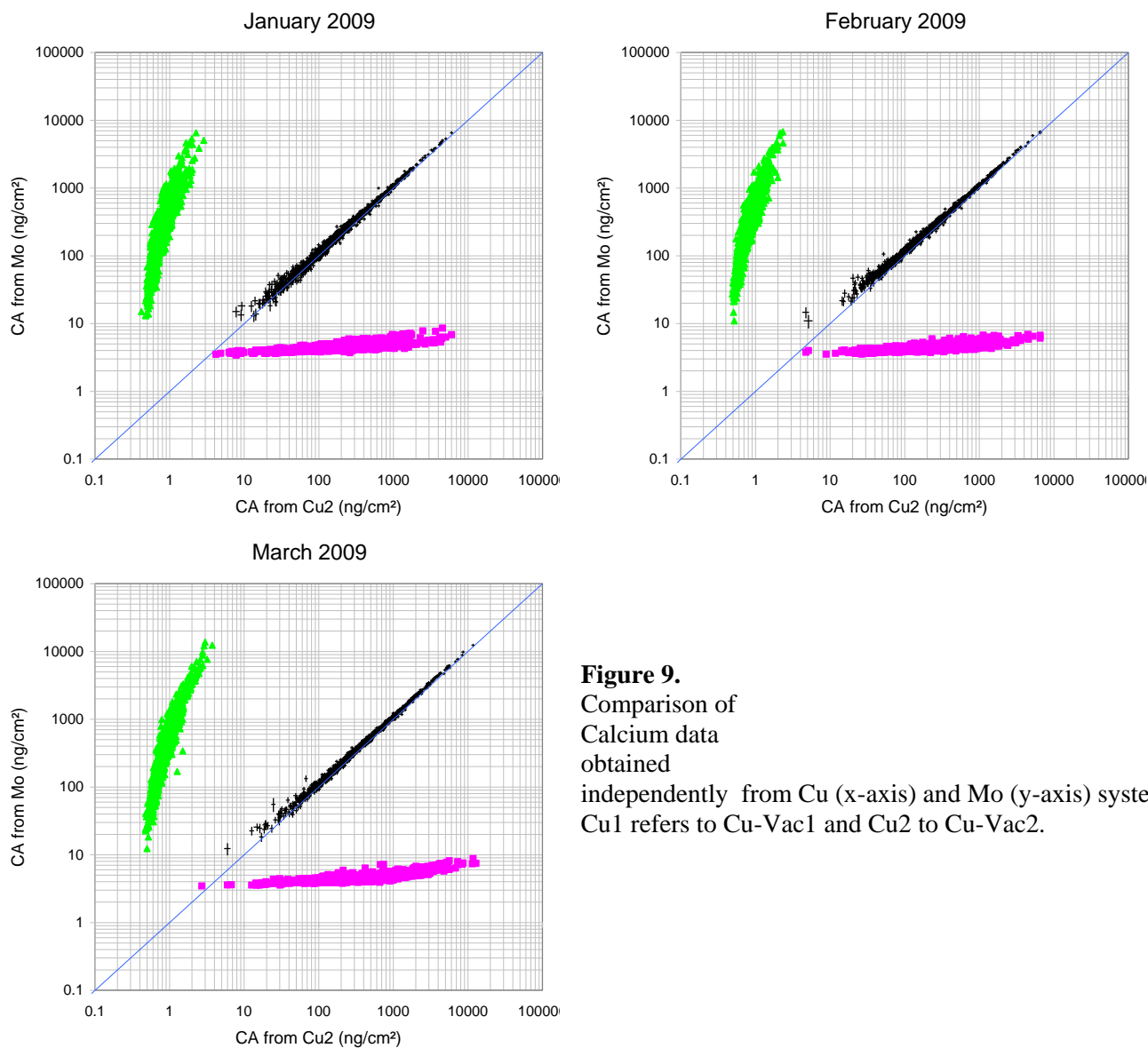Cu1 refers to Cu-Vac1 and Cu2 to Cu-Vac2.

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

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

Thirty four field blanks for January 2009, 40 field blanks for February 2009 and 38 field blanks for March 2009 samples were exposed at selected sites on selected sampling events. The field blanks were analyzed on both, XRF-Mo and 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 January, February and March 2009. Loadings are considered well measured when their uncertainties are less than 10%. Thus, the 95th percentile field blank loading for Fe (Feb 2009 samples) was at or above about 7.3% (7.8% on Mo) of all well measured sample loadings on the Cu system.

Cu anode

Jan 2009	Na	Mg	Al	Si	P	S	Cl	K	Ca	Ti	V	Cr	Mn	Fe
95 %ile	0.0%	0.0%	0.0%	6.8%	0.0%	0.0%	17.3%	8.1%	45.8%	9.9%	0.0%	0.0%	0.0%	4.9%
90 %ile	0.0%	0.0%	0.0%	3.1%	0.0%	0.0%	14.4%	5.0%	40.7%	4.3%	0.0%	0.0%	0.0%	3.4%
75 %ile	0.0%	0.0%	0.0%	1.0%	0.0%	0.0%	5.8%	1.3%	14.5%	0.0%	0.0%	0.0%	0.0%	0.9%
Feb 2009	Na	Mg	Al	Si	P	S	Cl	K	Ca	Ti	V	Cr	Mn	Fe
95 %ile	0.0%	0.0%	0.0%	6.3%	0.0%	0.0%	18.0%	7.2%	41.6%	3.3%	0.0%	0.0%	0.0%	7.3%
90 %ile	0.0%	0.0%	0.0%	2.7%	0.0%	0.0%	12.1%	4.8%	17.0%	0.1%	0.0%	0.0%	0.0%	2.6%
75 %ile	0.0%	0.0%	0.0%	0.6%	0.0%	0.0%	1.9%	1.1%	10.0%	0.0%	0.0%	0.0%	0.0%	1.0%
Mar 2009	Na	Mg	Al	Si	P	S	Cl	K	Ca	Ti	V	Cr	Mn	Fe
95 %ile	0.0%	0.0%	0.0%	8.6%	0.0%	0.0%	10.3%	3.0%	6.2%	0.5%	0.0%	0.0%	0.0%	2.9%
90 %ile	0.0%	0.0%	0.0%	1.6%	0.0%	0.0%	6.2%	2.1%	4.0%	0.1%	0.0%	0.0%	0.0%	1.1%
75 %ile	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.3%	0.0%	0.4%	0.0%	0.0%	0.0%	0.0%	0.1%

Mo anode

Jan 2009	Fe	Ni	Cu	Zn	As	Pb	Se	Br	Rb	Sr	Zr
95 %ile	4.8%	0.0%	0.0%	34.8%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%
90 %ile	3.9%	0.0%	0.0%	31.5%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%
75 %ile	0.4%	0.0%	0.0%	17.9%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%

Feb 2009	Fe	Ni	Cu	Zn	As	Pb	Se	Br	Rb	Sr	Zr
95 %ile	7.8%	0.0%	0.0%	37.8%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%
90 %ile	2.3%	0.0%	0.0%	25.6%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%
75 %ile	0.6%	0.0%	0.0%	9.6%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%

Mar 2009	Fe	Ni	Cu	Zn	As	Pb	Se	Br	Rb	Sr	Zr
95 %ile	2.5%	0.0%	0.0%	55.1%	0.0%	0.3%	0.0%	0.0%	0.0%	0.0%	0.0%
90 %ile	0.9%	0.0%	0.0%	36.4%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%
75 %ile	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%

Field blank loadings are negligible compared to samples for all elements except for Si, K, Ca, Ti, Fe and Zn in Jan-Mar 2009.