Data report for elemental analysis of IMPROVE samples collected during January, February, March 2006
UC Davis
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SUMMARY

This report summarizes the quality assurance performed during elemental analysis of the IMPROVE samples collected in January, February and March of 2006. 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

The procedures and their results are presented below.
Jan 2006 samples were analyzed on the additional Cu-anode system Cu-Vac2 (see previous report for details) and Feb – Mar 2006 samples were analyzed on the first Cu-anode system, Cu-Vac1. As of 2/1/07 more frequent (weekly) calibration checks were performed on both Cu systems. A new calibration was done on the Cu-Vac1 on 2/13/07 to reflect work done on the system. No new calibrations were performed on the Cu-Vac2 system.
All routine calibration checks on the Mo system were within our criteria.

Section 1. Overview of Elemental Analysis Systems

The elements Na and Mg (considered qualitative only) and Al to Fe are reported from one of 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 to analyze Jan-Mar 2006 samples.

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

The PESA system operates under vacuum (< 10 microns Hg) 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 typical current value of approximately 50 nA collected on a Faraday cup.

Section 2. General Statistics of January, February and March 2006 data

XRF and PESA analyses were carried out on 1678 samples collected in January 2006, 1682 samples collected in February 2006 and 1669 samples collected in March 2006. All samples were analyzed between 30 June 2006 and 13 September 2006 on the Mo-anode XRF system,

between 18 January 2007 and 18 March 2007 on Cu-Vac1, between 1 February 2007 and 2 March 2007 on Cu-Vac2, and from 2/27/07 to 2/28/07 and from 3/19/07 to 3/20/07 and from 3/20/07 to 3/23/07 on the PESA system.

Table 1 summarizes the first quarter 2006 detection rates on the three systems, with rates for December 2005 included for comparison.

PESA					
Z	*element*	*1-2006*	*2-2006*	*3-2006*	*12-2005*
1	H	98%	100%	100%	99%

Cu-anode XRF					
Z	*element*	*1-2006*	*2-2006*	*3-2006*	*12-2005*
11	Na	72%	44%	41%	62%
12	Mg	45%	20%	19%	31%
13	Al	76%	73%	72%	65%
14	Si	95%	96%	99%	92%
15	P	3%	1%	0%	3%
16	S	100%	100%	100%	100%
17	Cl	28%	13%	15%	15%
19	K	100%	100%	100%	99%
20	Ca	100%	100%	100%	99%
22	Ti	94%	97%	98%	92%
23	V	88%	91%	84%	78%
24	Cr	54%	62%	37%	50%
25	Mn	95%	98%	98%	93%
26	Fe	100%	100%	100%	100%

Mo-anode XRF					
Z	*element*	*1-2006*	*2-2006*	*3-2006*	*12-2005*
28	Ni	40%	37%	43%	46%
29	Cu	74%	85%	93%	76%
30	Zn	98%	100%	100%	99%
33	As	44%	53%	50%	46%
34	Se	77%	84%	82%	75%
35	Br	100%	100%	100%	99%
37	Rb	60%	68%	82%	68%
38	Sr	90%	94%	95%	91%
40	Zr	25%	26%	25%	16%
82	Pb	99%	95%	97%	94%

Table 1. Percentage of cases in which the element was detected on each system. December 2005 data included for reference.

Section 3. Quality Control

3.1 Concentration calibration and verification (calibration checks)

Both XRF systems are calibrated with thin film foil standards produced by Micromatter. The standards used for samples from the first quarter of 2006 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 the XRF-Cu systems and 10mA on the XRF-Mo system) to maintain counting live times comparable with those of actual IMPROVE samples.

Standard	Certified Elemental Concentrations +/- 5% ($\mu g/cm^2$)	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. .Some standards (*) have variable stoichiometry; they are not use directly in calibration of the systems but serve only as "indicators".

Spectra from the foil standards are processed and analyzed by the same software used for samples. Calibration factors relating spectral counts to elemental concentrations are determined from the ratio of an element's observed peak area to the concentration quoted by Micromatter.

During the time of Jan-Mar 2006 samples analyses, the performance of all systems was monitored weekly (bi-weekly on Cu systems). Fifteen standards are analyzed on the Cu system and 19 on the Mo system, and the ratios of reported to quoted values are calculated. 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.

Figures 1 to 3 below show the calibration checks and system recalibrations performed during the period in which samples of interest were analyzed on each system. The analysis dates for each sample month are listed in the legends. December 2005 samples analysis dates are included for reference. The y-axes indicate the ratio of the values reported for each standard to the value quoted by Micromatter.
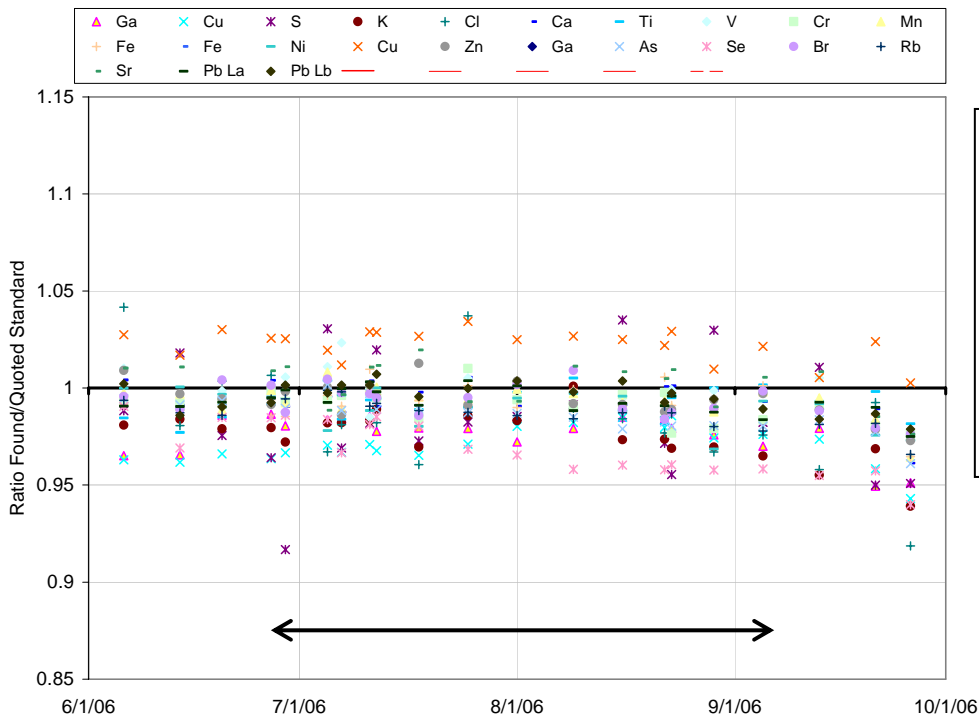
Figure 1

Legend:
Ga, Cu, S, K, Cl, Ca, Ti, V, Cr, Mn
Fe, Fe, Ni, Cu, Zn, Ga, As, Se, Br, Rb
Sr, Pb La, Pb Lb

Y-axis: Ratio Found/Quoted Standard
X-axis: 6/1/06, 7/1/06, 8/1/06, 9/1/06, 10/1/06

sample	analysis
Dec 2005	6/1/06 - 6/29/06
Jan 2006	6/30/06 - 7/24/06
Feb 2006	7/24/06 - 8/19/06
Mar 2006	8/19/06 -9/13/06

Figure 1. Mo XRF system performance chart based on standards

Figure 2

Legend:
Na, Cl, Mg, Al, Si, P, S, Cl
K, Ca, Ti, V, Cr, Mn, Fe, Ni
new cal, new cal, new cal, new cal, new cal, new cal, new cal, new cal

Y-axis: Ratio Found/Quoted Standard
X-axis: 12/1/06, 1/1/07, 2/1/07, 3/1/07, 4/1/07

sample	analysis
Nov 2005	12/4/06 - 1/12/07
Feb 2006	1/18/07 - 2/10/07
Mar 2006	2/21/07 – 3/18/07
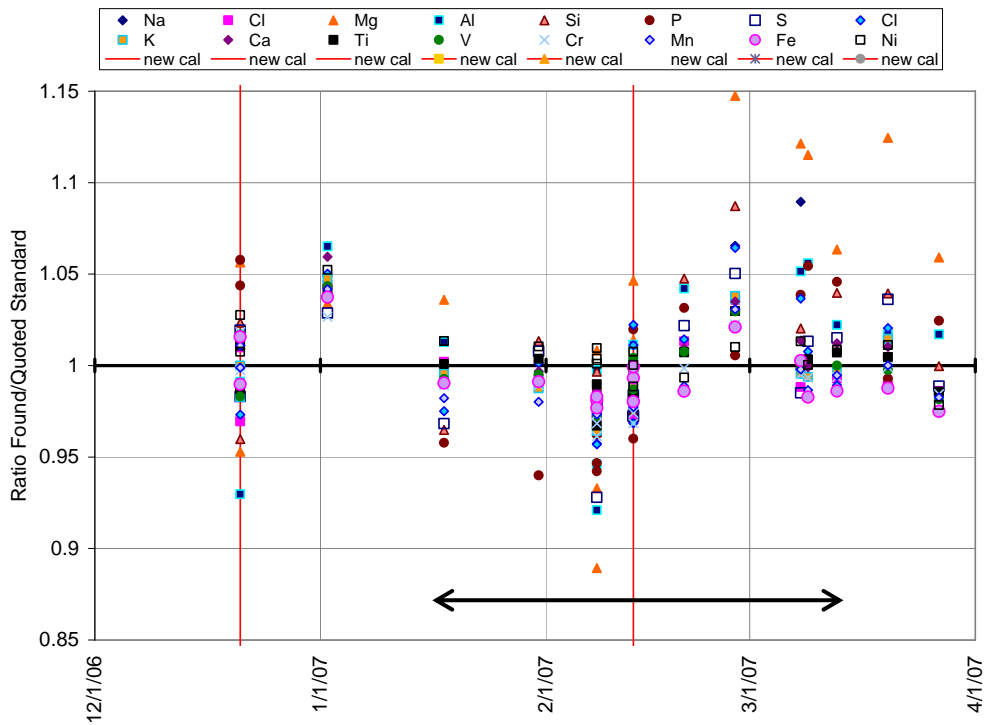
Figure 2. XRF Cu-Vac1 system performance chart based on standards.
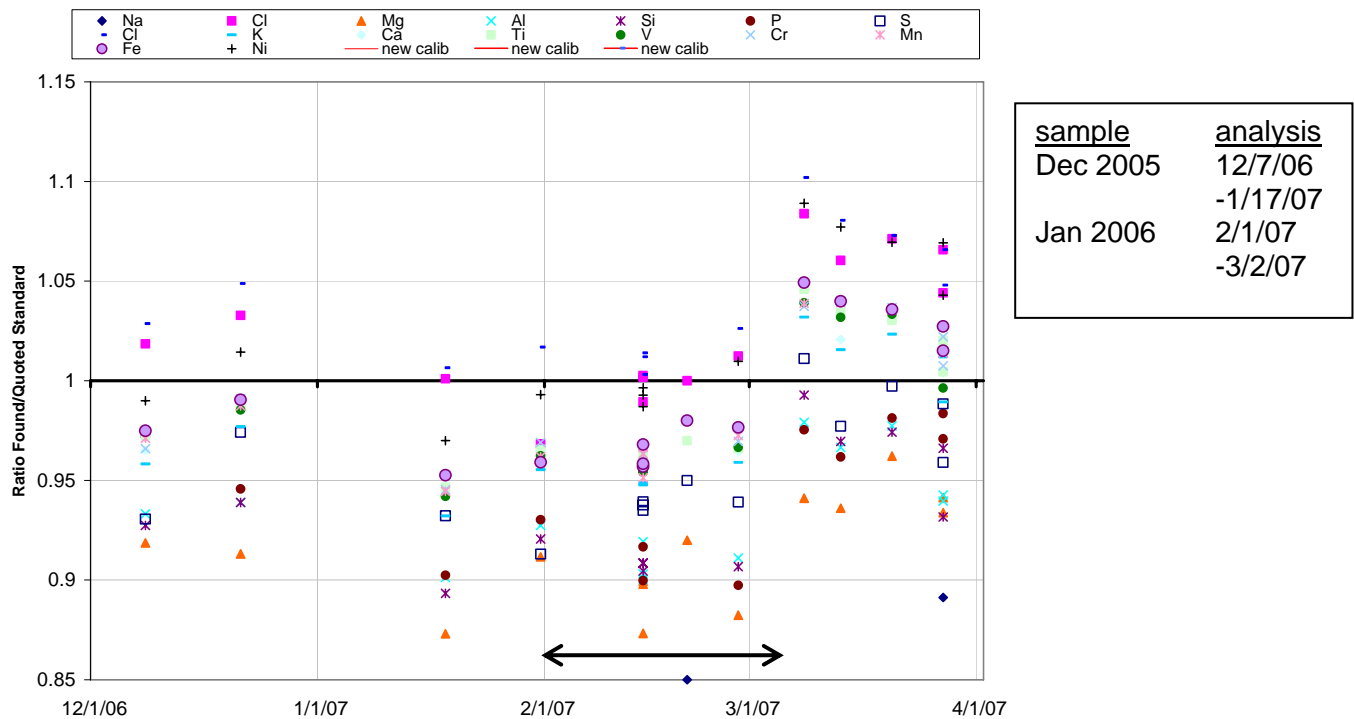
Figure 3. XRF Cu-Vac2 system performance chart based on standards.

All calibration checks on the Mo system during the analysis of Jan-Mar 2006 samples were within our criteria.

February and March 2006 samples were analyzed on the XRF Cu-Vac1 system. A new calibration of the system took place on 2/13/07 as a result of work performed on the system. All calibration checks performed during analysis of the samples of interest met our criteria.

January 2006 samples were analyzed on the XRF Cu-Vac2 system. During the analysis, the calibration checks with standards show low values for all elements, reaching the minimum acceptable criteria (0.9) for some elements i.e. Si, Al, P.

The PESA system is calibrated with six 1/8 mil thick Mylar blanks whose areal densities are determined from their weights and the chemical composition of Mylar. These foils have served as the PESA calibration standards for many years. The average hydrogen concentration for these PESA standards is calculated to be 20 µg/cm^2. As with XRF, the calibration factor is based on the ratio of observed counts for the six PESA standards to their calculated H concentration.

The PESA system is recalibrated at the beginning of every analytical session, because of variations in the ion source production, amplitude harmonics, and optics. The six Mylar blanks used as calibration standards are reanalyzed approximately every 200 samples to verify the calibration throughout the session. If the ratio of reported to calculated concentrations for these standards drifts outside the 0.95-1.05 range during an analysis run., the cyclotron is re-tuned, system is recalibrated, and samples reanalyzed. Figure 4 shows calibration verifications during the analysis of Jan-Mar 2006 samples.

1/8 mil Mylar standards
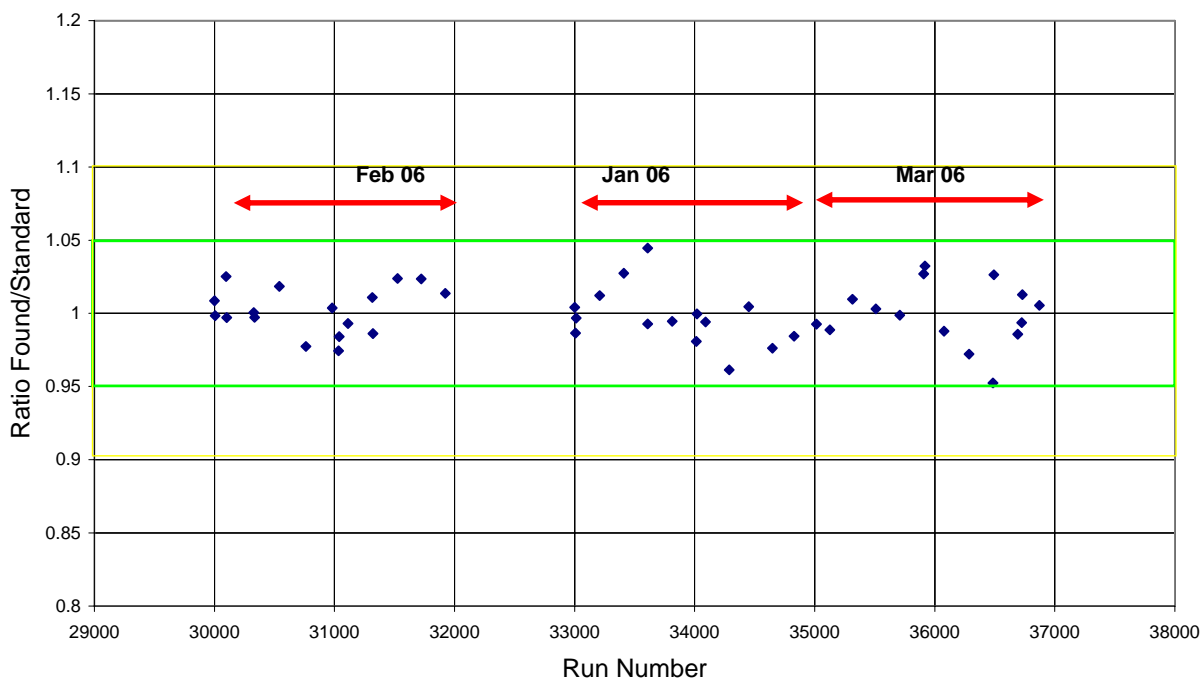January, February, March 2006 samples

Figure 4. PESA standards for Jan-Mar 2006 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 each system to establish relationships of the 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
										full	
intercept	slope	full scale	*from Nov*	intercept	slope	full scale	*from Dec*	intercept	slope	scale	*from Dec*
				-0.0358	0.01716	8.750	*0.00%*	-0.08490	0.03605	18.372	*-0.03%*
-0.0414	0.01667	8.494	*0.00%*					-0.07822	0.03604	18.375	*-0.02%*
-0.0377	0.01667	8.497	*0.04%*					-0.09336	0.03606	18.371	*-0.04%*

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 2006 samples, 26 SAFOX, SAMAX, TRCRX filters from Oct 2005 were reanalyzed twice. Similarly, reanalyses for Feb 2006 and Mar 2006

samples were performed, respectively, on 26 SAFOX, SAMAX AND TRCRX filters from August 2005 twice and 30 MEVEX, OLYMX and PMRFX filters from November 2005, three times. Figure 5 compares the original and repeat analyses.
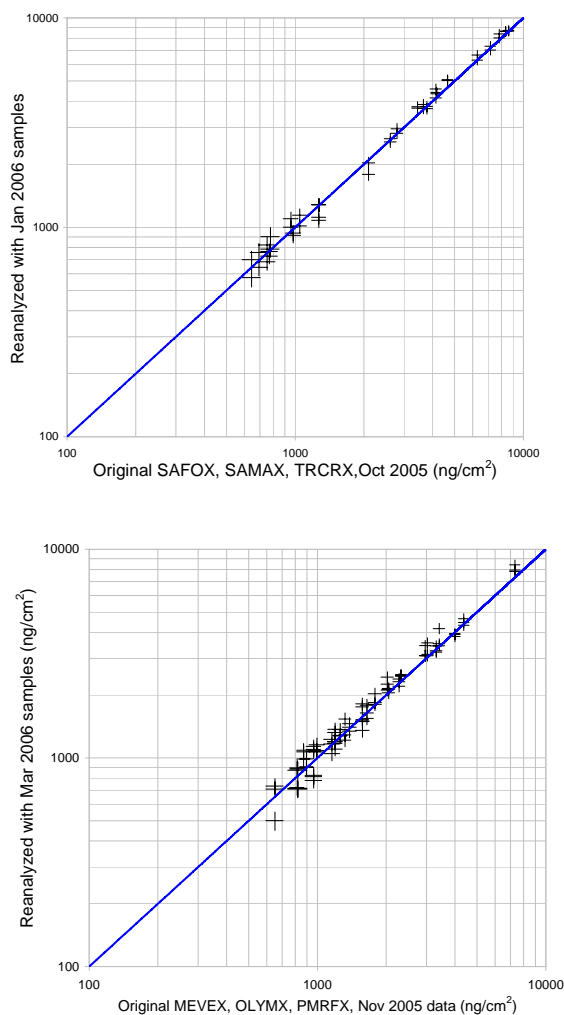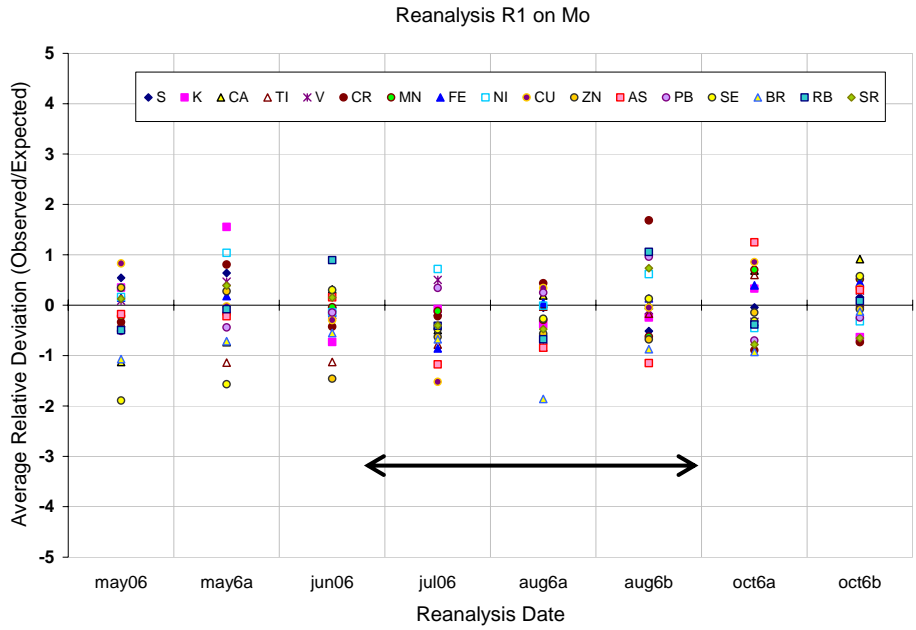

Figure 5. PESA reanalysis of selected Aug, Oct and Nov 2005 samples during analyses of Jan-Mar 2006 network samples.
Reported uncertainties are indicated by error bars; agreement is indicated by sloping lines.

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 with the XRF-Mo and both vacuum XRF-Cu systems (Cu-Vac1 and Cu-Vac2) approximately monthly during 2006/2007 analyses of Jan-Mar 2006 samples.
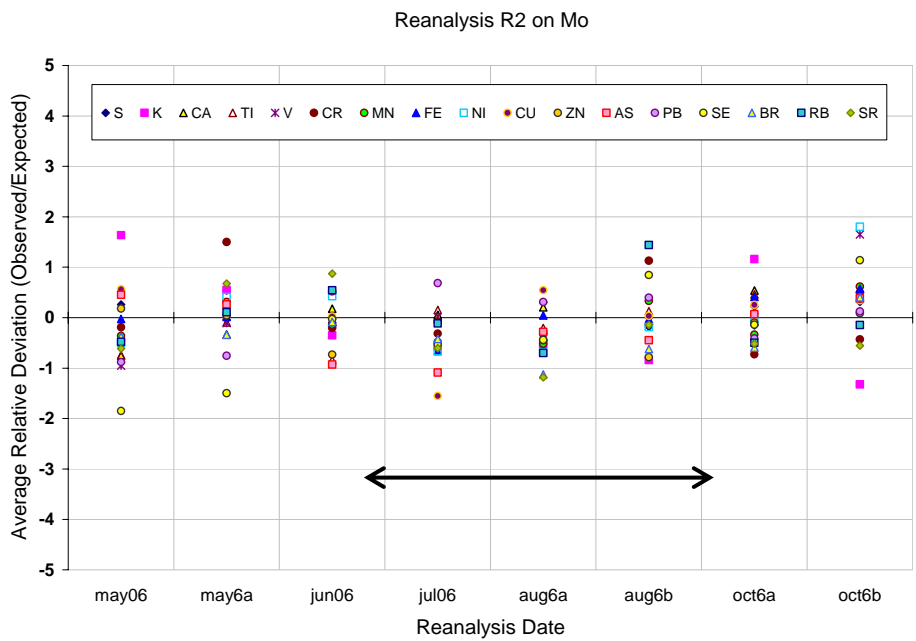The results are summarized in the figures 6-11 below.
For the Mo and Cu-Vac1 systems the mean loadings calculated based on 12 consecutive runs (about a year of data) are used as a benchmark for comparison. The average ratio of observed deviations (from mean) to reported measured uncertainties for each element is calculated and shown on vertical axis.

This format highlights any systematic trend in the measurements and provides a test, at actual sample loadings, of the stability of calibrations based on the heavily-loaded foil standards.
At present, sample reanalysis is used as a qualitative check on system performance.

Figure 6. Reanalyses of REANAL1 samples on XRF-Mo system. Horizontal arrow indicates when Jan-Mar 2006 network samples were analyzed.
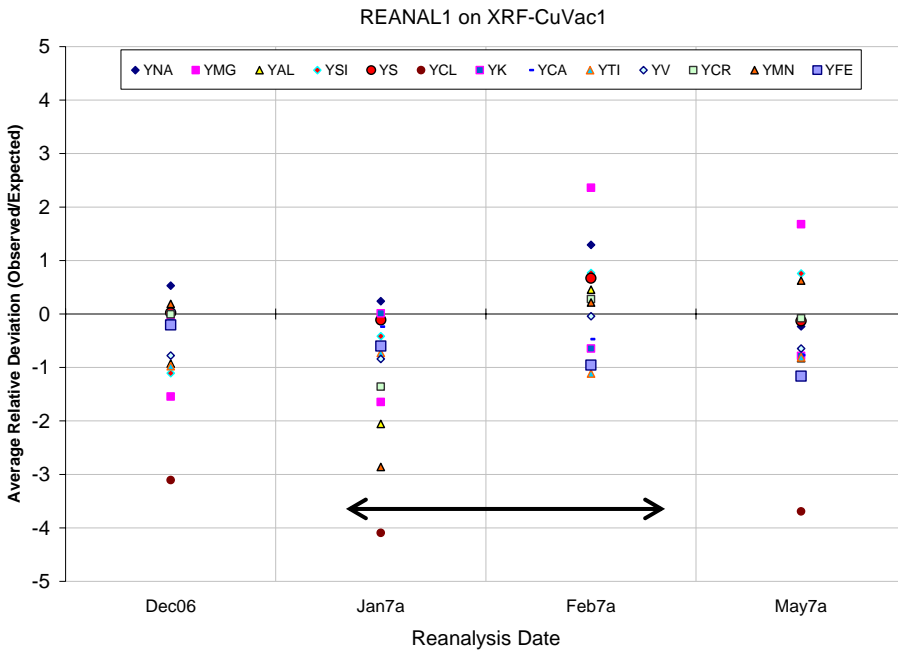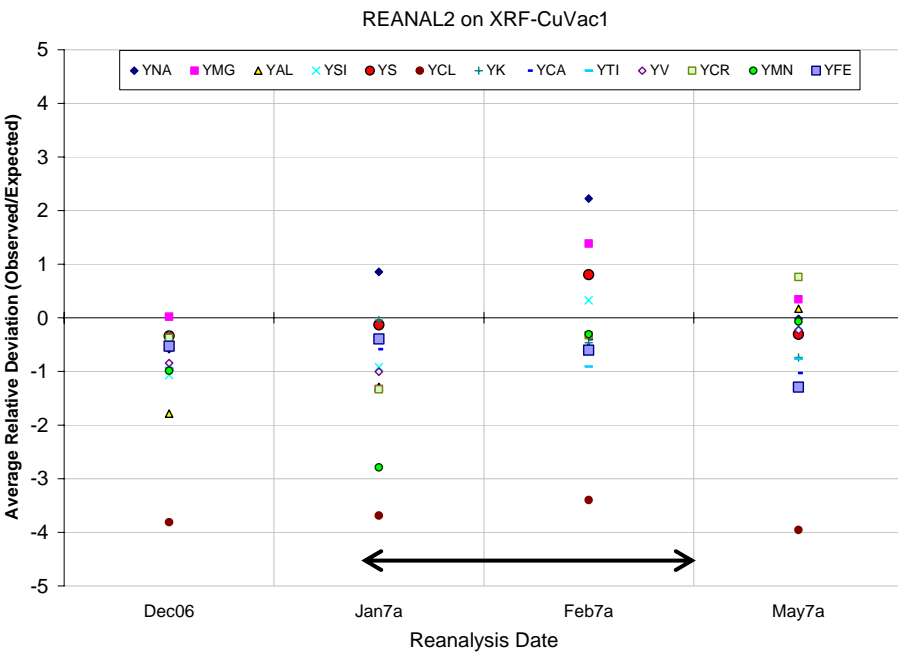

Figure 7. Reanalyses of REANAL2 samples on XRF-Mo system. Horizontal arrow indicates when Jan-Mar 2006 network samples were analyzed.

Figure 8. Reanalyses of REANAL1 samples on XRF-Cu1 system. Horizontal arrow indicates when Feb-Mar 2006 network samples were analyzed.

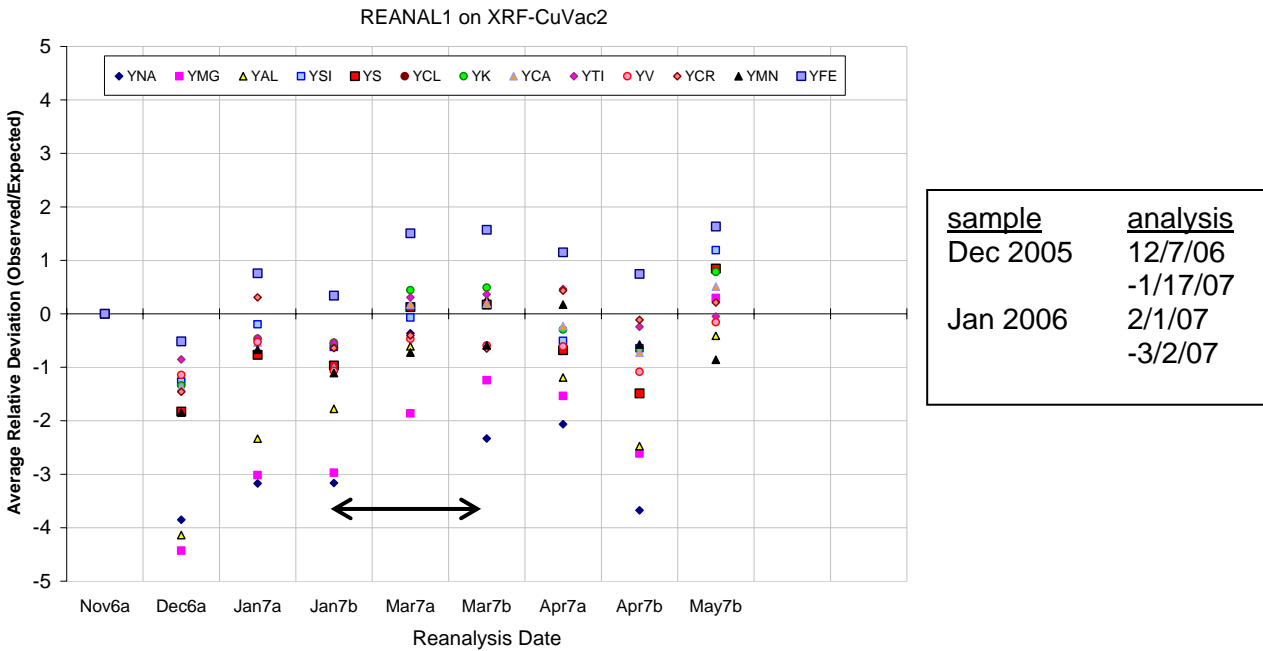
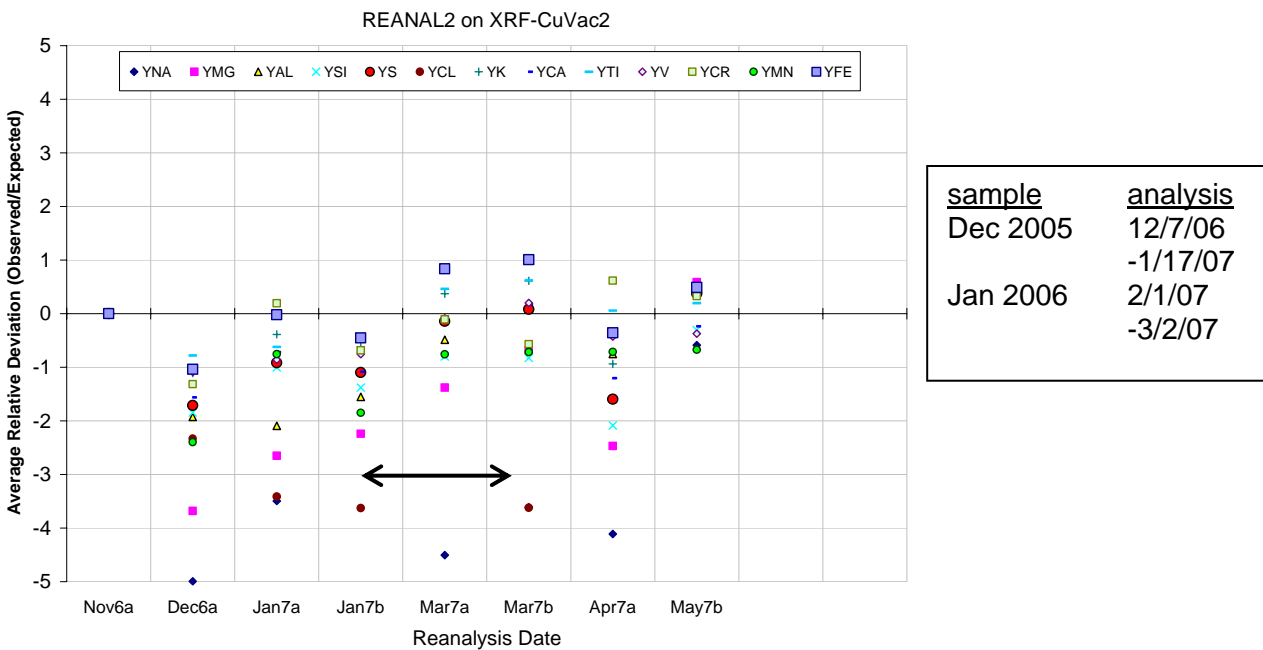**Figure 9.** Reanalyses of REANAL2 samples on XRF-Cu1 system. Horizontal arrow indicates when Feb-Mar 2006 network samples were analyzed.

Because of the limited number of reanalysis done on the Cu-Vac2 system (system is operational from Sep 2006) the choice was made to present the current reanalysis using the first (original) reanalysis performed in Nov 2006 as a baseline for comparison instead of the previously chosen average of all available reanalysis data at the time.


Figure 10. Reanalyses of REANAL1 samples on XRF-Cu2 system. Horizontal arrow indicates when Jan 2006 network samples were analyzed.


Figure 11. Reanalyses of REANAL2 samples on XRF-Cu2 system. Horizontal arrow indicates when Jan 2006 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 12 and 13 compare the two measurements of these two elements for the samples from Jan-Mar 2006. 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.
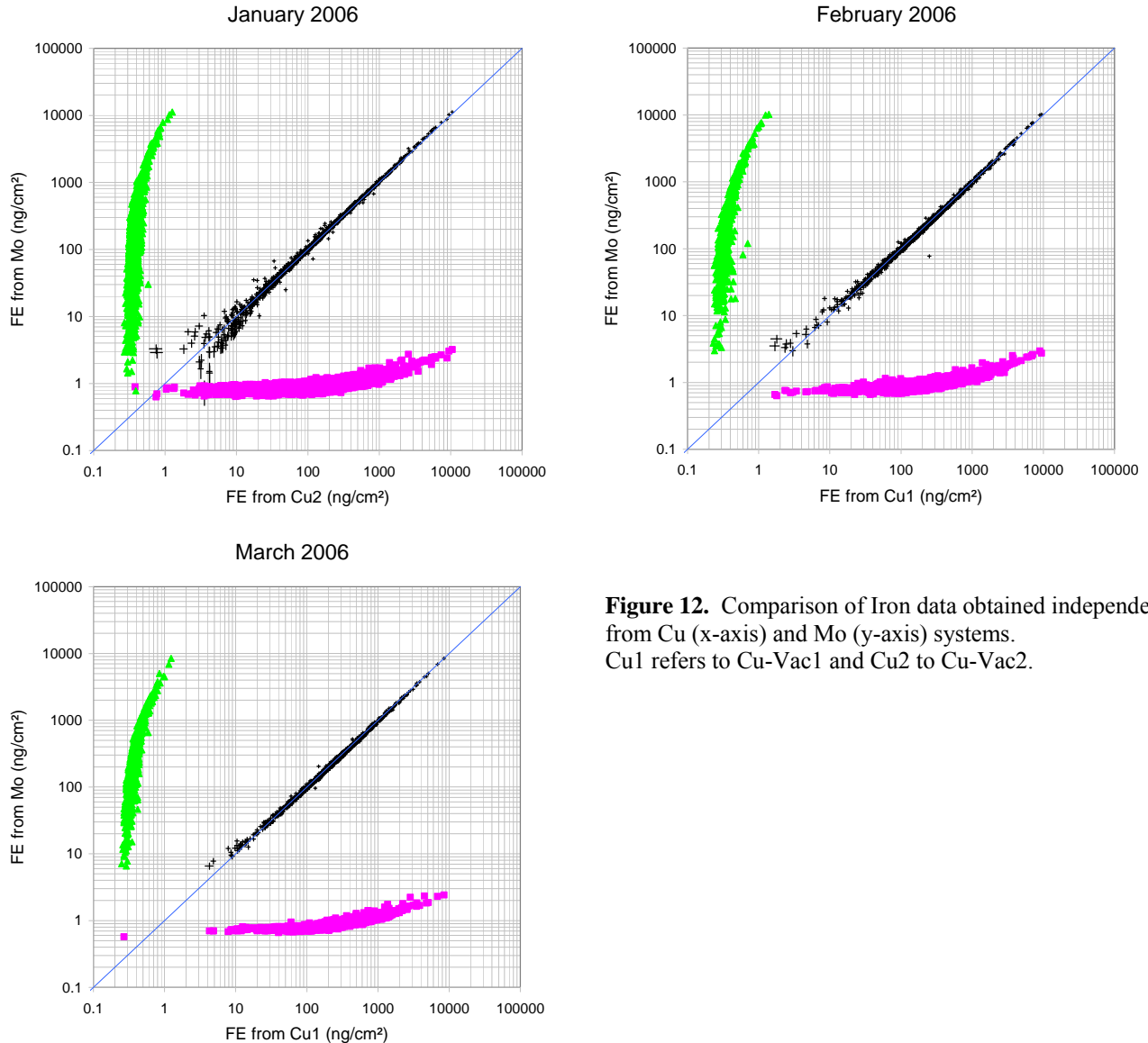
Figure 12. Comparison of Iron data obtained independently from Cu (x-axis) and Mo (y-axis) systems.
Cu1 refers to Cu-Vac1 and Cu2 to Cu-Vac2.

January 2006

February 2006

March 2006
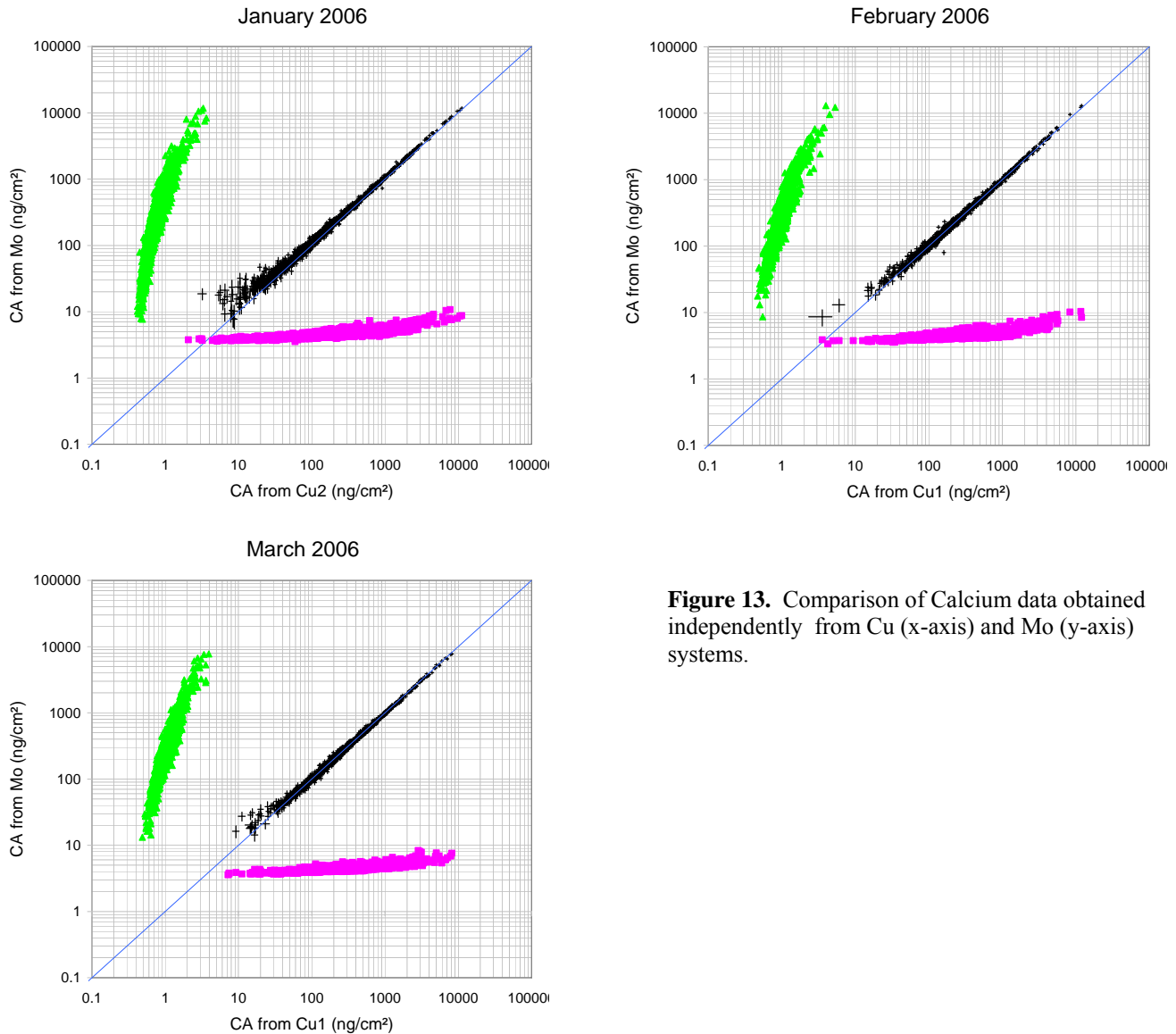
Figure 13. Comparison of Calcium data obtained independently from Cu (x-axis) and Mo (y-axis) systems.

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

Twenty three field blanks for January 2006, 16 field blanks for February 2006 and 24 field blanks for March 2006 samples were exposed at selected sites on selected sampling events. The Cu anode system used for analysis of the field blanks was the same system used for the corresponding samples.

Ninty-fifth, 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 2006. Loadings are considered well measured when their uncertainties are less than 10%.

Thus, the 95th percentile field blank loading for Fe (Feb 2006 samples) was greater than about 1.3% of all well measured sample loadings on both the Cu anode and Mo anode systems.

Cu anode

Jan 2006	Na	Mg	Al	Si	P	S	Cl	K	Ca	Ti	V	Cr	Mn	Fe
95 %ile	0%	0%	0%	2.0%	0%	0%	0.7%	1.2%	2.6%	0%	0%	0%	0%	6.8%
90 %ile	0%	0%	0%	0.1%	0%	0%	0.3%	0%	2.3%	0%	0%	0%	0%	4.1%
75 %ile	0%	0%	0%	0%	0%	0%	0%	0%	0.1%	0%	0%	0%	0%	0.7%

Feb 2006	Na	Mg	Al	Si	P	S	Cl	K	Ca	Ti	V	Cr	Mn	Fe
95 %ile	0%	0%	0%	10.7%	0%	0.1%	0%	0.5%	0.1%	0%	0%	0%	0%	1.3%
90 %ile	0%	0%	0%	6%	0%	0%	0%	0%	0%	0%	0%	0%	0%	0.5%
75 %ile	0%	0%	0%	0%	0%	0%	0%	0%	0%	0%	0%	0%	0%	0.1%

The field blank data from Cu system for March 2006 samples are not available at this time.

Mo anode

Jan 2006	Fe	Ni	Cu	Zn	As	Pb	Se	Br	Rb	Sr	Zr
95 %ile	13.1%	0%	0%	23.8%	0%	0%	0%	0%	0%	0%	0%
90 %ile	2.2%	0%	0%	22.9%	0%	0%	0%	0%	0%	0%	0%
75 %ile	0%	0%	0%	5.1%	0%	0%	0%	0%	0%	0%	0%

Feb 2006	Fe	Ni	Cu	Zn	As	Pb	Se	Br	Rb	Sr	Zr
95 %ile	1.3%	0%	0%	66.3%	0%	0%	0%	0%	0%	0%	0%
90 %ile	0.5%	0%	0%	61.4%	0%	0%	0%	0%	0%	0%	0%
75 %ile	0%	0%	0%	8%	0%	0%	0%	0%	0%	0%	0%

Mar 2006	Fe	Ni	Cu	Zn	As	Pb	Se	Br	Rb	Sr	Zr
95 %ile	0.1%	0%	0%	20.0%	0%	0%	0%	0%	0%	0%	0%
90 %ile	0%	0%	0%	4.8%	0%	0%	0%	0%	0%	0%	0%
75 %ile	0%	0%	0%	0%	0%	0%	0%	0%	0%	0%	0%

Previously noted Zn contamination still shows in the field blanks loadings for all the samples. The results suggest that for all the elements, with the exception of Zn, the field blanks loadings are negligible compared to samples.