

Data report for elemental analysis of IMPROVE samples collected during
April, May, June 2006
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SUMMARY

This report summarizes the quality assurance performed during elemental analysis of the IMPROVE samples collected in April, May and June 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

Analysis details and key events are summarized below.

Apr and Jun 2006 samples were analyzed on the second Cu-anode system Cu-Vac2, and May 2006 samples were analyzed on the first Cu-anode system Cu-Vac1. A new calibration was performed on Cu-Vac2 on 4/20/07 (June 2006 samples) to reflect work done on the system. No new calibrations were performed on the Cu-Vac1 system.

The Mo system was recalibrated to reflect maintenance (alignment and securing of the detector collimator, and window cleaning) on 10/5/06 (April 2006 samples). During the analysis of Apr-Jun 2006 samples all routine calibration checks on the Mo system were within criteria.

A new set of standards (Mylar foils) was introduced for PESA calibration and calibration checks on April 26, 2007.

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 April, May and June 2006 data

XRF and PESA analyses were carried out on 1649 samples collected in April 2006, 1685 samples collected in May 2006, and 1609 samples collected in June 2006. All samples were analyzed between 14 September 2006 and 4 December 2006 on the Mo-anode XRF system, between 18 March 2007 and 17 April 2007 on Cu-Vac1, between 8 March 2007 and 13 May 2007 on Cu-Vac2, and on 3/23/07, 4/26-27/07, 5/1-2/07, and 5/21-22/07 on the PESA system.

Table 1 summarizes the second quarter 2006 detection rates on the three systems, with rates for March 2006 included for comparison.

PESA					
Z	element	4-2006	5-2006	6-2006	3-2006
1	H	100%	97%	100%	100%

Cu-anode XRF					
Z	element	4-2006	5-2006	6-2006	3-2006
11	Na	60%	38%	63%	41%
12	Mg	77%	23%	71%	19%
13	Al	97%	82%	93%	72%
14	Si	100%	96%	100%	99%
15	P	2%	0%	3%	0%
16	S	100%	98%	100%	100%
17	Cl	20%	9%	15%	15%
19	K	100%	98%	100%	100%
20	Ca	100%	98%	100%	100%
22	Ti	100%	97%	99%	98%
23	V	98%	82%	97%	84%
24	Cr	90%	32%	82%	37%
25	Mn	100%	98%	100%	98%
26	Fe	100%	98%	100%	100%

Mo-anode XRF					
Z	element	4-2006	5-2006	6-2006	3-2006
28	Ni	57%	53%	58%	43%
29	Cu	89%	95%	96%	93%
30	Zn	100%	100%	100%	100%
33	As	70%	74%	58%	50%
34	Se	81%	91%	91%	82%
35	Br	100%	99%	100%	100%
37	Rb	86%	82%	80%	82%
38	Sr	96%	97%	97%	95%
40	Zr	30%	16%	20%	25%
82	Pb	94%	97%	100%	97%

Table 1. Percentage of cases in which the element was detected on each system. March 2006 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 second 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 XRF-Cu systems and 10mA on XRF-Mo system) to maintain counting live times comparable with those of actual IMPROVE samples.

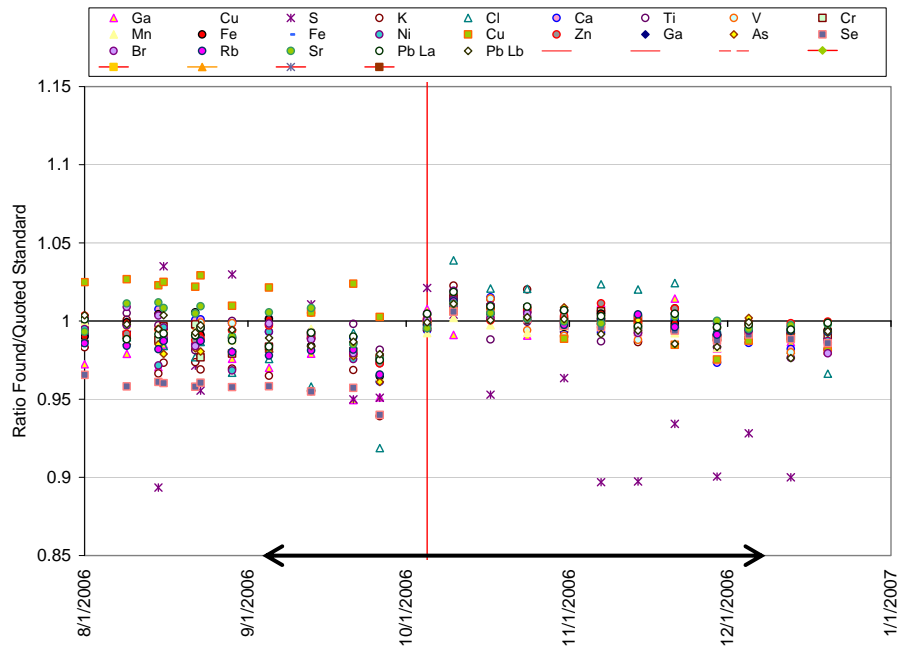
Standard	Certified Elemental Concentrations +/- 5% ($\mu\text{g}/\text{cm}^2$)	Serial #
NaCl	Na: 19.1, Cl: 29.4	16518
MgF ₂	Mg: 20.6	16519
Al	Al: 40.7	16520
SiO	Si: 23.9	16521
GaP*	P: 4.5	16500
CuS _x	S: 12.9 Cu: 37.6	16523
KCl	Cl: 22.5 K: 24.9	16296
CaF ₂	Ca: 24.9	16525
Ti	Ti: 13.7	16504
V	V: 12.2	16505
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. 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.

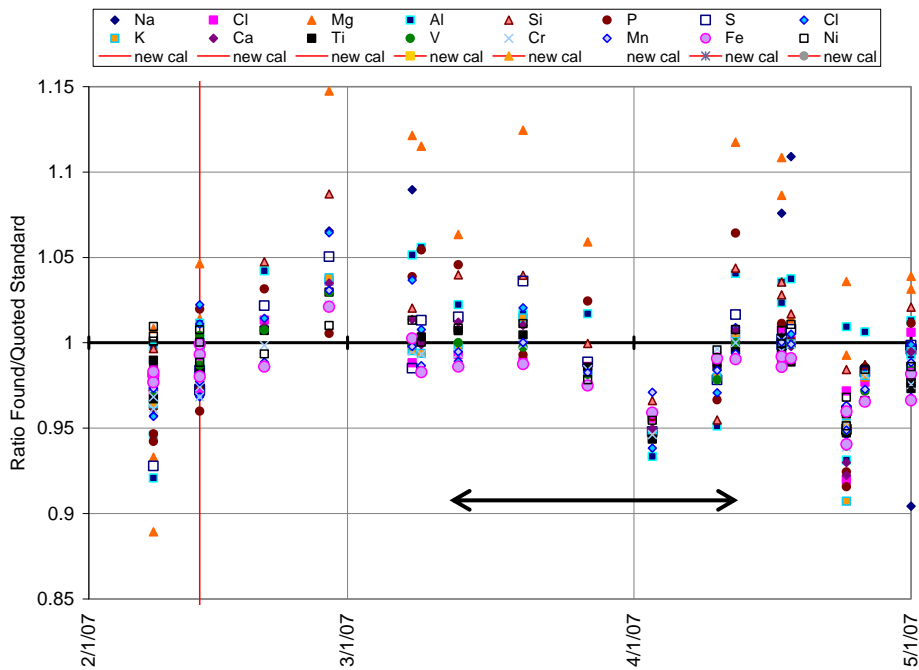
During the analyses of Apr-Jun 2006 samples, the performance of all systems was monitored weekly. Fifteen standards are analyzed on the Cu system and 19 on the Mo system, and the ratios of reported to quoted values are calculated. If the ratios lie within the acceptance limits 0.9 – 1.1 for all quantitative 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. March 2006 sample 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.



<u>sample</u>	<u>analysis</u>
Mar 2006	8/19/06 -9/13/06
Apr 2006	9/14/06- 10/16/06
May 2006	10/17/06- 11/10/06
Jun 2006	11/10/06- 12/4/06

Figure 1. Mo XRF system performance chart based on standards



<u>sample</u>	<u>analysis</u>
Mar 2006	2/21/07 – 3/18/07
May 2006	3/18/07- 4/17/07

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

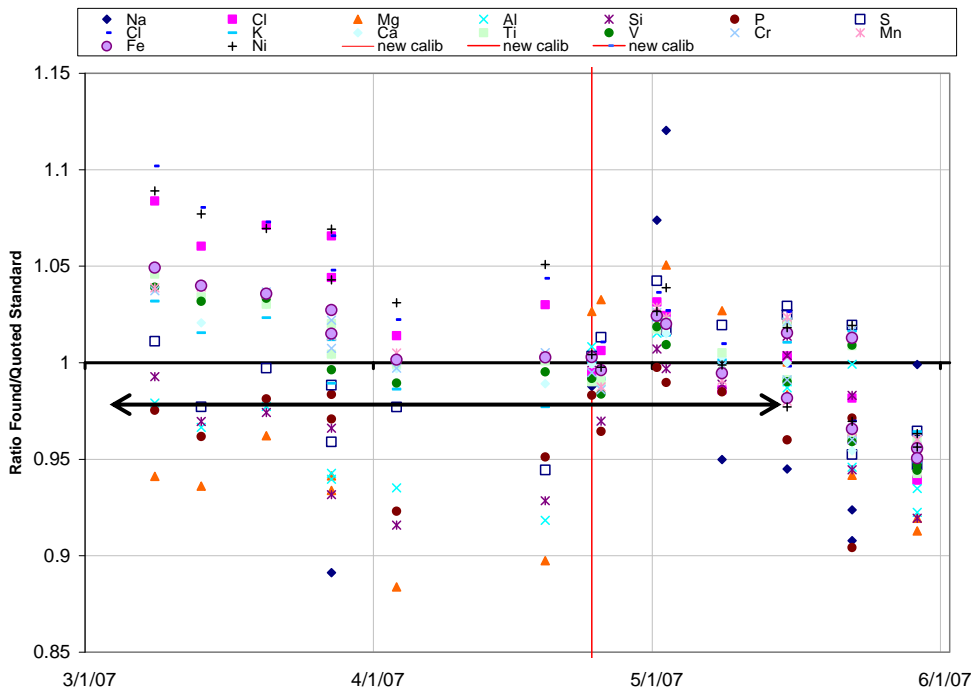


Figure 3. XRF Cu-Vac2 system performance chart based on standards.

A descending trend of standards ratios was observed on the XRF-Mo system between 8/16/06 and 9/26/06. Even though the standards ratios did not exceed acceptance limits, the system was recalibrated on October 5, 2006 to reflect maintenance done on the system, including cleaning of the detector window and collimator adjustment. All calibration checks on the Mo system during the analysis of Apr-Jun 2006 samples were within our criteria.

May 2006 samples were analyzed on the XRF Cu-Vac1 system. A failing socket adaptor for the X-ray tube was replaced toward the end of this analysis run. A descending trend of standards ratios was observed during the time of analysis, but no recalibration was performed as all ratios met the acceptance criteria. Unusually low detection rates were obtained for several elements (*e.g.* Cr) as was also the case with March 2006 samples, the previous group analyzed on Cu-Vac1. The entire March and May 2006 sample collection was reanalyzed on the CuVac2 system to assure the quality of these data. The reanalyses yielded no grounds to invalidate the original results.

April and June 2006 samples were analyzed on XRF Cu-Vac2 system. New calibration factors on April 24th, 2007 were the result of the repairs on the system. Descending trends were noted in ratios, especially for Fe. During the analysis, all calibration checks for quantitative elements met criteria.

On April 26, 2007, six new Mylar foils (thicknesses 2.5, 3.5 and 9.3 microns) were combined with two previously used foils (1/8 mil thick) to form a new set of references for PESA system calibrations and calibration checks. The hydrogen concentration for each of these standards was determined based on their weights and chemical composition of the Mylar. The calculated values for each PESA standard are listed below:

PESA Standard	1	2	3	4	5	6	7	8
Calculated H amount (ug/cm ²)	19.80	19.80	36.73	36.73	23.78	23.78	17.59	17.59

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, 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 the 0.95-1.05 range during an analysis run., the cyclotron is re-tuned, the system is recalibrated, and the samples are reanalyzed. Figure 4 shows calibration verifications during the analysis of Apr-Jun 2006 samples. During analysis of Apr 2006 and May 2006 samples (circled points) the average ratio of all standards had fallen below acceptable criteria twice. The analyses were continued and the affected samples were reanalyzed during a subsequent PESA analysis run on July 25th, 2007.

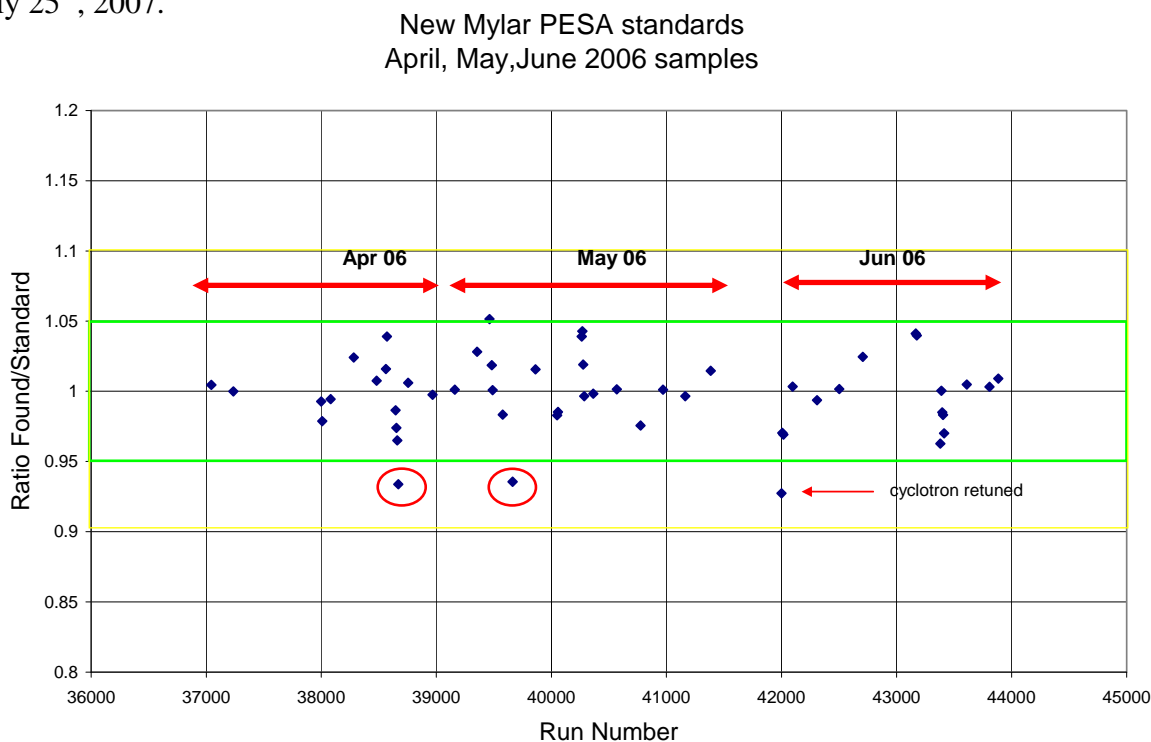


Figure 4. PESA standards for Apr-Jun 2006 samples

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
intercept	slope	full scale	from Jun05		intercept	slope	full scale	from Oct05		intercept	slope	full scale	from Jun05
Apr-06					-0.0358	0.01716	8.750	0.00%		-0.08626	0.036033	18.362	-0.03%
May-06	-0.0377	0.01667	8.497	0.08%						-0.08789	0.036027	18.358	-0.05%
Jun-06					-0.0358	0.01716	8.750	0.00%		-0.07943	0.036008	18.357	-0.06%

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 Apr 2006 samples, 24 MEVEX, OLYMX, PMRFX filters from Sep 2005 were reanalyzed four times. For May 2006 samples, 29 MEVEX, OLYMX, PMRFX filters from Nov 2005 were reanalyzed three times. Similarly, reanalyses for June 2006 samples were performed on 28 SAFOX, SAMAX AND TRCRX filters from Dec 2005 three times. Figure 5 compares the original and repeat analyses.

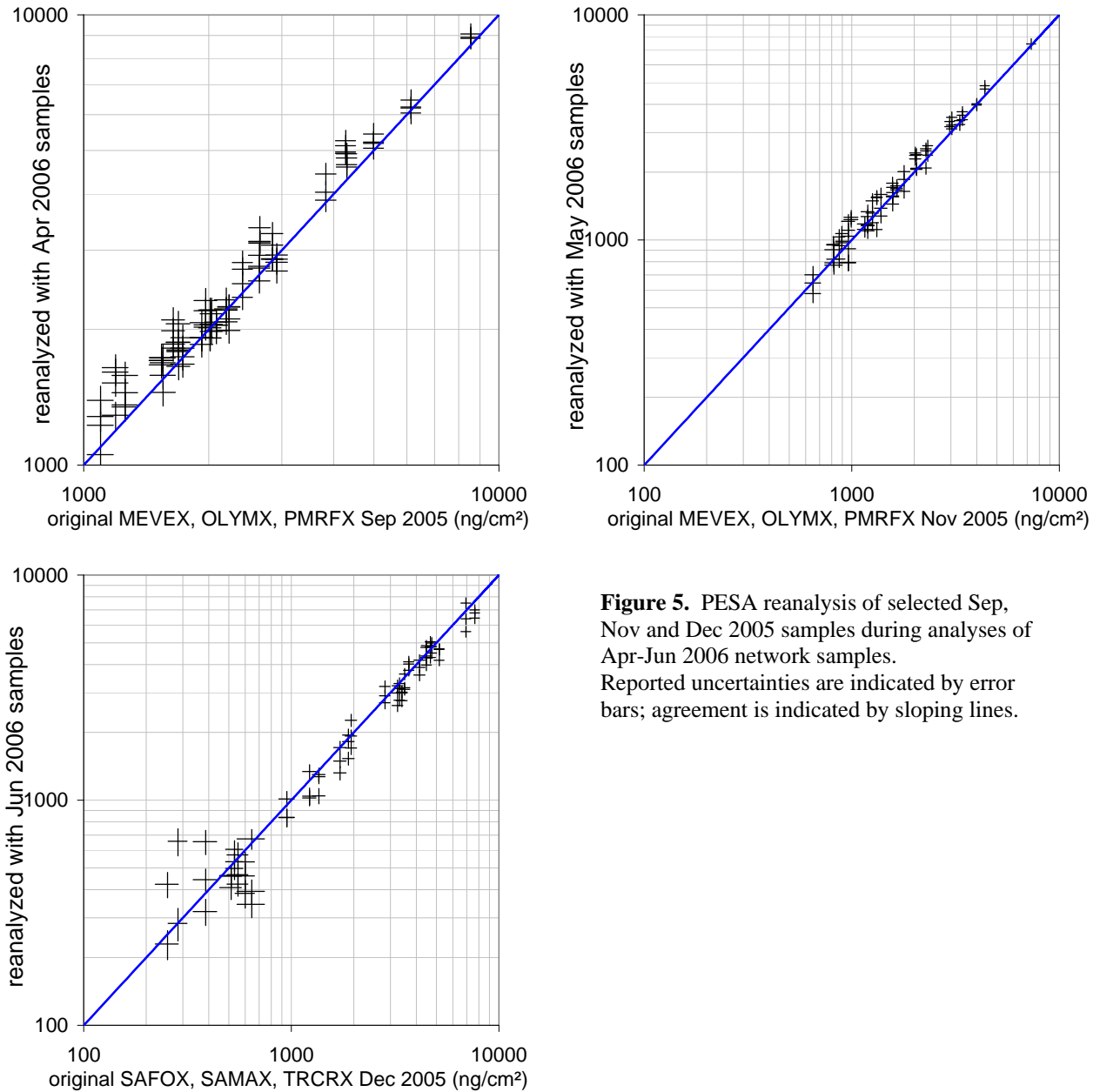


Figure 5. PESA reanalysis of selected Sep, Nov and Dec 2005 samples during analyses of Apr-Jun 2006 network samples. Reported uncertainties are indicated by error bars; agreement is indicated by sloping lines.

XRF reanalyses were performed on the same fixed collection of samples employed in previous reports. The collection, denoted trays REANAL1 and REANAL2, was reanalyzed with the XRF-Mo and Cu-Vac2 systems approximately monthly during analyses of Apr-Jun 2006 samples. The trays were not reanalyzed on the Cu-Vac1 system during analysis of May 2006 samples, so the figures 8 and 9 show the available reanalysis results before and after period of interest. All 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. As in previous reports, the original run (Nov06) on Cu-Vac2 serves as a baseline for the newer system. The average ratio of observed deviations (from mean or original) 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.

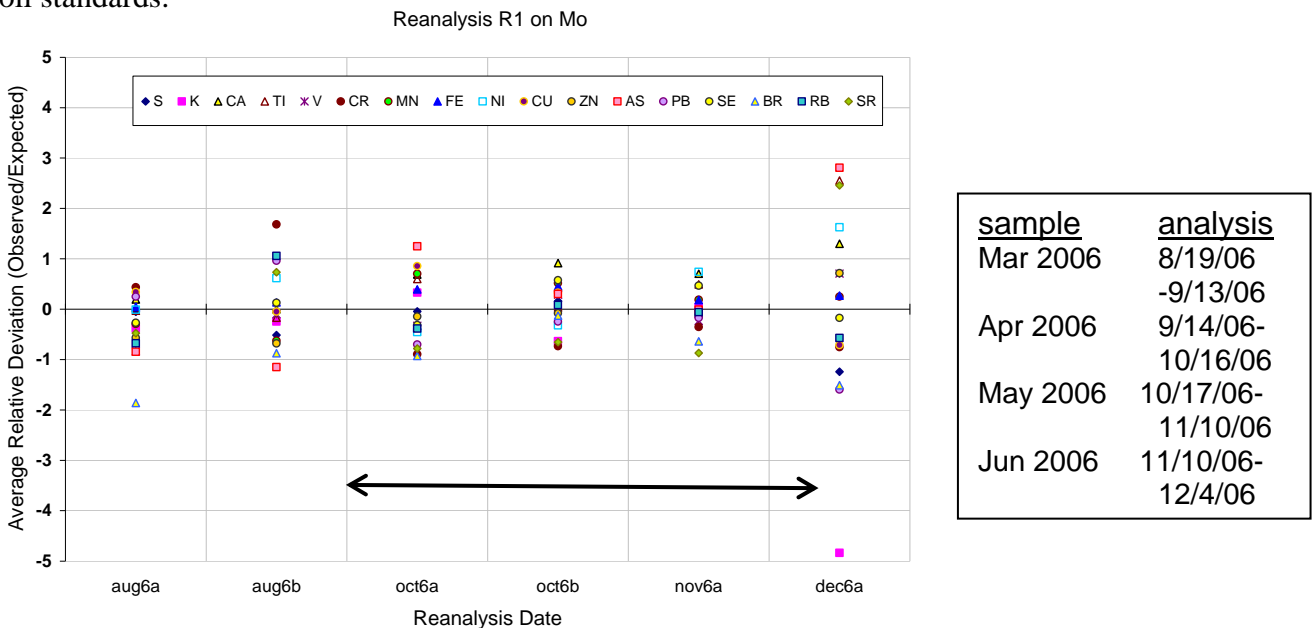


Figure 6. Reanalyses of REANAL1 samples on XRF-Mo system. Horizontal arrow indicates when Apr-Jun 2006 network samples were analyzed.

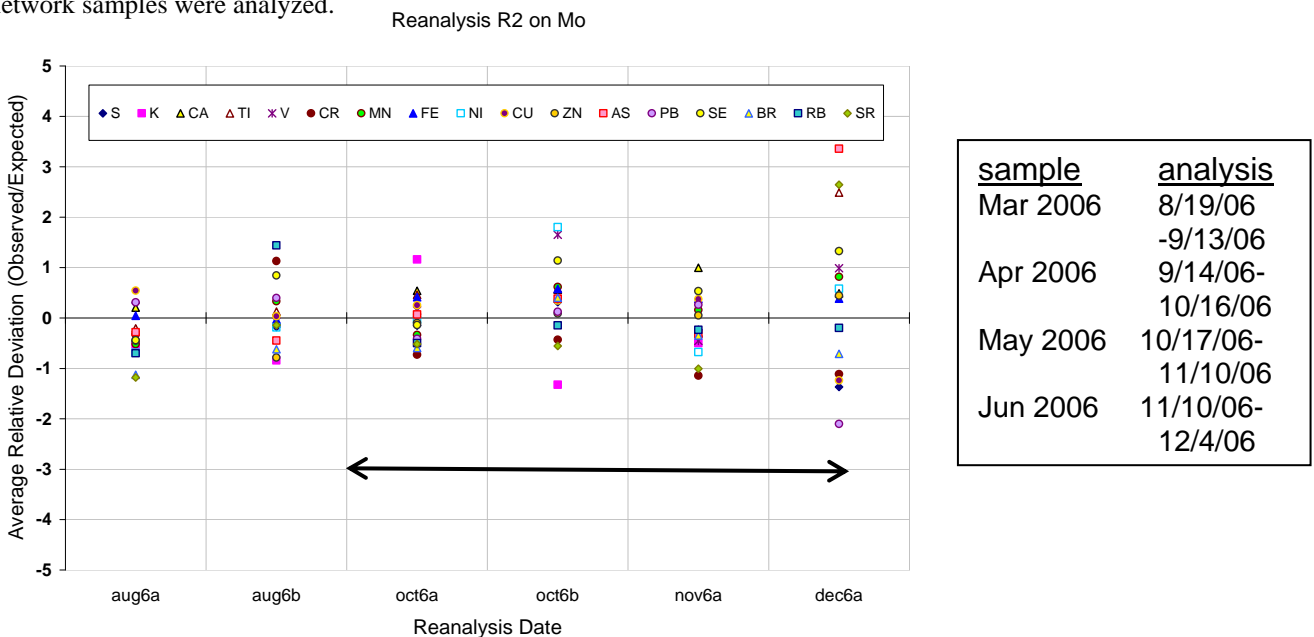
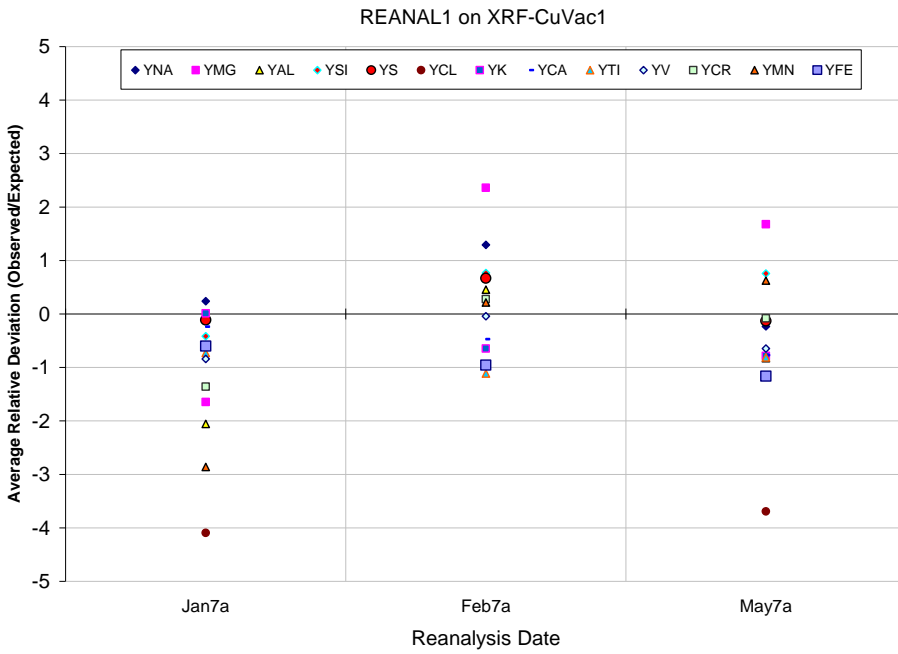
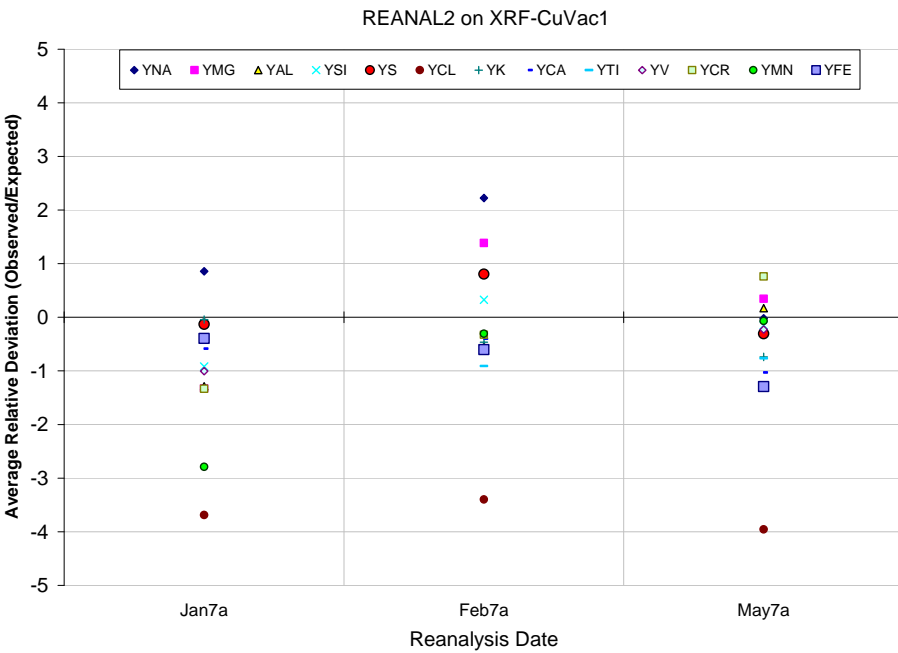


Figure 7. Reanalyses of REANAL2 samples on XRF-Mo system. Horizontal arrow indicates when Apr-Jun 2006 network samples were analyzed.



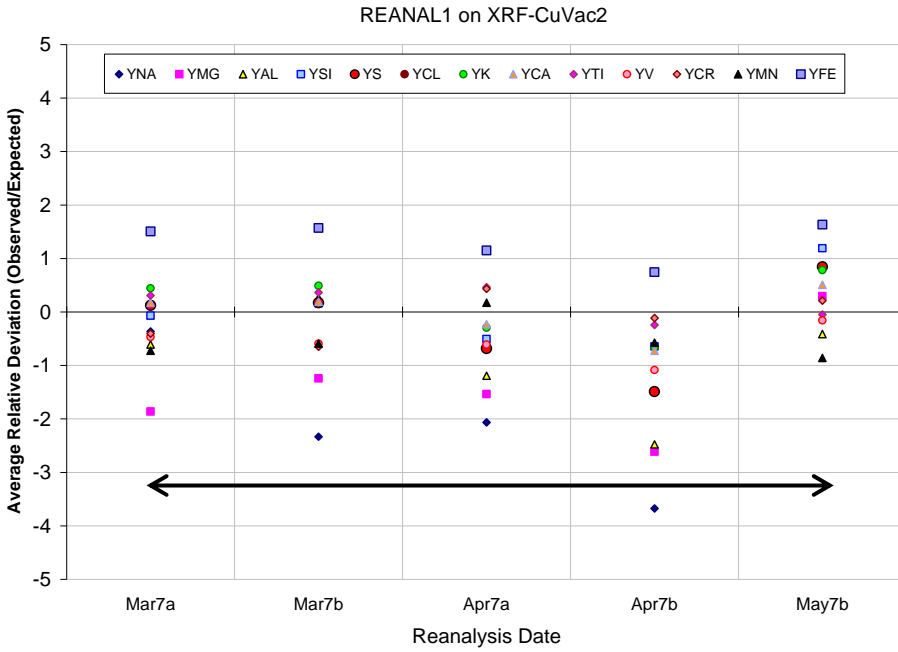
sample	analysis
Mar 2006	2/21/07 – 3/18/07
May 2006	3/18/07- 4/17/07

Figure 8. Reanalyses of REANAL1 samples on XRF-Cu1 system.



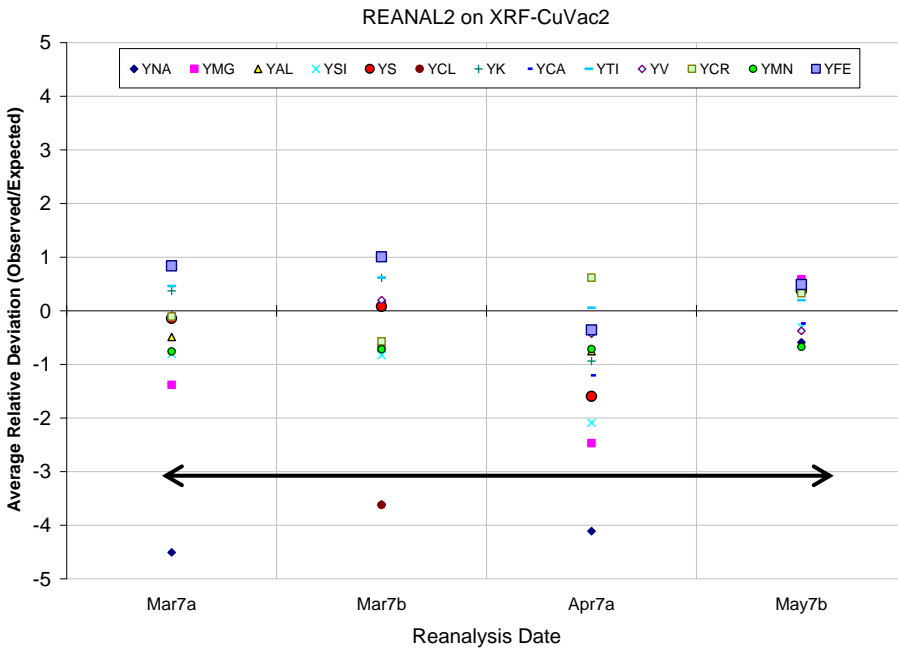
sample	analysis
Mar 2006	2/21/07 – 3/18/07
May 2006	3/18/07- 4/17/07

Figure 9. Reanalyses of REANAL2 samples on XRF-Cu1 system.



sample	analysis
Jan 2006	2/1/07
	-3/2/07
Apr 2006	3/8/07-
	4/3/07
Jun 2006	4/20/07-
	5/13/07

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



sample	analysis
Jan 2006	2/1/07
	-3/2/07
Apr 2006	3/8/07-
	4/3/07
Jun 2006	4/20/07-
	5/13/07

Figure 11. Reanalyses of REANAL2 samples on XRF-Cu2 system. Horizontal arrow indicates when Apr and Jun 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 Apr-Jun 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.

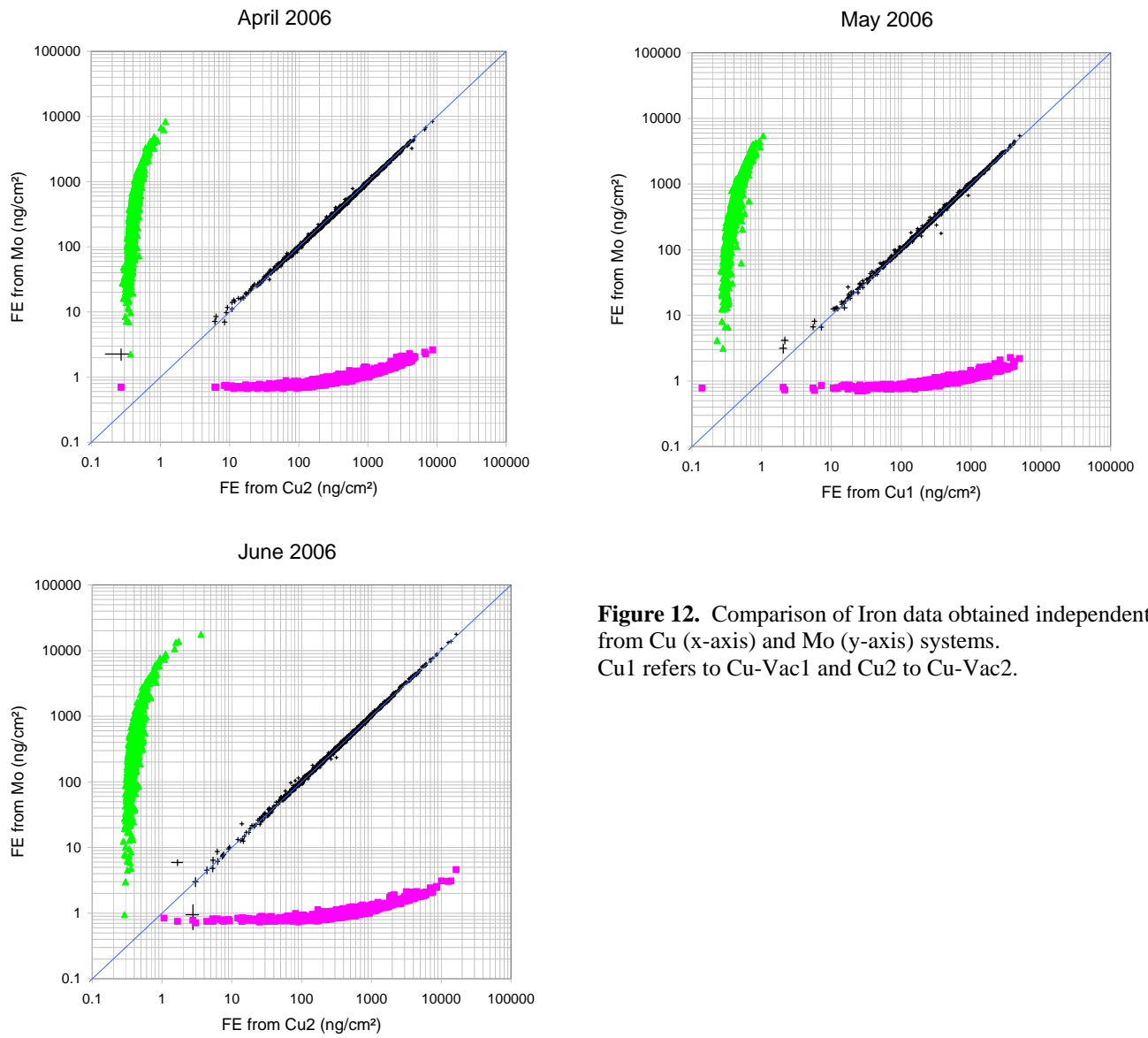


Figure 12. Comparison of Iron data obtained independently from Cu (x-axis) and Mo (y-axis) systems. Cu1 refers to Cu-Vac1 and Cu2 to Cu-Vac2.

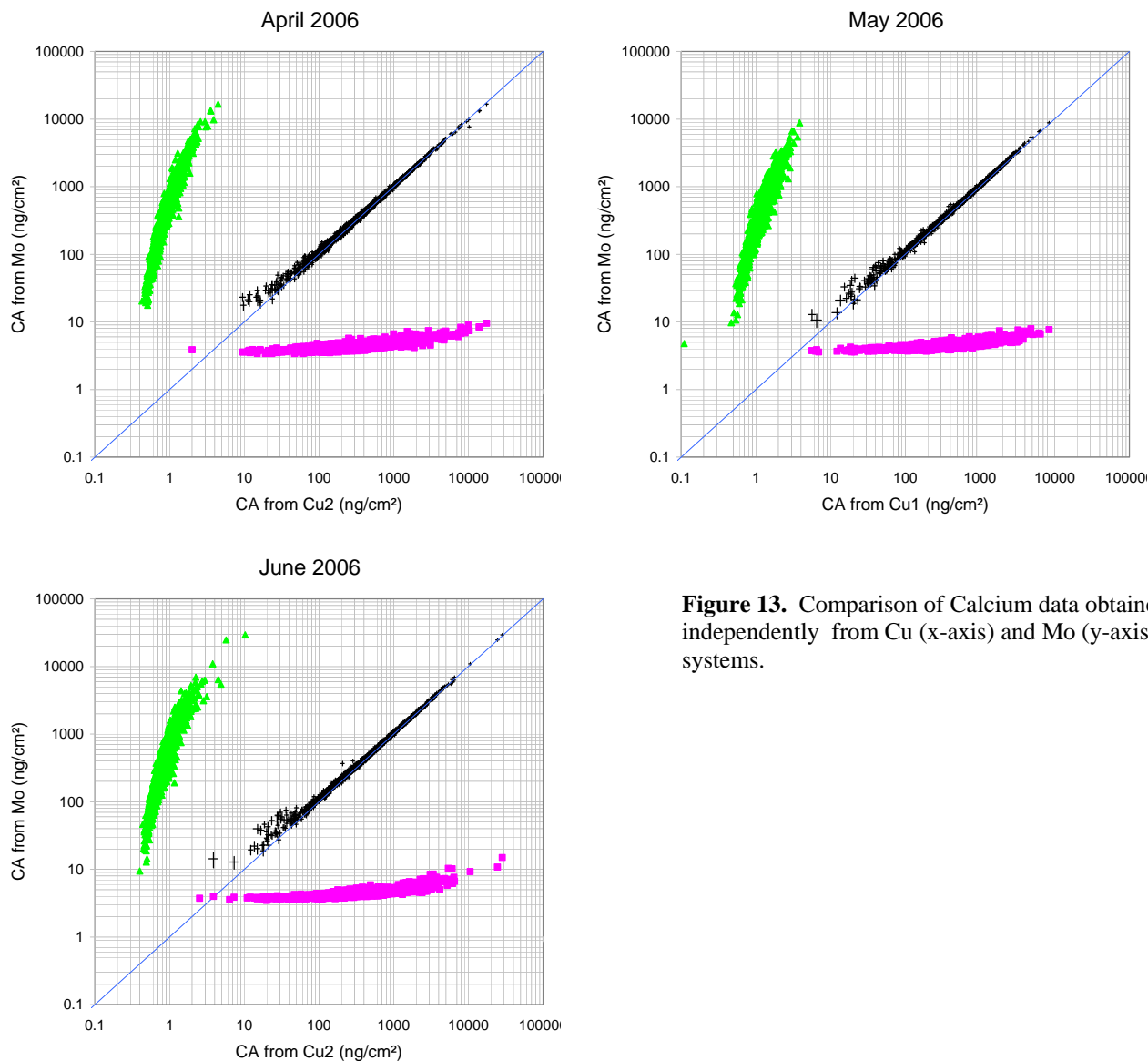


Figure 13. Comparison of Calcium data obtained independently from Cu (x-axis) and Mo (y-axis) systems.

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 field blanks for April 2006, 21 field blanks for May 2006 and 19 field blanks for June 2006 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 April, May and June 2006. Loadings are considered well measured when their uncertainties are less than 10%. Thus, the 95th percentile field blank loading for Fe (Apr 2006 samples) was at or above about 0.5% of all well measured sample loadings on the Cu system (0.2% on the Mo system).

Cu anode

Apr 2006	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%	0.1%	0.3%	0.2%	0.0%	0.0%	0.0%	0.5%
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%	0.1%
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%	0.0%

The field blanks data from Cu system for May and June 2006 samples are not yet available.

Mo anode

Apr 2006	Fe	Ni	Cu	Zn	As	Pb	Se	Br	Rb	Sr	Zr
95 %ile	0.2%	0.0%	0.0%	28.8%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%
90 %ile	0.2%	0.0%	0.0%	28.1%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%
75 %ile	0.0%	0.0%	0.0%	5.2%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%
May 2006											
95 %ile	1.4%	0.0%	0.0%	48.5%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%
90 %ile	1.0%	0.0%	0.0%	29.3%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%
75 %ile	0.0%	0.0%	0.0%	11.5%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%
Jun 2006											
95 %ile	1.4%	0.0%	0.0%	43.5%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%
90 %ile	0.7%	0.0%	0.0%	33.7%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%
75 %ile	0.2%	0.0%	0.0%	1.7%	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 Zn, as noted in previous reports.