

Data report for elemental analysis of IMPROVE samples collected during
July, August, September 2006
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SUMMARY

This report summarizes the quality assurance performed during elemental analysis of the IMPROVE samples collected in July, August and September 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.

Jul and Sep 2006 samples were analyzed on Cu-Vac1 and Aug 2006 samples were analyzed on Cu-Vac2. Both Cu systems were recalibrated on June 12th, 2007 (Aug and Sep 2006 samples) to reflect repairs and maintenance performed on both systems..

The detector in the Mo system was replaced on Jan 29th, 2007 (Sep 2006 samples), and the system was recalibrated. During the analysis of Jul-Sep 2006 samples all routine calibration checks on the Mo system for all reported elements were within criteria. (As noted in previous reports, higher variations were observed for S, which is not reported from this system).

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 July, August and September 2006 data

XRF and PESA analyses were carried out on 1751 samples collected in July 2006, 1569 samples collected in August 2006 and 1619 samples collected in September 2006. All samples were analyzed between 4 December 2006 and 27 February 2007 on the Mo-anode XRF system, between 20 April 2007 and 9 July 2007 on Cu-Vac1, between 16 May 2007 and 7 July 2007 on Cu-Vac2, and on 5/22-23/07 and 6/6-7/07 (Jul06 samples) and 7/23-26/07 (Aug06 and Sep06 samples) on the PESA system.

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

PESA					
Z	element	7-2006	8-2006	9-2006	6-2006
1	H	99%	100%	98%	100%

Cu-anode XRF					
Z	element	7-2006	8-2006	9-2006	6-2006
11	Na	37%	67%	36%	63%
12	Mg	32%	47%	39%	71%
13	Al	86%	83%	77%	93%
14	Si	97%	98%	94%	100%
15	P	1%	1%	2%	3%
16	S	100%	100%	100%	100%
17	Cl	9%	12%	11%	15%
19	K	100%	100%	99%	100%
20	Ca	100%	100%	100%	100%
22	Ti	99%	99%	97%	99%
23	V	93%	95%	85%	97%
24	Cr	52%	64%	55%	82%
25	Mn	99%	99%	99%	100%
26	Fe	100%	100%	100%	100%

Mo-anode XRF					
Z	element	7-2006	8-2006	9-2006	6-2006
28	Ni	57%	60%	51%	58%
29	Cu	96%	95%	93%	96%
30	Zn	100%	100%	100%	100%
33	As	36%	33%	48%	58%
34	Se	93%	93%	93%	91%
35	Br	100%	100%	100%	100%
37	Rb	73%	68%	78%	80%
38	Sr	97%	97%	96%	97%
40	Zr	16%	16%	26%	20%
82	Pb	100%	100%	100%	100%

Table 1. Percentage of cases in which the element was detected on each system. June 2006 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 third 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

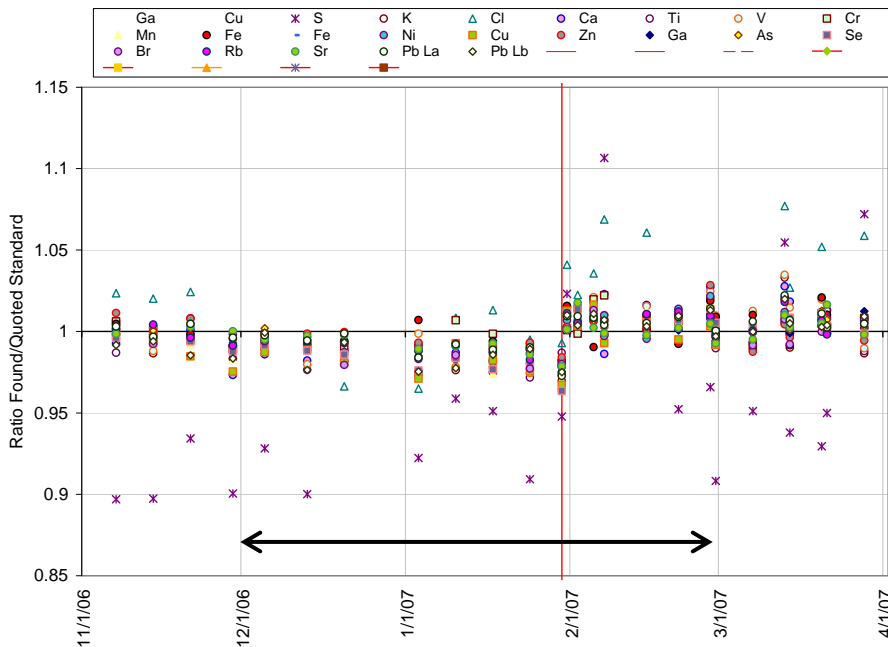
Table 2. Micromatter standard foils used for all analyses. Standards (*) with variable stoichiometry.

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, with exception of Zr, As and Zn. For these elements, where no standards are available or the standards are [non stoichiometric](#), the calibration factor is obtained by plotting instrument response versus atomic number (or energy), generating the smooth curve and interpolating the factor for the specific element of interest. This change in calibration procedure affects samples from September 2006.

During the analyses of Jul-Sep 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.

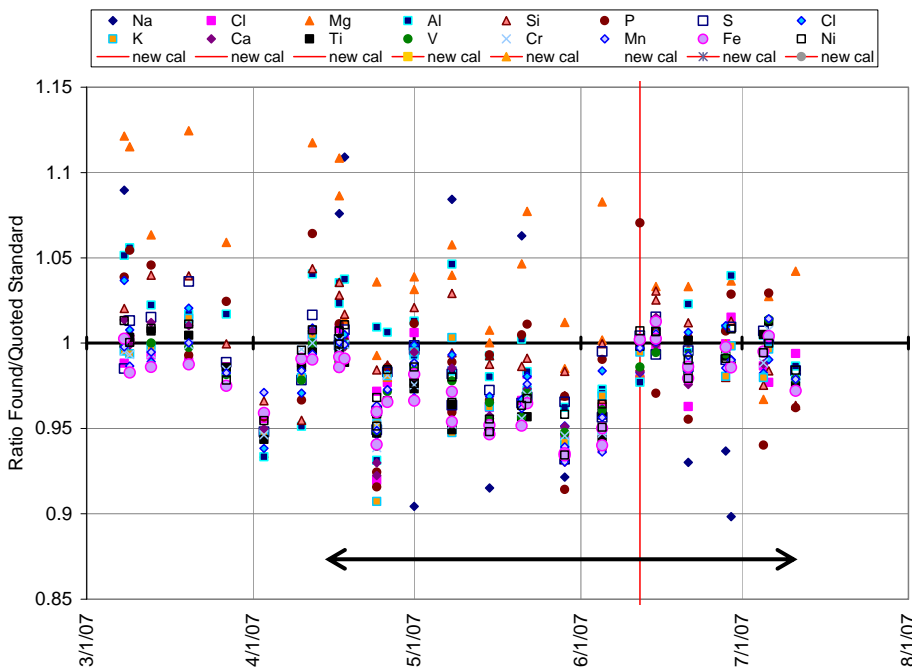
Figures 1 to 3 below show the calibration checks and system recalibrations performed during the period in which samples of interest were analyzed on each system. The analysis dates for each

sample month are listed in the legends. June 2006 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.



<u>sample</u>	<u>analysis</u>
Jun 2006	11/10/06- 12/4/06
Jul 2006	12/4/06- 1/3/07
Aug 2006	1/3/07- 1/29/07
Sep 2006	2/3/07- 2/27/07

Figure 1. Mo XRF system performance chart based on standards



<u>sample</u>	<u>analysis</u>
May 2006	3/18/07- 4/17/07
Jul 2006	4/20/07- 5/18/07
Sep 2006	5/20/07- 7/9/07

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

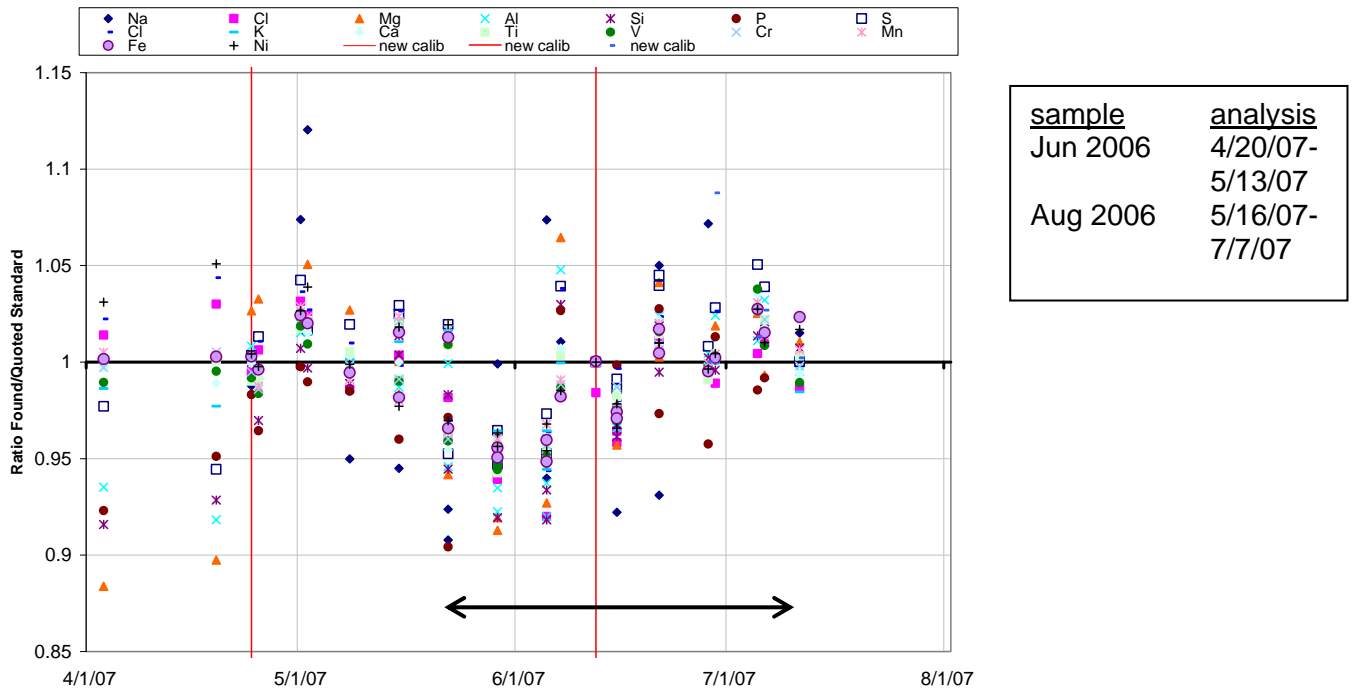


Figure 3. XRF Cu-Vac2 system performance chart based on standards.

None of the standards ratios exceeded acceptance limits during the analysis of Jul-Sep 2006 samples on the Mo system. The system was recalibrated on 1/29/07 because the detector was replaced,. At this time the above-noted new calibration procedure for non stoichiometric standards was introduced. The calibration factors for Zr (standard not available), As and Zn were calculated based on the curve best fitting the instrumental response (energy vs. calibration factor) for all elements of interest.

July and September 2006 samples were analyzed on the XRF Cu-Vac1 system and August 2006 samples were analyzed on the XRF Cu-Vac2 system. Both systems were recalibrated on June 12th, 2007 to reflect repairs and maintenance performed on both systems. Because of an observed drop in standards ratios (Figure 3), all the samples analyzed between May 22nd, 2007 and June 12th, 2007 were reanalyzed.

Eight Mylar foils (thicknesses 2.5, 3.2, 3.5 and 9.3 microns) were used for calibrations and calibration checks of PESA system. Due to damage, the standard foil #2 (19.8 ug/cm²) was replaced with another 3.2 micron foil (21.50ug/cm²) on July 23th, 2007 (starting with Aug 2006 network samples). 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) 21.50	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 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 Jul-Sep 2006 samples.

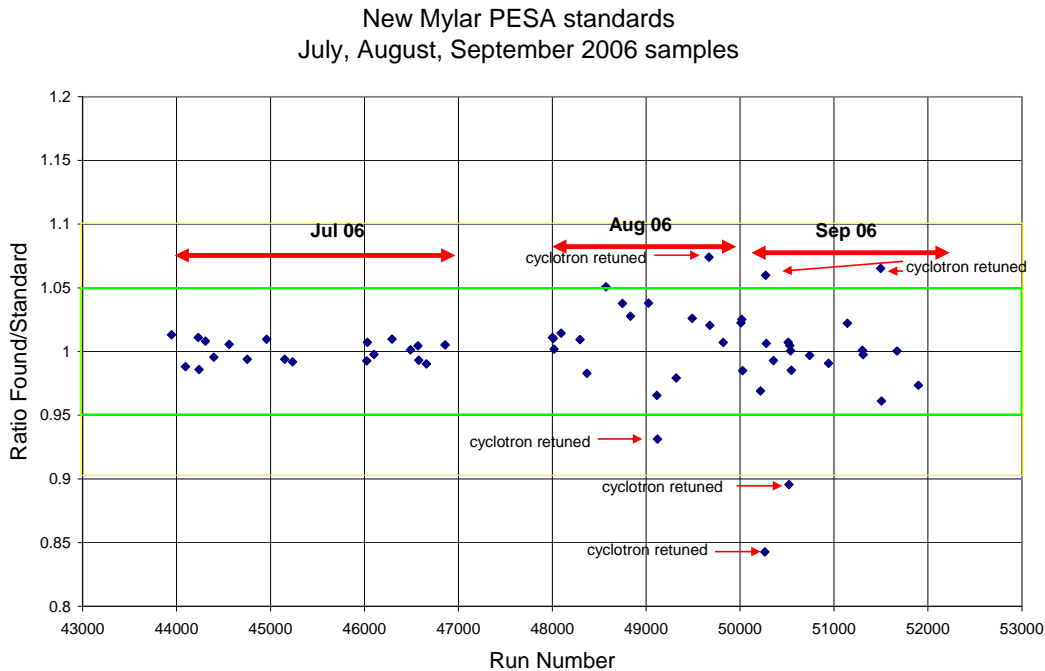


Figure 4. PESA standards for Jul-Sep 2006 samples

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 Mo system. For Cu systems, the energy calibrations were performed only when determined by spectroscopist to be necessary. 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 Jun05	
Jul-06	-0.0386	0.01665	8.488	-0.03%						-0.07943	0.036008	18.357	-0.06%	
Aug-06					-0.0358	0.01716	8.750	0.00%		-0.08087	0.036024	18.363	-0.02%	
Sep-06	-0.0386	0.01665	8.488	-0.03%						-0.0581	0.03567	18.205	-0.89%	

Note, the higher change in energy calibration for Sep 2006 samples on Mo (0.89%) does reflect the change of detector in the Mo system.

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 Jul 2006 samples, 28 MEVEX, OLYMX, PMRFX filters from Jan 2006 were reanalyzed four times. For Aug 2006 samples, 30 SAFOX, SAMAX, TRCRX from Feb 2006 were reanalyzed twice. Similarly, reanalyses for Sep 2006 samples were performed on 29 SAFOX, SAMAX AND TRCRX filters from Apr 2006 three times. Figure 5 compares the original and repeat analyses.

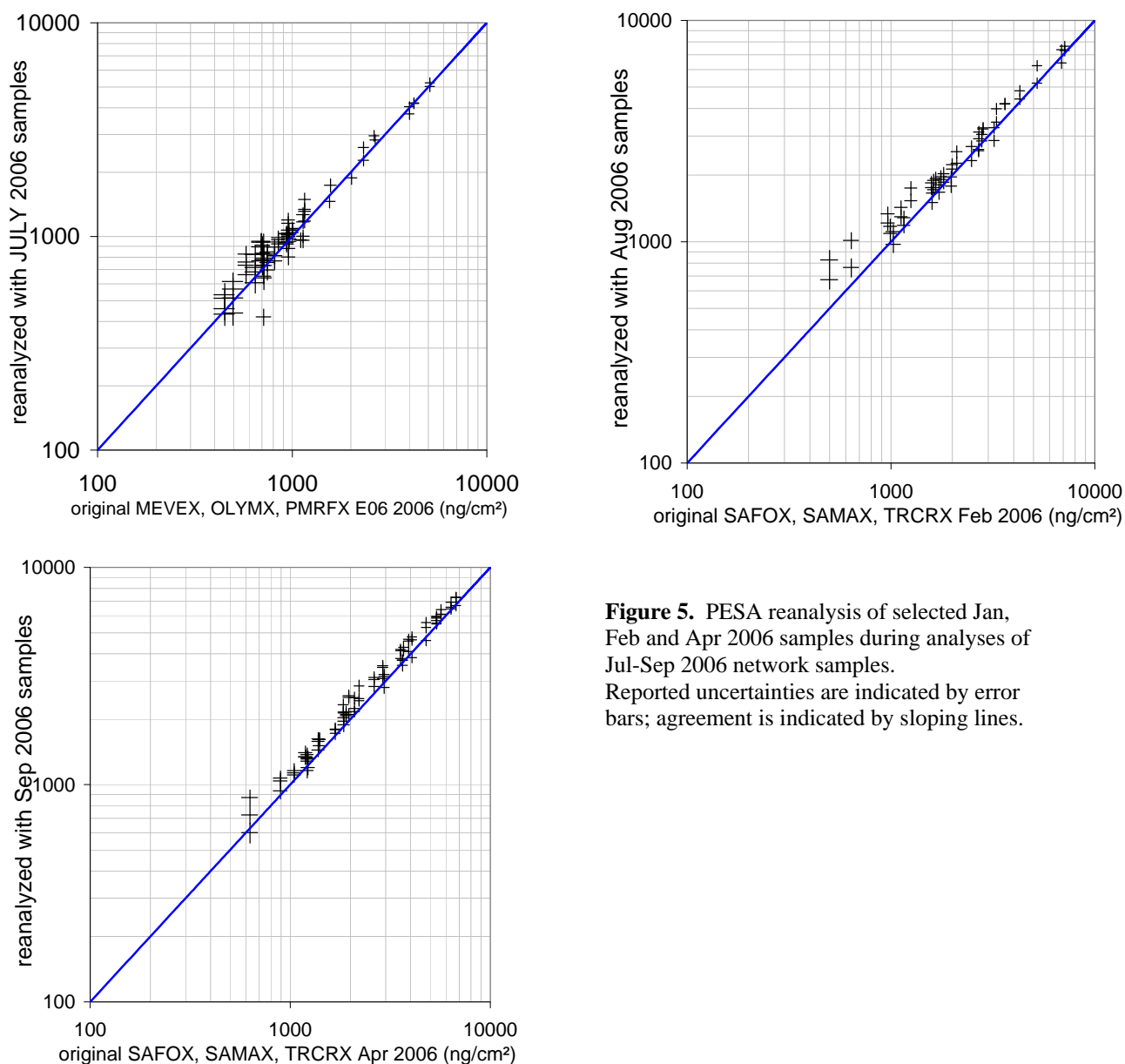
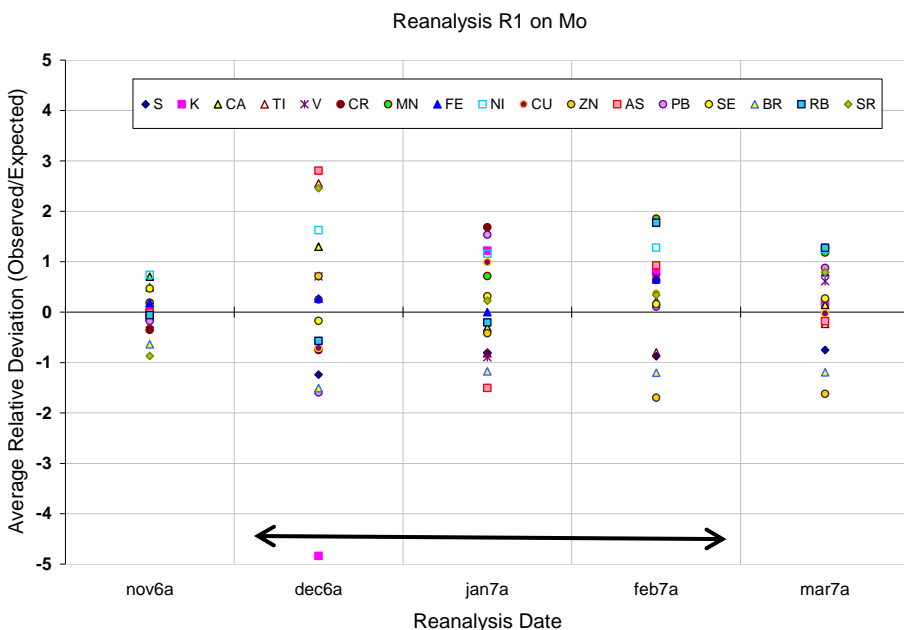


Figure 5. PESA reanalysis of selected Jan, Feb and Apr 2006 samples during analyses of Jul-Sep 2006 network samples. Reported uncertainties are indicated by error bars; agreement is indicated by sloping lines.

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

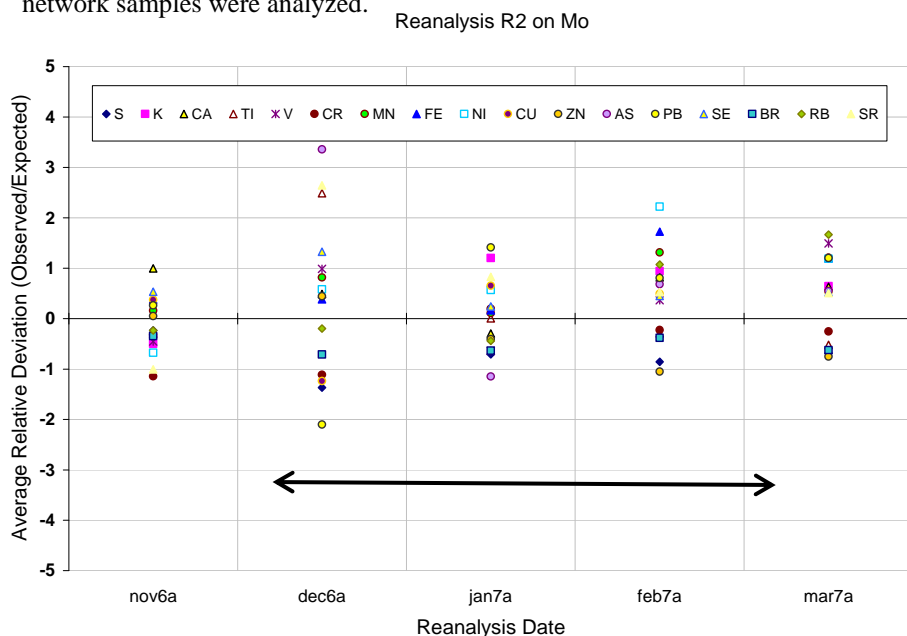
approximately monthly (bi-monthly on Cu-Vac1) on the systems during 2006/2007 analyses of Jul-Sep 2006 samples. All results are summarized in the figures 6-11 below.

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. At present, sample reanalysis is used as a qualitative check on system performance.



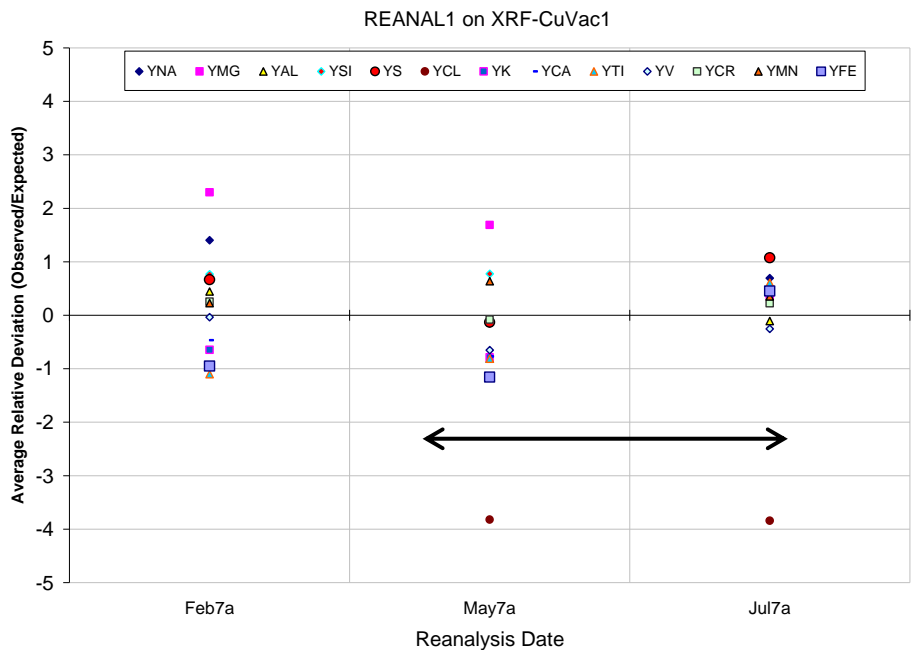
sample	analysis
Jun 2006	11/10/06- 12/4/06
Jul 2006	12/4/06- 1/3/07
Aug 2006	1/3/07- 1/29/07
Sep 2006	2/3/07- 2/27/07

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



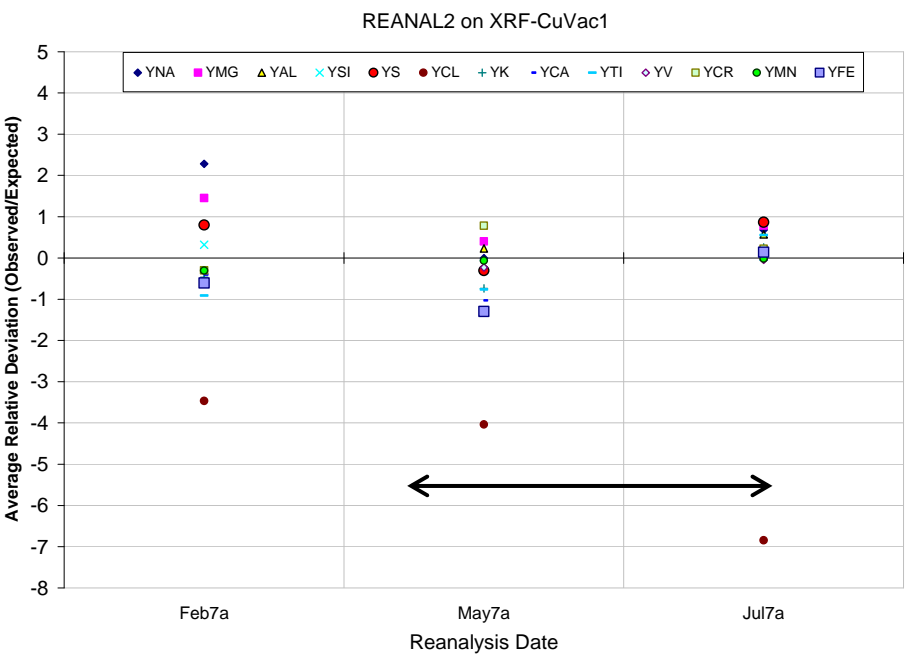
sample	analysis
Jun 2006	11/10/06- 12/4/06
Jul 2006	12/4/06- 1/3/07
Aug 2006	1/3/07- 1/29/07
Sep 2006	2/3/07- 2/27/07

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



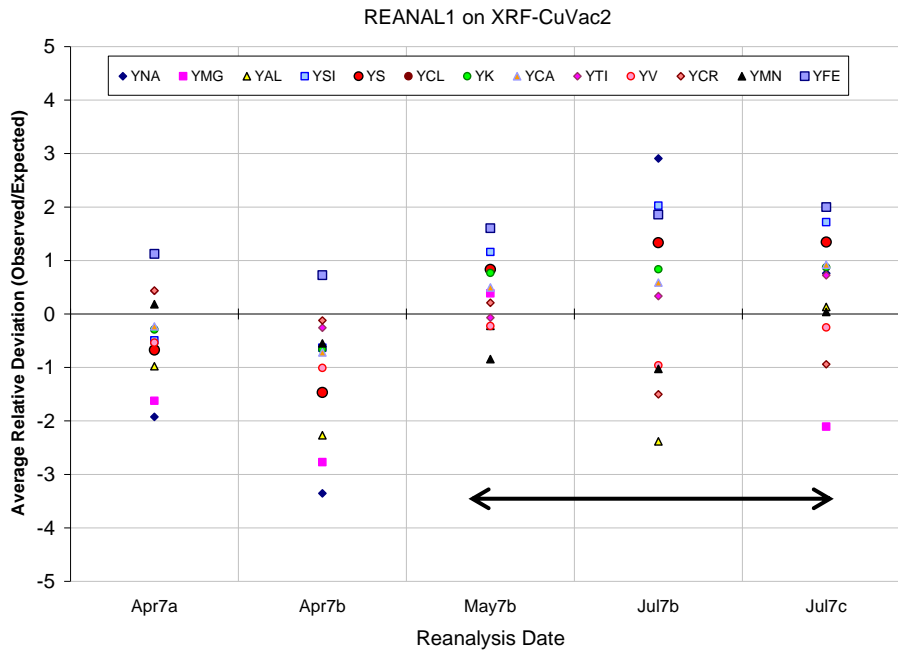
<u>sample</u>	<u>analysis</u>
May 2006	3/18/07-4/17/07
Jul 2006	4/20/07-5/18/07
Sep 2006	5/20/07-7/9/07

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



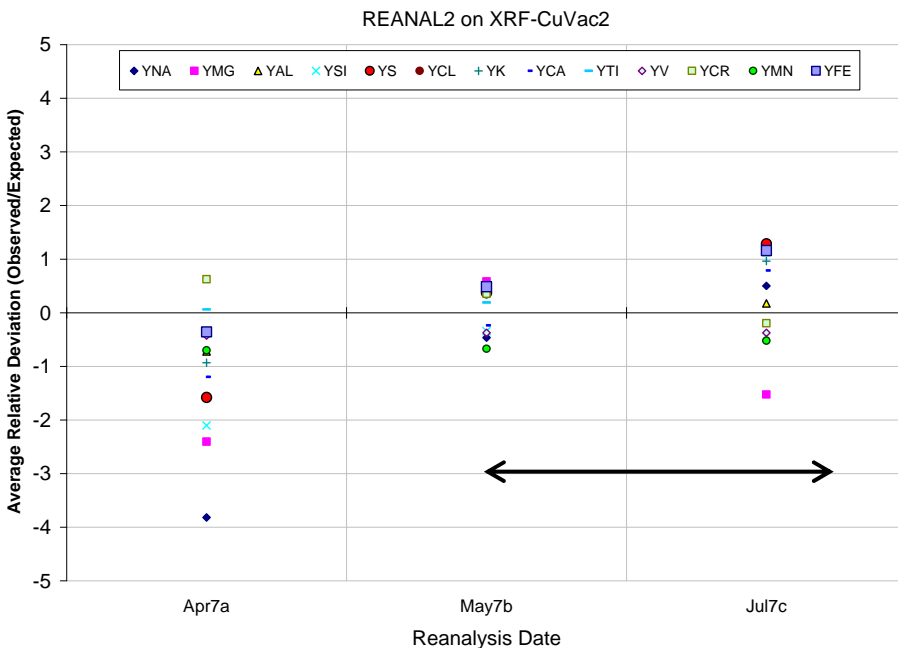
<u>sample</u>	<u>analysis</u>
May 2006	3/18/07-4/17/07
Jul 2006	4/20/07-5/18/07
Sep 2006	5/20/07-7/9/07

Figure 9. Reanalyses of REANAL2 samples on XRF-Cu1 system. Horizontal arrow indicates when Jul and Sep 2006 network samples were analyzed.



sample	analysis
Jun 2006	4/20/07- 5/13/07
Aug 2006	5/16/07- 7/7/07

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



sample	analysis
Jun 2006	4/20/07- 5/13/07
Aug 2006	5/16/07- 7/7/07

Figure 11. Reanalyses of REANAL2 samples on XRF-Cu2 system. Horizontal arrow indicates when Aug 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 Jul-Sep 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.

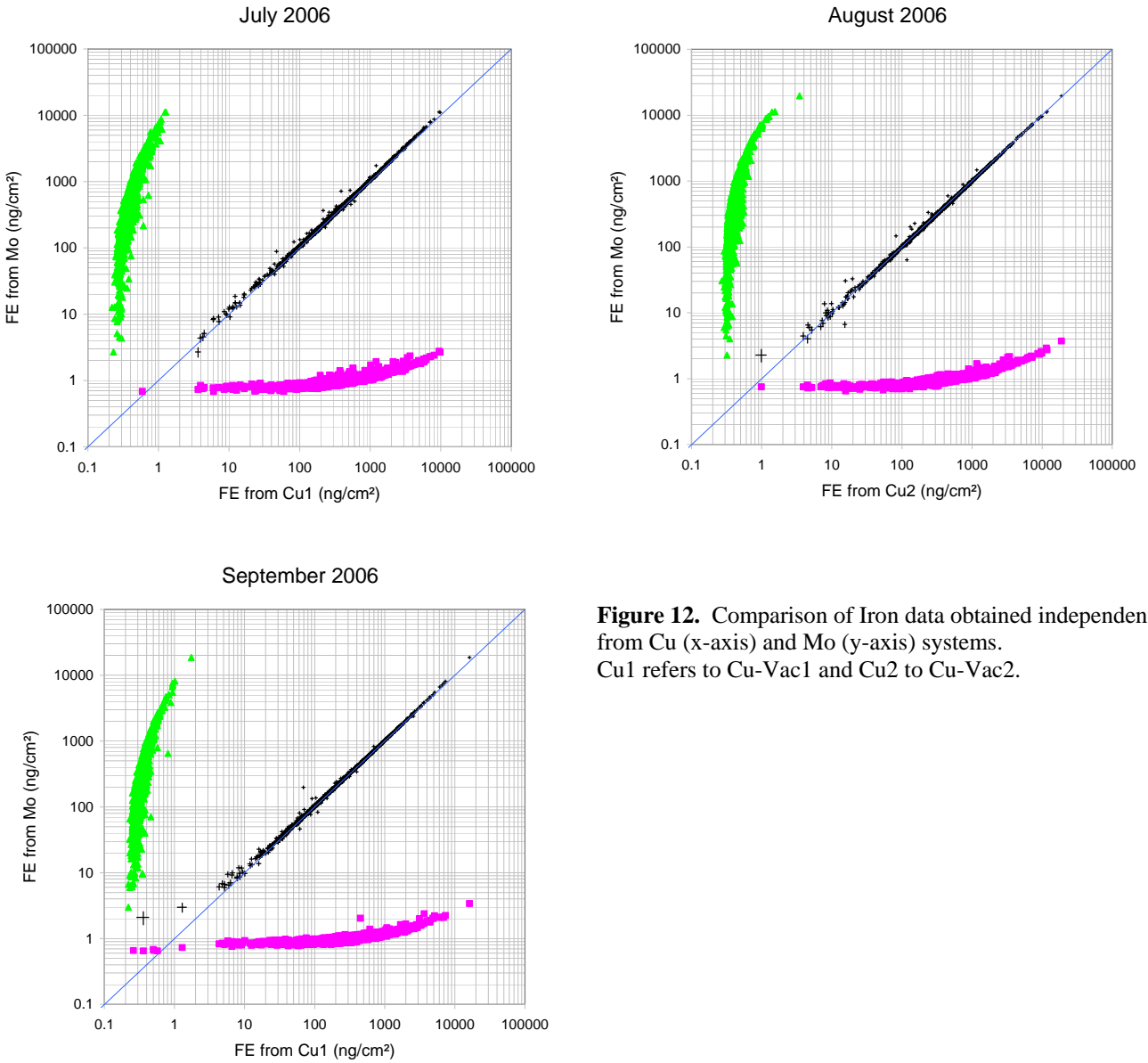


Figure 12. Comparison of Iron data obtained independently from Cu (x-axis) and Mo (y-axis) systems. Cu1 refers to Cu-Vac1 and Cu2 to Cu-Vac2.

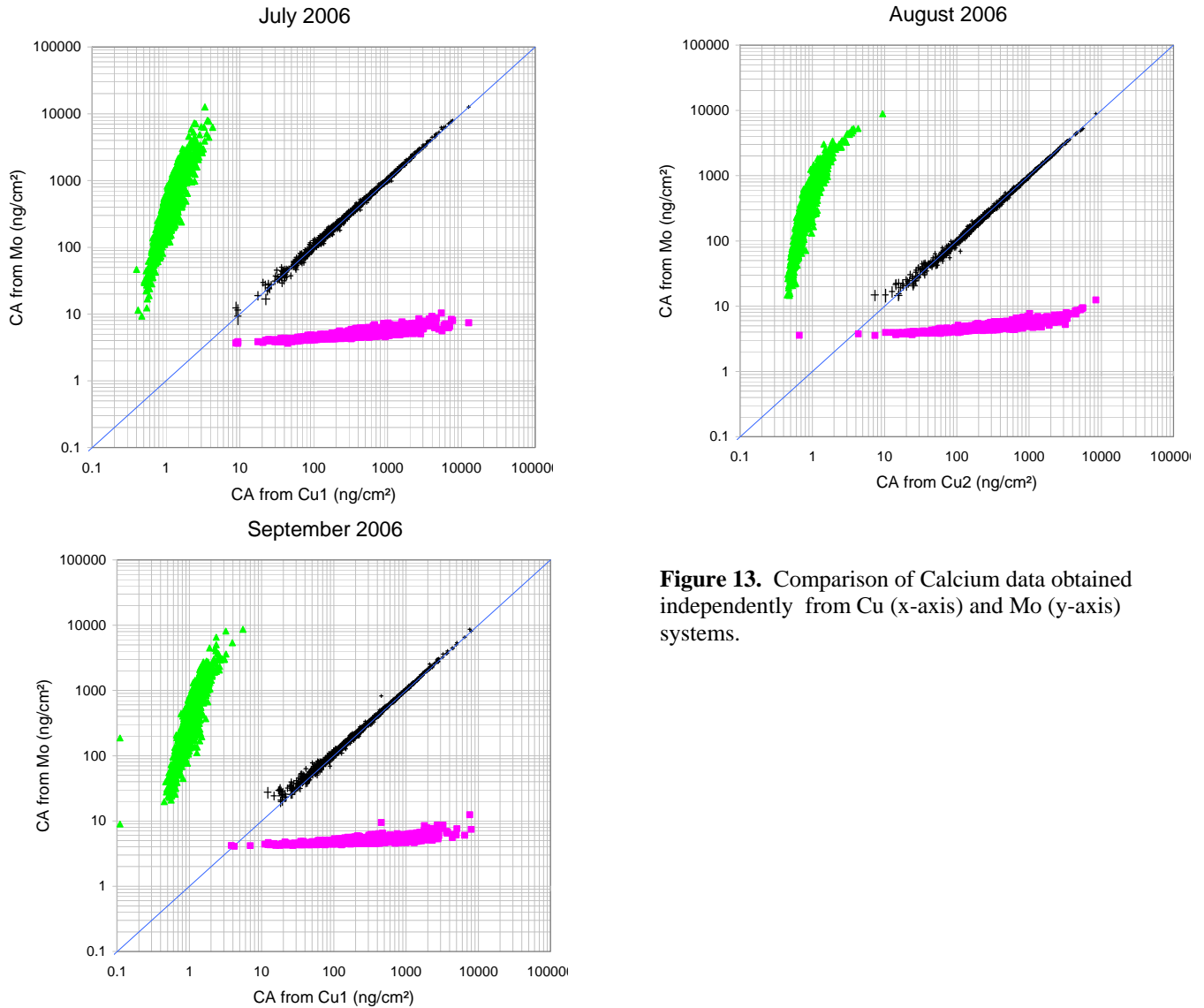


Figure 13. Comparison of Calcium data obtained independently from Cu (x-axis) and Mo (y-axis) systems.

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

Fifteen field blanks for July 2006, 21 field blanks for August 2006 and 13 field blanks for September 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 July, August and September 2006. Loadings are considered well measured when their uncertainties are less than 10%. Thus, the 95th percentile field blank loading for

Fe (Sep 2006 samples) was at or above about 3.7% of all well measured sample loadings on Cu system (3.0% on Mo system).

Cu anode

Jul 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%	0.0%	0.1%	0.0%	0.0%	0.0%	0.0%	0.4%
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%	0.3%
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%
Aug 2006	Na	Mg	Al	Si	P	S	Cl	K	Ca	Ti	V	Cr	Mn	Fe
95 %ile	0.0%	0.0%	0.0%	0.5%	0.0%	0.0%	0.0%	0.0%	0.1%	0.1%	0.0%	0.0%	0.0%	1.2%
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%	1.2%
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%
Sep 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%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	3.7%
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%	0.9%
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%	0.1%

Mo anode

Jul 2006	Fe	Ni	Cu	Zn	As	Pb	Se	Br	Rb	Sr	Zr
95 %ile	0.5%	0.0%	0.0%	15.6%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%
90 %ile	0.3%	0.0%	0.0%	6.9%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%
75 %ile	0.0%	0.0%	0.0%	1.5%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%
Aug 2006	Fe	Ni	Cu	Zn	As	Pb	Se	Br	Rb	Sr	Zr
95 %ile	1.0%	0.0%	0.0%	60.1%	0.0%	0.6%	0.0%	0.0%	0.0%	0.0%	0.0%
90 %ile	0.6%	0.0%	0.0%	17.1%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%
75 %ile	0.0%	0.0%	0.0%	5.1%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%
Sep 2006	Fe	Ni	Cu	Zn	As	Pb	Se	Br	Rb	Sr	Zr
95 %ile	3.0%	0.0%	0.0%	3.3%	0.0%	1.5%	0.0%	0.0%	0.0%	0.0%	0.0%
90 %ile	0.6%	0.0%	0.0%	3.1%	0.0%	0.8%	0.0%	0.0%	0.0%	0.0%	0.0%
75 %ile	0.0%	0.0%	0.0%	0.0%	0.0%	0.2%	0.0%	0.0%	0.0%	0.0%	0.0%

Field blank loadings are negligible compared to samples for all elements with the exception of Zn, as noted in previous reports.