

Data report for elemental analysis of IMPROVE samples collected during
OCTOBER, NOVEMBER, DECEMBER 2005
UC Davis

SUMMARY

This report summarizes the quality assurance performed during elemental analysis of the IMPROVE samples collected in October, November and December of 2005. 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. Two significant changes were introduced in the XRF analysis of October - December 2005 samples. One was the placing into operation of an additional Cu-anode system, as described in a [data advisory](#). The added system has already increased analytical throughput. The second change was to the calibration procedures for the Mo-anode system ; the current used for single-element foils was raised from 2.6 mA to 10 mA to better match the livetimes encountered with actual samples.

Section 1. Overview of Elemental Analysis Systems

The elements Na and Mg (considered qualitative only) and Al to Fe are reported from an XRF system with a Cu-anode grounded X-ray tube. This system operates under vacuum (< 350 microns Hg). There are now two Cu systems, which will be distinguished hereafter as Cu-Vac1 and Cu-Vac2. Data acceptance is based solely on each system's performance for single-element calibration foils; as the [data advisory](#) noted, the systems exhibit some detectable differences for actual samples. All July 2005 samples were analyzed on both systems, with results that are shown in Attachment 1.

Cu-Vac1 was used to analyze the samples from November 2005, and Cu-Vac2 was used to analyze the samples from October 2005 and December 2005. All October-December 2005 samples were analyzed for 1000 seconds at 10 mA and 20 kV (default settings for sample analysis).

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 October, November and December 2005 data

XRF and PESA analyses were carried out on 1851 samples collected in October 2005, 1637 samples collected in November 2005 and 1688 samples collected in December 2005. All samples collected in the fourth quarter of 2005 were analyzed between 6 April 2006 and 29 June 2006 on the Mo-anode XRF system, between 4 December 2006 and 12 January 2007 on the Cu-anode XRF system (Cu-Vac1), between 2 November 2006 and 17 January 2007 on Cu-Vac2, and on December 20th, 2006 and from January 16th to January 18th, 2007 on the PESA system. Table 1 summarizes the fourth quarter 2005 detection rates on the three systems, with rates for September 2005 included for comparison.

PESA					
Z	element	10-2005	11-2005	12-2005	9-2005
1	H	99%	99%	99%	100%

Cu-anode XRF					
Z	element	10-2005	11-2005	12-2005	9-2005
11	Na	56%	31%	62%	40%
12	Mg	37%	17%	31%	20%
13	Al	76%	61%	65%	78%
14	Si	96%	93%	92%	94%
15	P	3%	1%	3%	1%
16	S	99%	100%	100%	100%
17	Cl	14%	12%	15%	9%
19	K	99%	100%	99%	100%
20	Ca	98%	100%	99%	100%
22	Ti	96%	95%	92%	98%
23	V	88%	81%	78%	94%
24	Cr	41%	37%	50%	42%
25	Mn	95%	94%	93%	98%
26	Fe	99%	100%	100%	100%

Mo-anode XRF					
Z	element	10-2005	11-2005	12-2005	9-2005
28	Ni	44%	41%	46%	62%
29	Cu	81%	78%	76%	94%
30	Zn	99%	100%	99%	100%
33	As	65%	63%	46%	27%
34	Se	76%	64%	75%	90%
35	Br	99%	99%	99%	100%
37	Rb	54%	52%	68%	63%
38	Sr	91%	92%	91%	94%
40	Zr	14%	12%	16%	33%
82	Pb	99%	99%	94%	99%

Table 1. Percentage of cases in which the element was detected on each system. September 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 fourth quarter of 2005 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 used 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. For elements such as Cl, which are found in more than one standard, calibration factors are based on the average of the several ratios.

During the time of Oct-Dec 2005 samples analyses, the performance of the Mo XRF system was monitored by weekly calibration checks, and the performance of both Cu XRF systems was monitored once or twice a month. 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 elements, then the system is considered stable and the existing calibration factors continue to be used. Deviations beyond 10% for the quantitative reported elements 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. September 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.

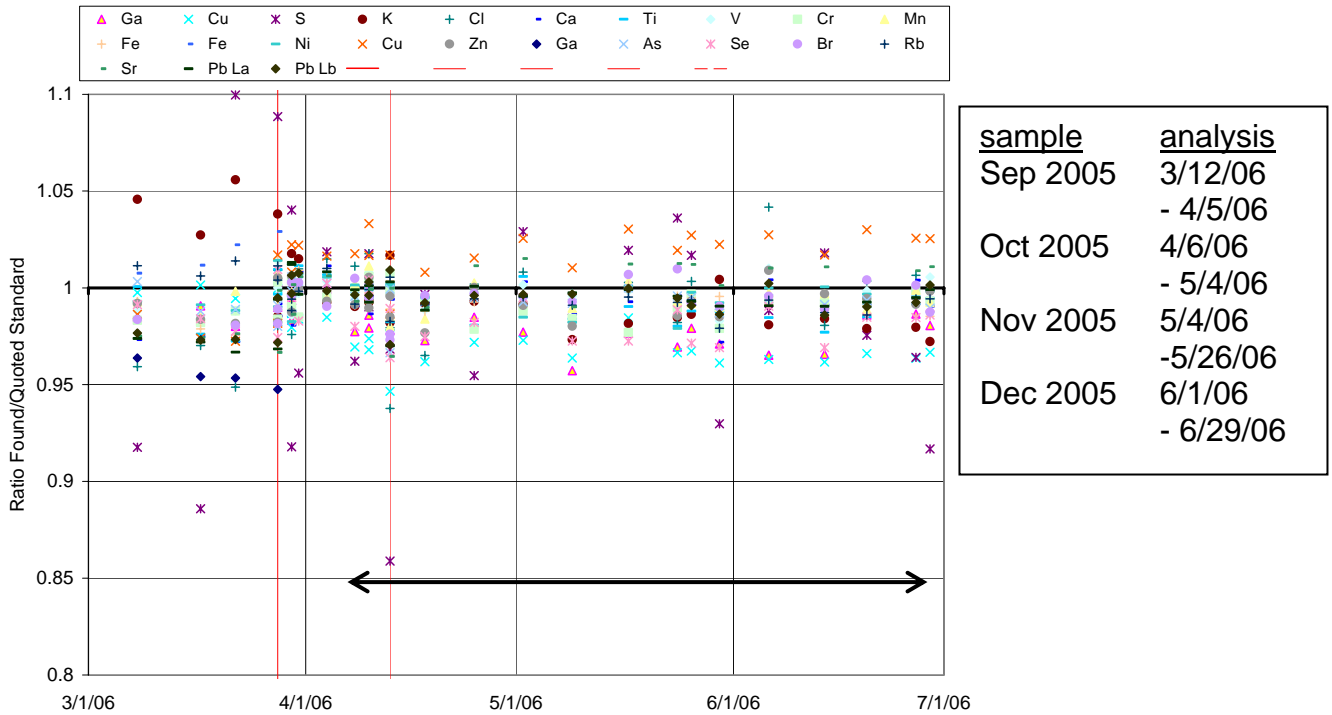


Figure 1. Mo XRF system performance chart based on standards

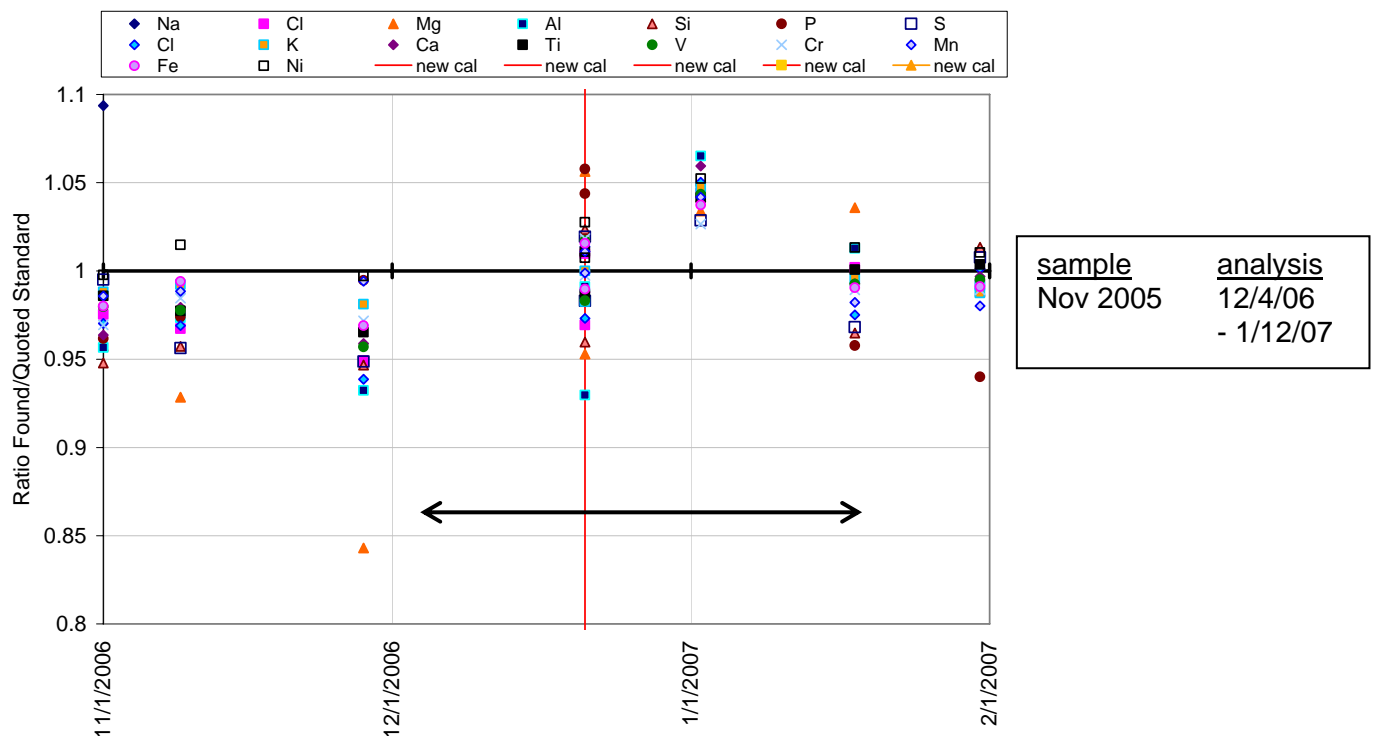


Figure 2. XRF Cu-Vac1 system performance chart based on standards.

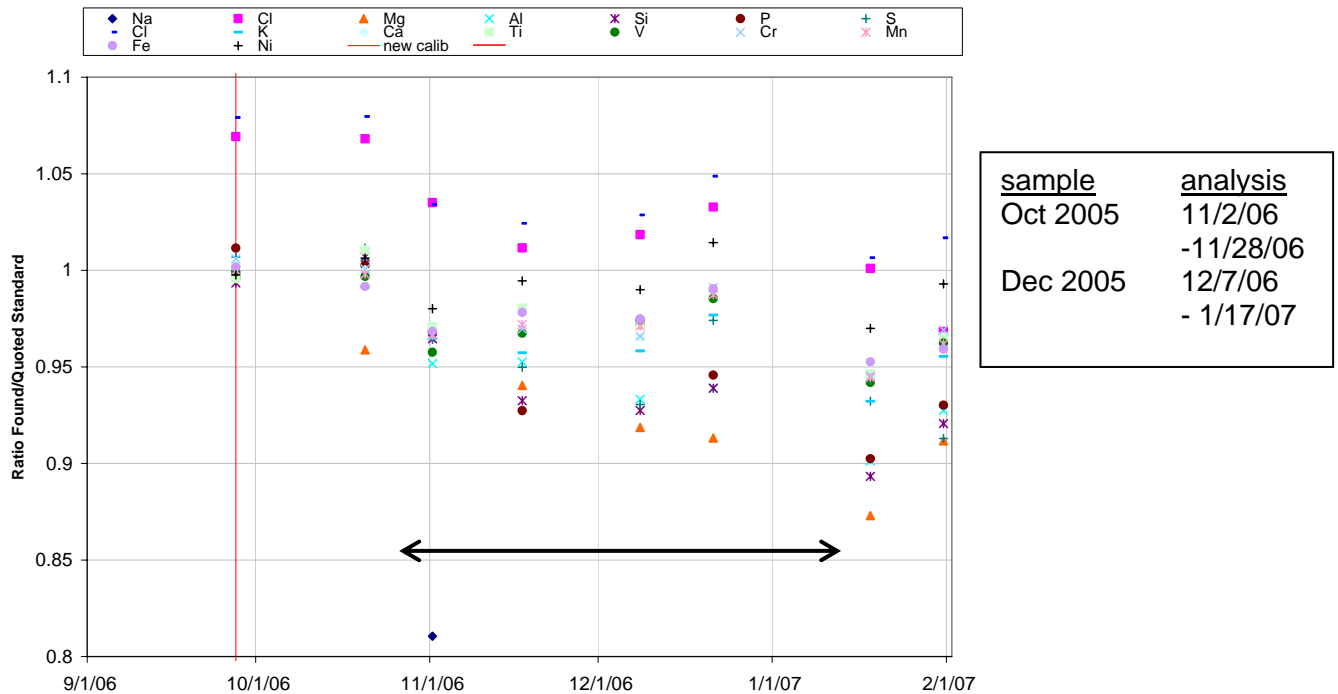


Figure 3. XRF Cu-Vac2 system performance chart based on standards.

The XRF-Mo system was recalibrated after change was made on April 13th 2006 to the operational parameters for standards. The current was changed from 2.6 mA to 10 mA to better reflect the livetimes for the IMPROVE samples. All calibration checks on the Mo system during the analysis of Oct-Dec 2005 samples were within our criteria.

November 2005 samples were analyzed on the XRF Cu-Vac1 system and processed with new concentration calibration factors obtained in December 2006 to reflect maintenance done on the system (including a change of the vacuum pump) in September 2006
 October and December 2005 samples were analyzed on XRF Cu-Vac2 system. This system was set up and calibrated in late September 2006. All calibration checks during the analysis of the October-December 2005 samples for the elements considered quantitative were successful. However, the following calibration check on January 18th 2007, showed the Si standard slightly falling below acceptable range (0.89). None of the samples were re-analyzed.

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 $\mu\text{g}/\text{cm}^2$. 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 and recalibrations during the analysis of Oct-Dec 2005 samples. The cyclotron was re-tuned twice

during analysis of these samples. One of the calibration checks on Jan 18th (run number 27839) resulted in the average ratio falling outside the criteria. The cyclotron was not returned. The following checks were all successful.

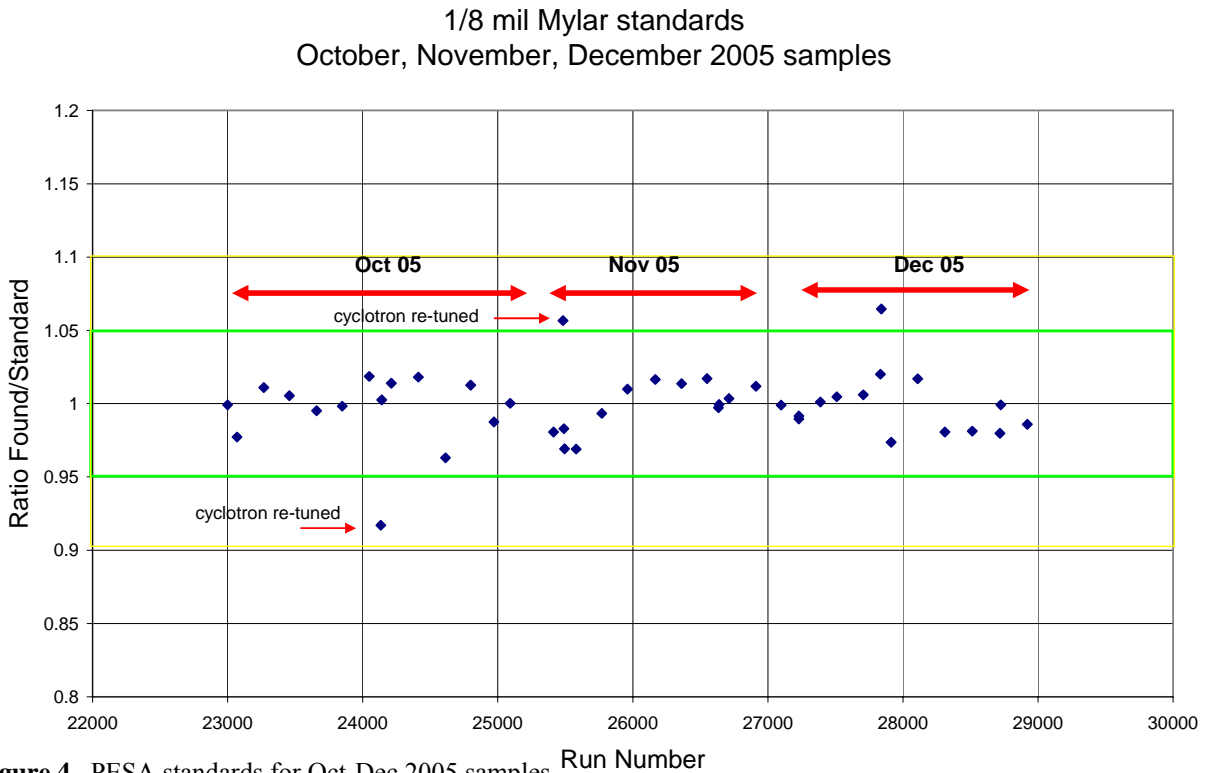


Figure 4. PESA standards for Oct-Dec 2005 samples

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 Sep		intercept	slope	full scale	from Sep		intercept	slope	full scale	from Sep	
Oct-05					-0.0358	0.01716	8.750	N/A		-0.0817	0.03607	18.385	0.09%	
Nov-05	-0.0414	0.01667	8.494	-0.02%						-0.0797	0.03604	18.374	0.04%	
Dec-05					-0.0358	0.01716	8.750	N/A		-0.0862	0.03606	18.378	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 Oct 2005 samples, 56 PMRFX and OLYMX filters from Jan-Feb and July 2005 were reanalyzed. Similarly, Nov 2005 and Dec 2005 reanalyses were performed, respectively, on 52 SAFOX, SAMAX AND TRCRX filters from August 2005 and 56 MEVEX, OLYMX and PMRFX filters from August 2005. Figure 5 compares the original and repeat analyses.

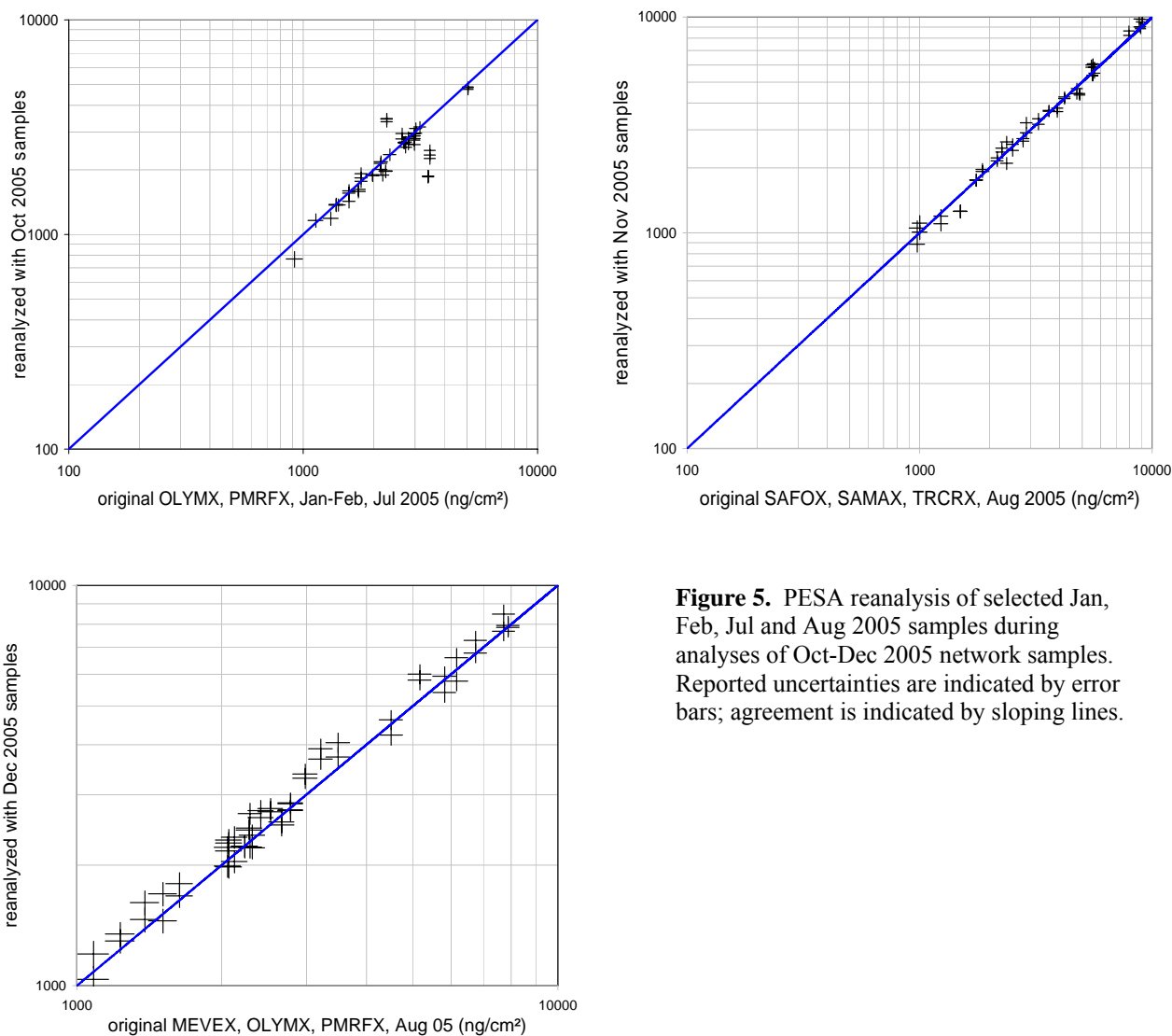


Figure 5. PESA reanalysis of selected Jan, Feb, Jul and Aug 2005 samples during analyses of Oct-Dec 2005 network samples. Reported uncertainties are indicated by error bars; agreement is indicated by sloping lines.

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 Oct-Dec 2005 samples.

The results are summarized in the figures below.

Figures 6-11 show the consistency of reanalysis results from both systems during the analysis of the Oct-Dec 2005 samples. The horizontal axis of each figure indicates the dates of successive reanalyses. The vertical axis shows for each element the average ratio, over all sample days, of observed deviations (from the mean of all reanalyses) to reported measurement uncertainties. 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.

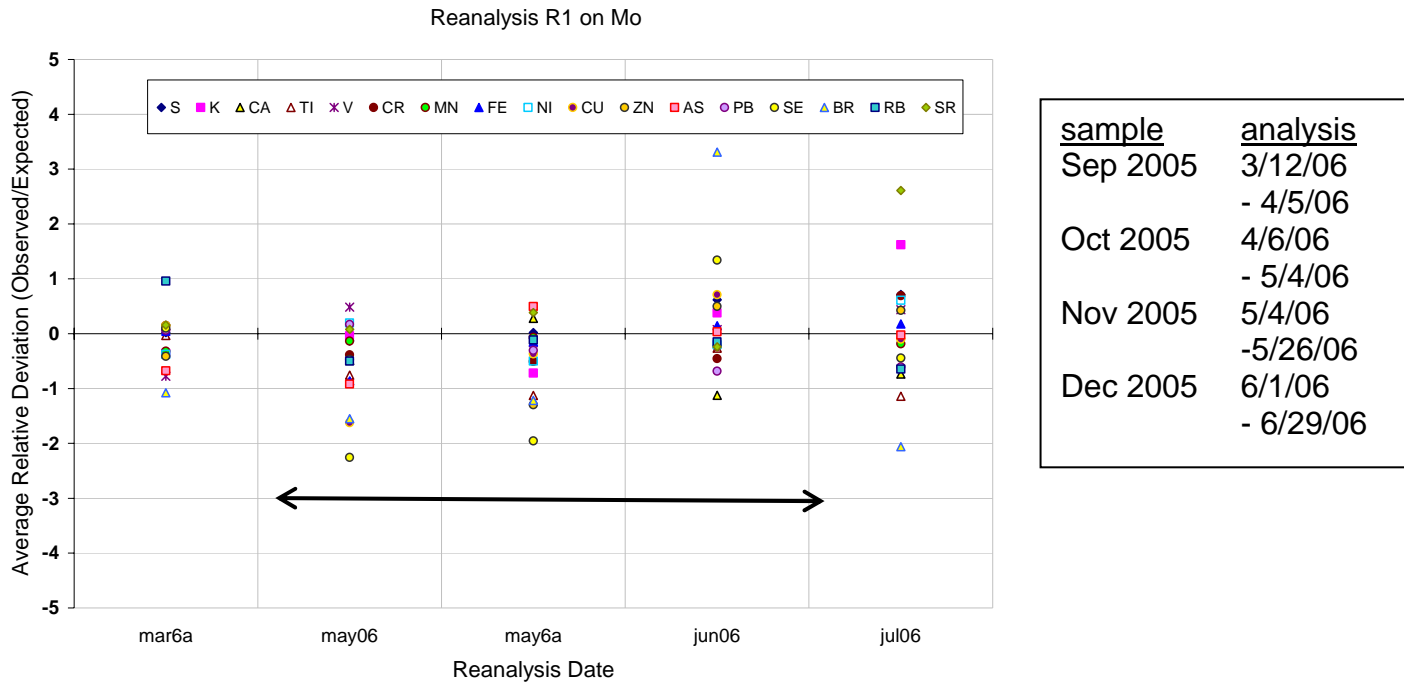


Figure 6. Reanalyses of REANAL1 samples on XRF-Mo system. Horizontal arrow indicates when Oct-Dec 2005 network samples were analyzed.

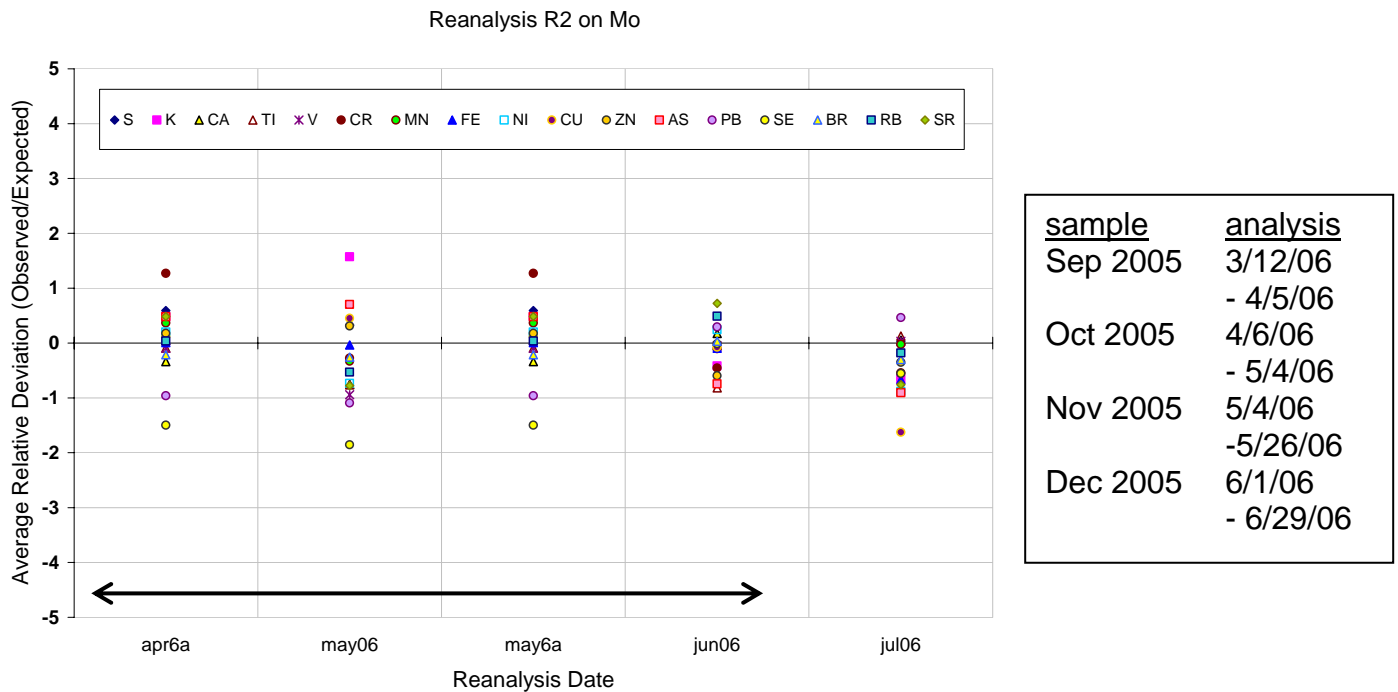


Figure 7. Reanalyses of REANAL2 samples on XRF-Mo system. Horizontal arrow indicates when Oct-Dec 2005 network samples were analyzed.

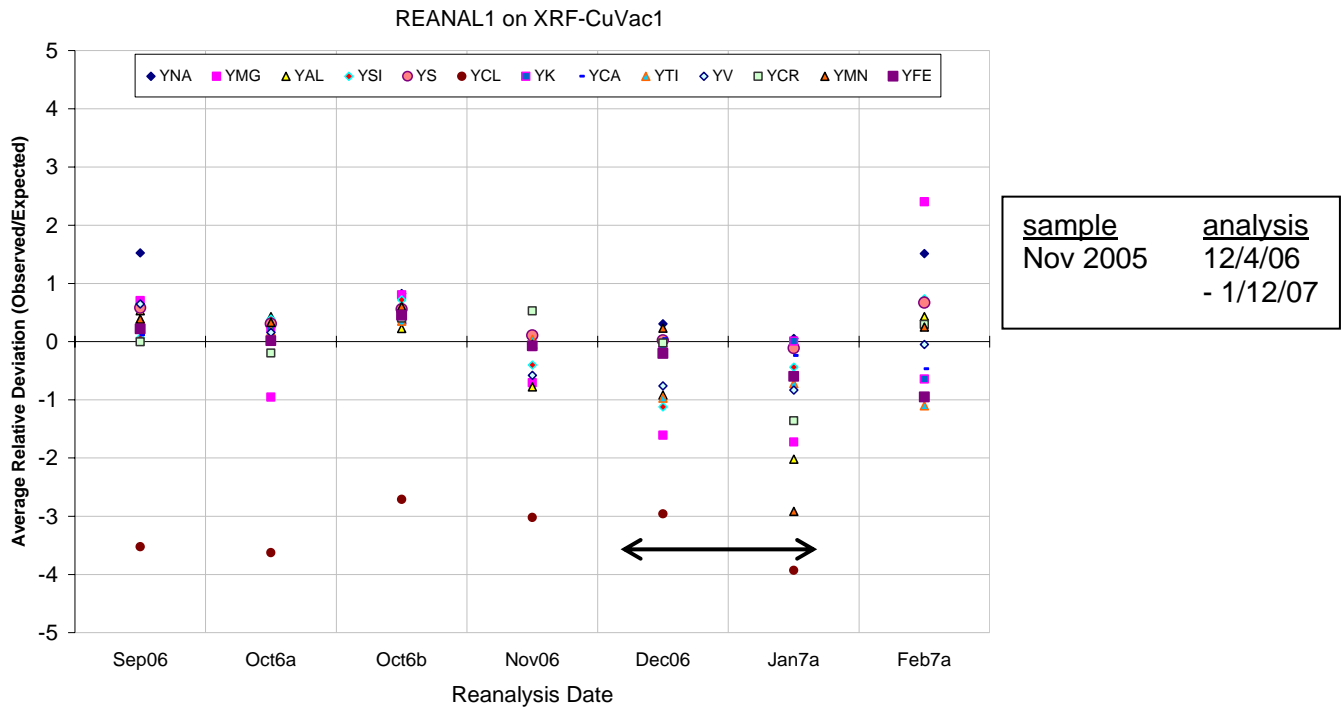


Figure 8. Reanalyses of REANAL1 samples on XRF-Cu1 system. Horizontal arrow indicates when Nov 2005 network samples were analyzed.

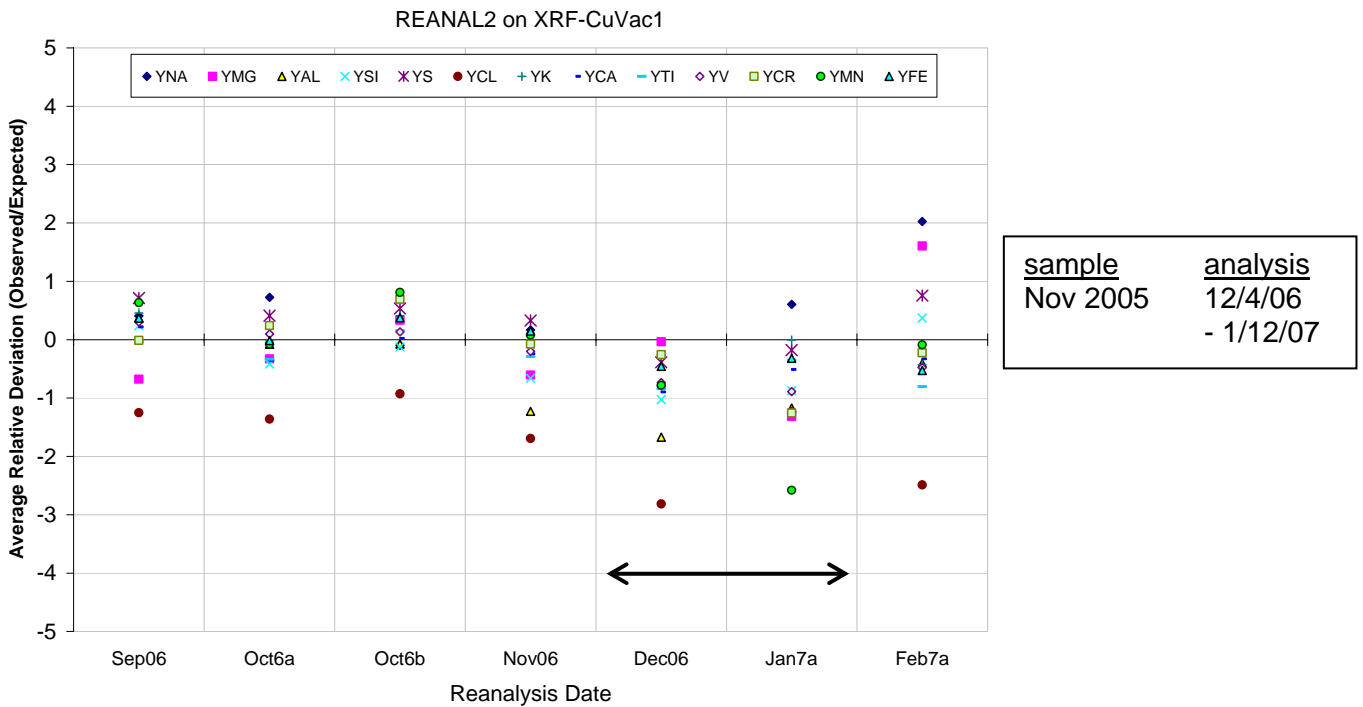
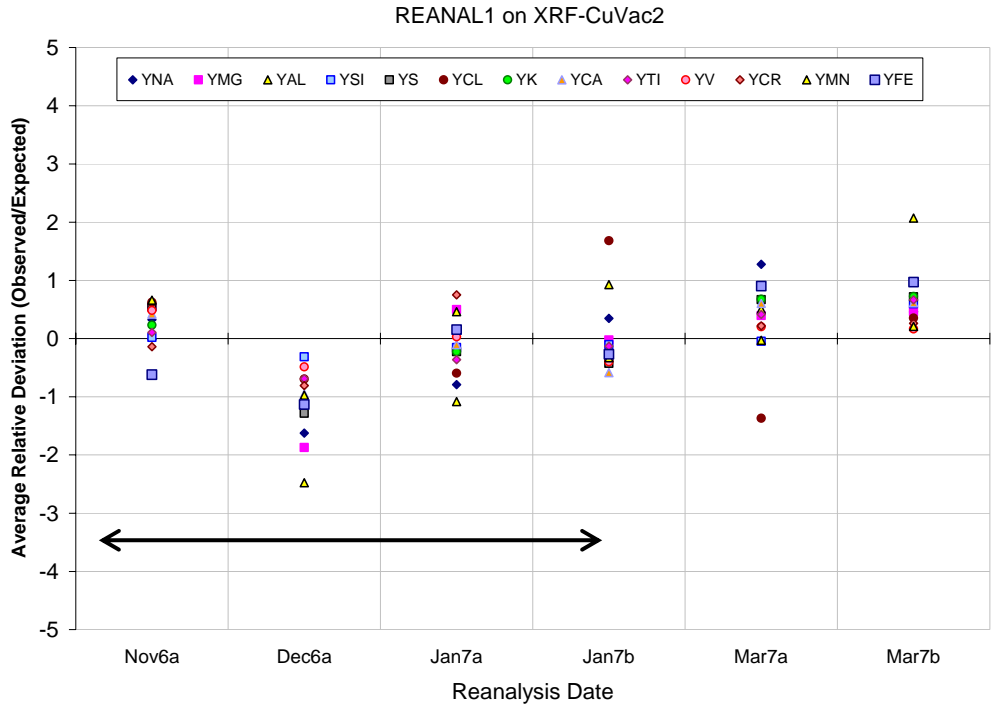
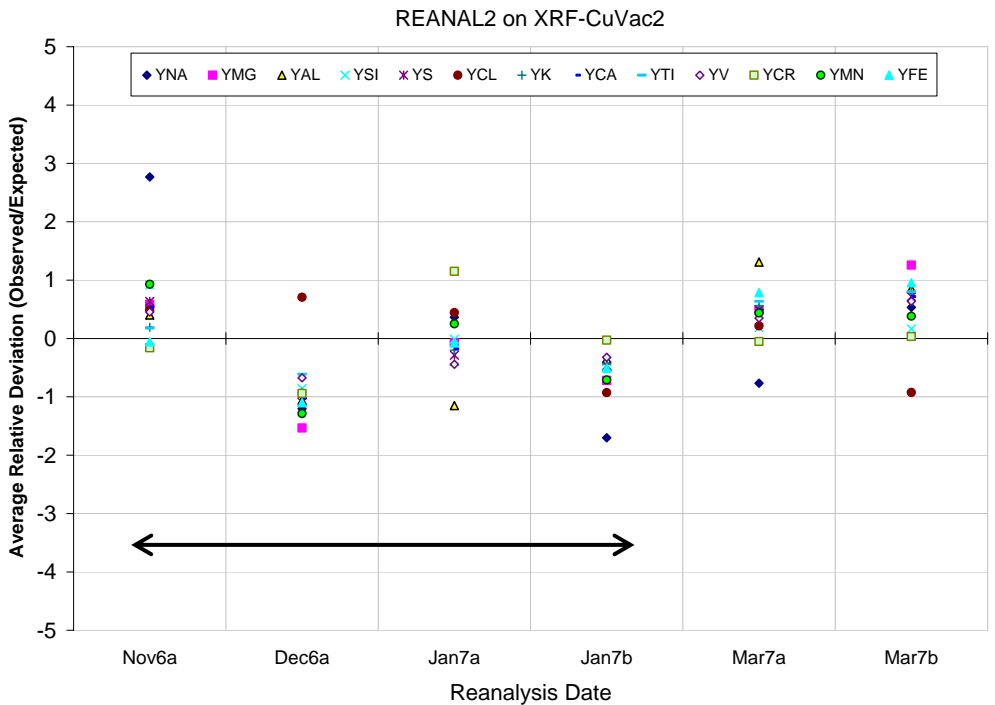


Figure 9. Reanalyses of REANAL2 samples on XRF-Cu1 system. Horizontal arrow indicates when Nov 2005 network samples were analyzed.



sample	analysis
Oct 2005	11/2/06 – 11/28/06
Dec 2005	12/7/06 – 1/17/07

Figure 10. Reanalyses of REANAL1 samples on XRF-Cu2 system. Horizontal arrow indicates when Oct, Dec 2005 network samples were analyzed.



sample	analysis
Oct 2005	11/2/06 – 11/28/06
Dec 2005	12/7/06 – 1/17/07

Figure 11. Reanalyses of REANAL2 samples on XRF-Cu2 system. Horizontal arrow indicates when Oct, Dec 2005 network samples were analyzed.

3.4 Systems comparison

Additional comparison between elements measured independently by the Cu and Mo systems allows identification of problems that may not be evident in repeated measurements by the same system. The elements Calcium and Iron are reported from the Cu system but are also quantified by the Mo system. Figures 12 and 13 compare the two measurements of these two elements for the samples from Oct-Dec 2005. Since the October 2005 samples are the first to be reported from Cu-Vac2 system, selected sites (ISLE1 - MEAD1) were reanalyzed on Cu-Vac1, and these comparisons are also shown. Additional comparisons between Cu-Vac1 and Cu-Vac2 are presented in Attachment 1.

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.

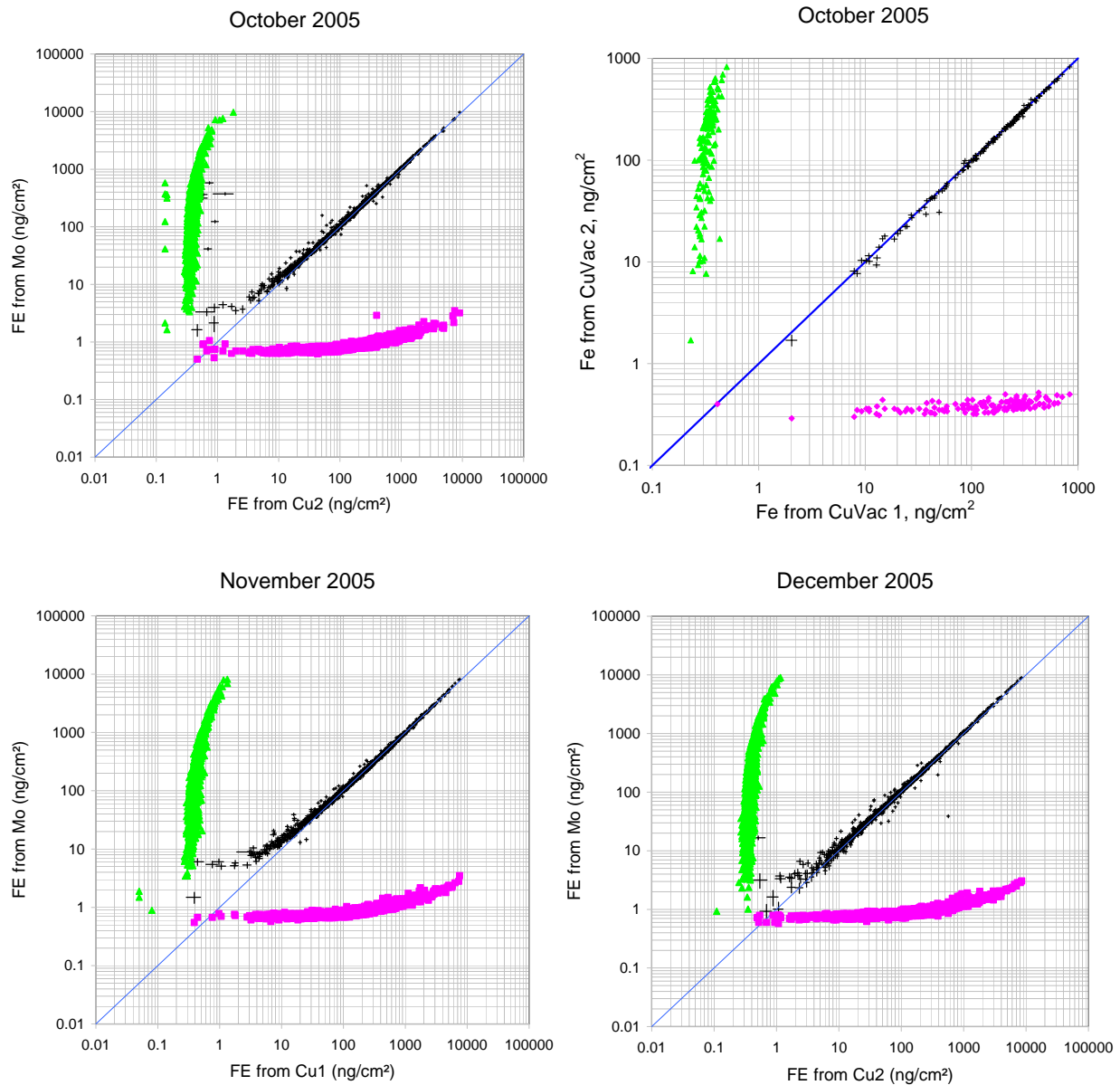


Figure 12. Comparison of Iron data obtained independently from Cu (x-axis) and Mo (y-axis) systems. Cu1 refers to Cu-Vac1 and Cu2 to Cu-Vac2.

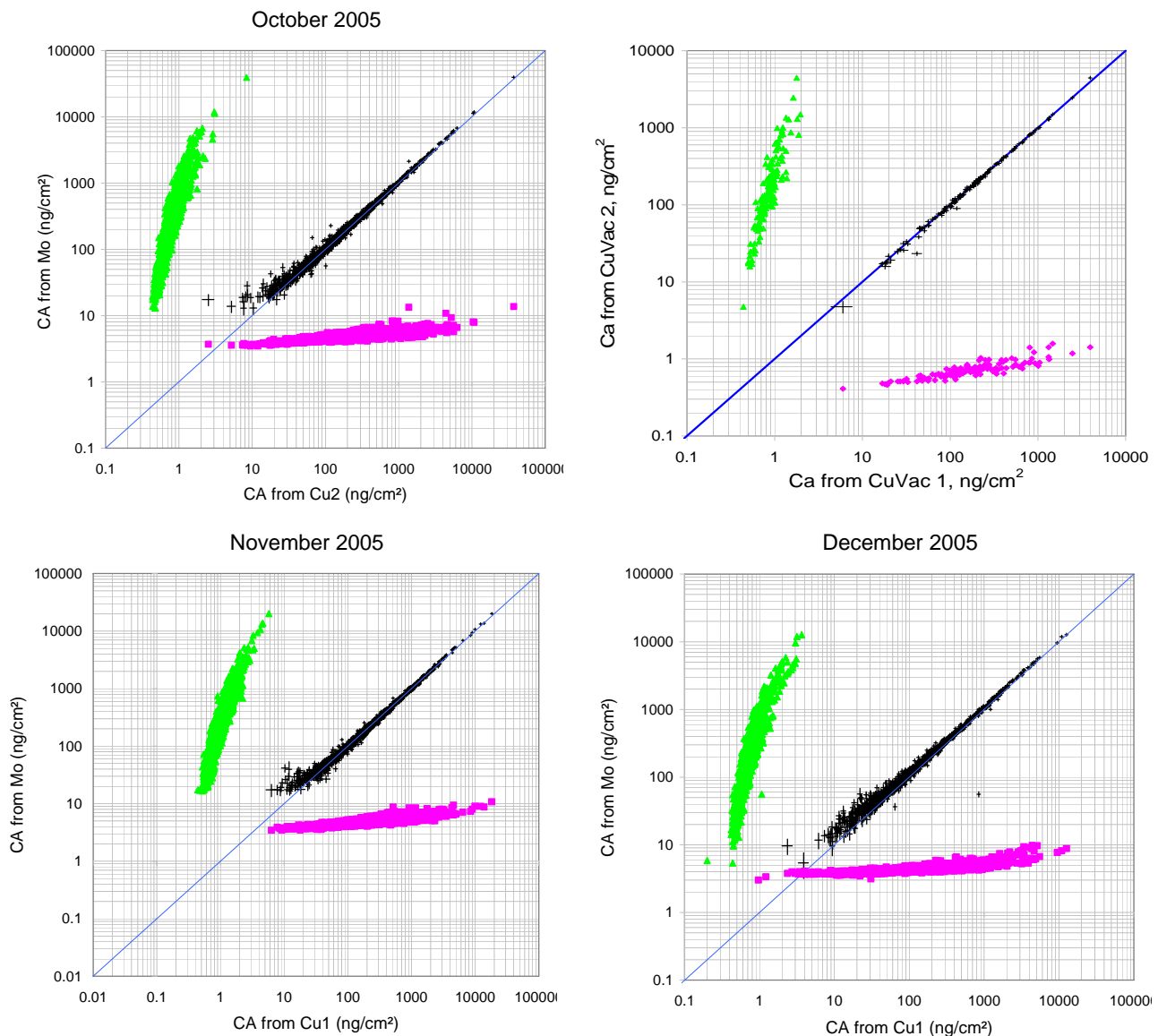


Figure 13. Comparison of Calcium data obtained independently from Cu (x-axis) and Mo (y-axis) systems.

Calcium and iron determinations by the Mo system contain more uncertainty than those from the Cu system, 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 four field blanks for November 2005 samples were exposed at selected sites on selected sampling events. The field blanks were analyzed on XRF-Mo system on March 16, 2006, but were not analyzed yet on the Cu system. Therefore, the results are from XRF-Mo analysis only.

Ninety-fifth, 90th and 75th percentile field blank loadings are shown in the table below. They are given as percentiles of well measured network sample loadings during November 2005. Loadings are considered well measured when their uncertainties are less than 10%.

Thus, the 95th percentile field blank loading for Fe was as large as 7% of all well measured sample loadings.

Field Blanks						
Nov 2005	Fe	Cu	Zn	Pb	Se	Br
95 %ile	7.1%	0.0%	36.5%	3.1%	0.0%	0.0%
90 %ile	0.7%	0.0%	23.7%	1.5%	0.0%	0.0%
75 %ile	0.0%	0.0%	4.6%	0.2%	0.0%	0.0%

In addition to field blanks, fifteen laboratory blanks were analyzed on the Mo system. Table below shows the percentages of values in the network below laboratory blank concentrations.

Laboratory Blanks						
Nov 2005	Fe	Cu	Zn	Pb	Se	Br
95 %ile	0.3%	0.0%	1.53%	0.0%	0.0%	0.0%
90 %ile	0.2%	0.0%	0.18%	0.0%	0.0%	0.0%
75 %ile	0.1%	0.0%	0.00%	0.0%	0.0%	0.0%

The results show that for all the elements, with the exception of Zn, the field and lab blanks loadings are negligible compared to samples. The field blank results for Zn suggest contamination that has been [noted](#) before.

Attachment 1

All July 2005 IMPROVE samples were analyzed on both Cu-anode XRF systems, the original (Cu-Vac1) and the duplicate (Cu-Vac2). The following is an album of comparisons for each CuXRF element. Each point is (Y1,Y2), where Y_i is val(i) if detected and mdl(i) if not detected. Samples with a non-detect in one analysis are plotted in red. Samples with non-detects in both analyses are not plotted.

