Data report for elemental analysis of IMPROVE samples collected during JULY, AUGUST, SEPTEMBER 2005
UC Davis

SUMMARY

This report summarizes the quality assurance performed during and after elemental analysis of the IMPROVE samples collected during the months of July, August and September of 2005. The elemental analyses include the determination of most elements with atomic numbers from 11 to 40 (Na-Zr) and 82 (Pb) with two energy dispersive X-ray fluorescence systems (XRF), and the determination of hydrogen by Proton Elastic Scattering Analysis (PESA) with the Crocker cyclotron. Our quality assurance is based on our review of the following:
- Concentration calibration and verification
- Energy calibration
- Laboratory replicates (reanalysis)
- Systems comparison

These procedures are described below, and their results are presented. The routine verifications of the calibration of each system were all successful during the period when July - September 2005 samples were analyzed. No new calibrations were performed on the Cu-anode XRF system although the system was modified part-way through the analyses, as discussed below. Two new calibrations of the Mo-anode XRF system were performed: on December 12th 2005, to account for collimator adjustment, and March 28th 2006, to calibrate the system with new set of standards.

Section 1.   Overview of Elemental Analysis Systems

The elements Na and Mg (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). All July-September 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+) 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 July, August and September 2005 data

XRF and PESA analyses were carried out on 1680 samples collected in July 2005, 1676 samples collected in August 2005 and 1635 samples collected in September 2005. All samples collected in the third quarter of 2005 were analyzed between 3 December 2005 and 5 April 2006 (with the exception of sites SENE1-SIPS1 which were reanalyzed on January 4-5, 2007) on the Mo-anode XRF system, between 2 September 2006 and 4 December 2006 on the Cu-anode XRF system, and between 1 November 2006 and 4 December 2006 on the PESA system.
Table 1 summarizes the third quarter 2005 detection rates on the three systems, with rates for June 2005 included for comparison.

PESA					
Z	element	6-2005	7-2005	8-2005	9-2005
1	H	98%	100%	100%	100%

Cu-anode XRF					
Z	element	6-2005	7-2005	8-2005	9-2005
11	Na	50%	44%	37%	40%
12	Mg	33%	26%	15%	20%
13	Al	89%	92%	88%	78%
14	Si	95%	96%	96%	94%
15	P	1%	2%	1%	1%
16	S	98%	100%	100%	100%
17	Cl	10%	9%	6%	9%
19	K	98%	100%	100%	100%
20	Ca	98%	100%	100%	100%
22	Ti	97%	99%	99%	98%
23	V	89%	97%	94%	94%
24	Cr	65%	56%	56%	42%
25	Mn	97%	99%	99%	98%
26	Fe	99%	100%	100%	100%

Mo-anode XRF					
Z	element	6-2005	7-2005	8-2005	9-2005
28	Ni	60%	51%	57%	62%
29	Cu	91%	94%	94%	94%
30	Zn	98%	100%	100%	100%
33	As	43%	52%	50%	27%
34	Se	86%	91%	91%	90%
35	Br	98%	100%	100%	100%
37	Rb	70%	77%	74%	63%
38	Sr	91%	96%	95%	94%
40	Zr	29%	25%	23%	33%
82	Pb	96%	97%	96%	99%

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

Section 3.   Quality Control

3.1   Concentration calibration and verification
Both XRF systems are calibrated with thin film foil standards produced by Micromatter. The standards used for samples from the third quarter of 2005 are listed below in Tables 2 and 3. Because their concentrations are relatively high, standards are analyzed at reduced X-ray tube current (2.6 mA) to maintain counting live times comparable with those of actual IMPROVE samples.

Standard	Certified Elemental Concentrations +/- 5% ($\mu g/cm^2$)	Serial #
NaCl	Na: 19.5, Cl: 29.3	12856
Mg	Mg: 41.2	12857
Al	Al: 43.5	12858
SiO	Si: 29.6	12859
GaP*	P: 18.4 Ga: 28.7	6522
CuS	S: 13.8 Cu: 41.2	12861
KCl	Cl: 22.8, K: 25.2	16296
CaF	Ca: 25.6	6523
Ti	Ti: 40.4	12865
V	V: 37.4	12864
Cr	Cr: 46.9	12866
Mn	Mn: 45.4	12867
Fe	Fe: 15.8	12139
Fe	Fe: 48.3	12868
Ni	Ni: 40.3	12869
Cu	Cu: 45.4	6742
Au	Au: 43.0 La	16202
Zn	Zn: 48.0	6743
GaAs*	Ga: 21.8, As: 23.5	6744
Se	Se: 46.7	6780
CsBr	Br: 17.8	6530
RbI	Rb: 19.2	6531
SrF2	Sr: 34.5	6532
Pb	Pb La: 41.2 Pb Lb: 41.2	6745

Table 2. Micromatter standard foils used for Mo analyses before 3/28/06. Some standards (*) have variable stoichiometry; they are not use directly in calibration of the systems but serve only as "indicators".

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 3. Micromatter standard foils used for all Cu analyses, and for Mo analyses from 3/28/06. 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. For elements such as Cl and Fe, which are found in more than one standard, calibration factors are based on the average of the several ratios.

The performance of the Mo XRF system is monitored by weekly calibration verification checks, and the performance of the Cu XRF system is 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 reported elements considered quantitative 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 and 2 show the calibration verifications and system recalibrations performed during the period in which samples from June 2005 (for context) and July-September 2005 were analyzed. The analysis dates for each sample month are listed in the legends. The y-axes indicate the ratio of the values reported for each standard to the value quoted by Micromatter.
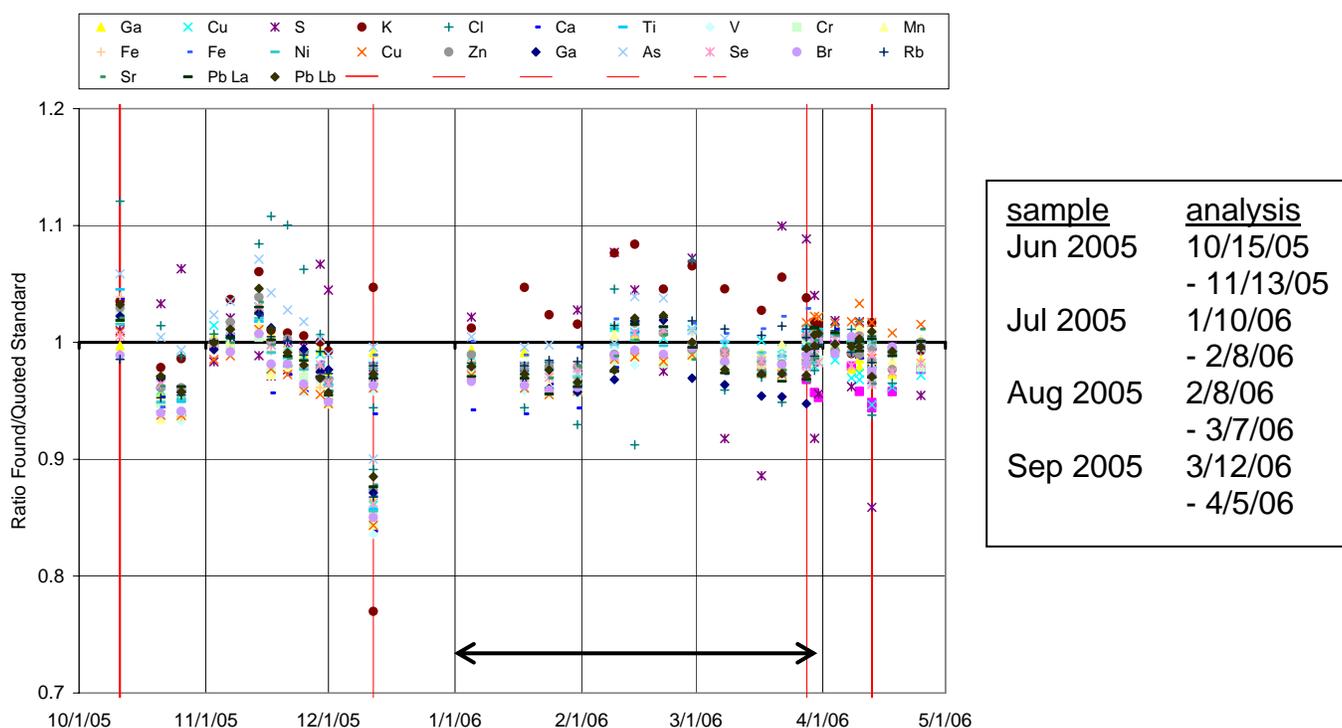

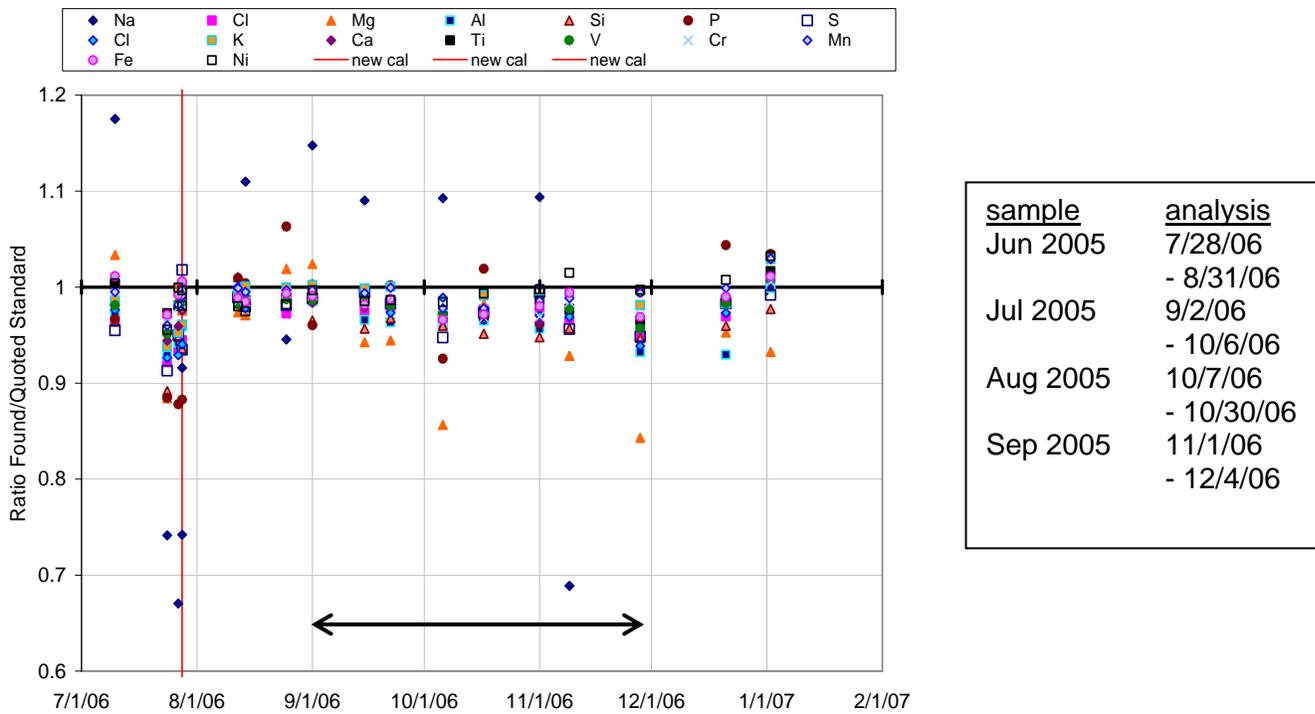**Figure 1.** Mo XRF system performance chart based on standards

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

The XRF-Mo system was reconfigured after collimator adjustment on 13 December 2005 and new calibration factors were applied to subsequent analyses starting with July 2005 samples. A new set of calibration standards was introduced on 3/28/06, and calibration factors for all subsequent analyses are based on the new standards. All calibration checks during the analysis of Jul-Sep 2005 samples were within our criteria, with the exception of the S value recorded on 3/17/06. Because ambient Ar (atomic number 18) can interfere with neighboring elements such as S (atomic number 16) in the open air XRF-Mo system, and because S concentrations are reported from the vacuum XRF-Cu system, no action was taken at the time.

The XRF-Cu system was partially disassembled on 9/14/06 to install a new vacuum pump. This opportunity was taken also to perform other routine maintenance, such as cleaning the detector window. A calibration check of the reassembled system was still within our criteria, as were all others during the period of Jul-Sep 2005 analysis. (As observed earlier, variations in measured reference values for Na and Mg were accepted because these elements are considered qualitative only.)

Based on the success of calibration checks on the reassembled system using the existing calibration factors, a decision was made to retain the existing calibration. The 9/14/06 modifications could nevertheless have introduced subtle changes into the performance of the Cu-anode system.

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 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 3 shows calibration verifications and recalibrations during the analysis of June 2005 (for reference) and Jul-Sep 2005 samples.

1/8 mil Mylar standards
July, August, September 2005 samples
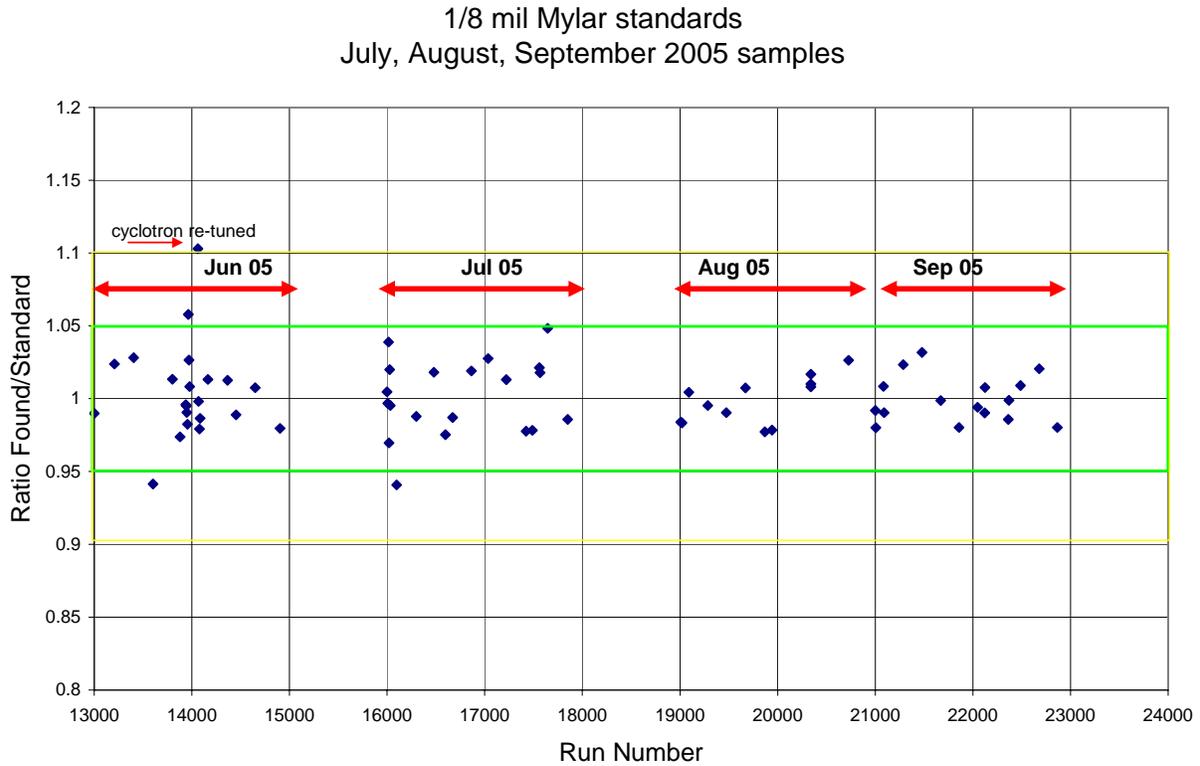
Figure 3. PESA standards for June, July, August and September 2005 samples

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-Cu			*change*	**XRF-Mo**			*change*
	intercept	slope	full scale	*from June*	intercept	slope	full scale	*from June*
Jul-05	-0.0385	0.01668	8.499	*0.10%*	-0.0774	0.03602	18.365	*-0.01%*
Aug-05	-0.0353	0.01665	8.491	*0.00%*	-0.0858	0.03610	18.398	*0.16%*
Sep-05	-0.0385	0.01667	8.496	*0.06%*	-0.0843	0.03605	18.374	*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. The proton beam used in PESA weakens the Teflon membrane, increasing the likelihood of damage in subsequent analyses and limiting the reanalyses that can be performed on a given filter to two or three. The X-ray beams of the XRF-Mo and XRF-Cu systems are effectively non-destructive, and XRF can be repeated hundreds of times on the same filter.

Filters to be reanalyzed by PESA are selected from the previous quarter's X-module (collocated A-module) samples. During the analysis of July 2005 samples, 29 MEVEX and OLYMX filters from April-May 2005 were reanalyzed. Similarly, August 2005 and September 2005 reanalyses were performed, respectively, on 29 MEVEX, OLYMX and PMRFX filters from June 2005 and 20 SAFOX and TRCRX filters from June 2005. Figure 4 compares the original and repeat analyses.
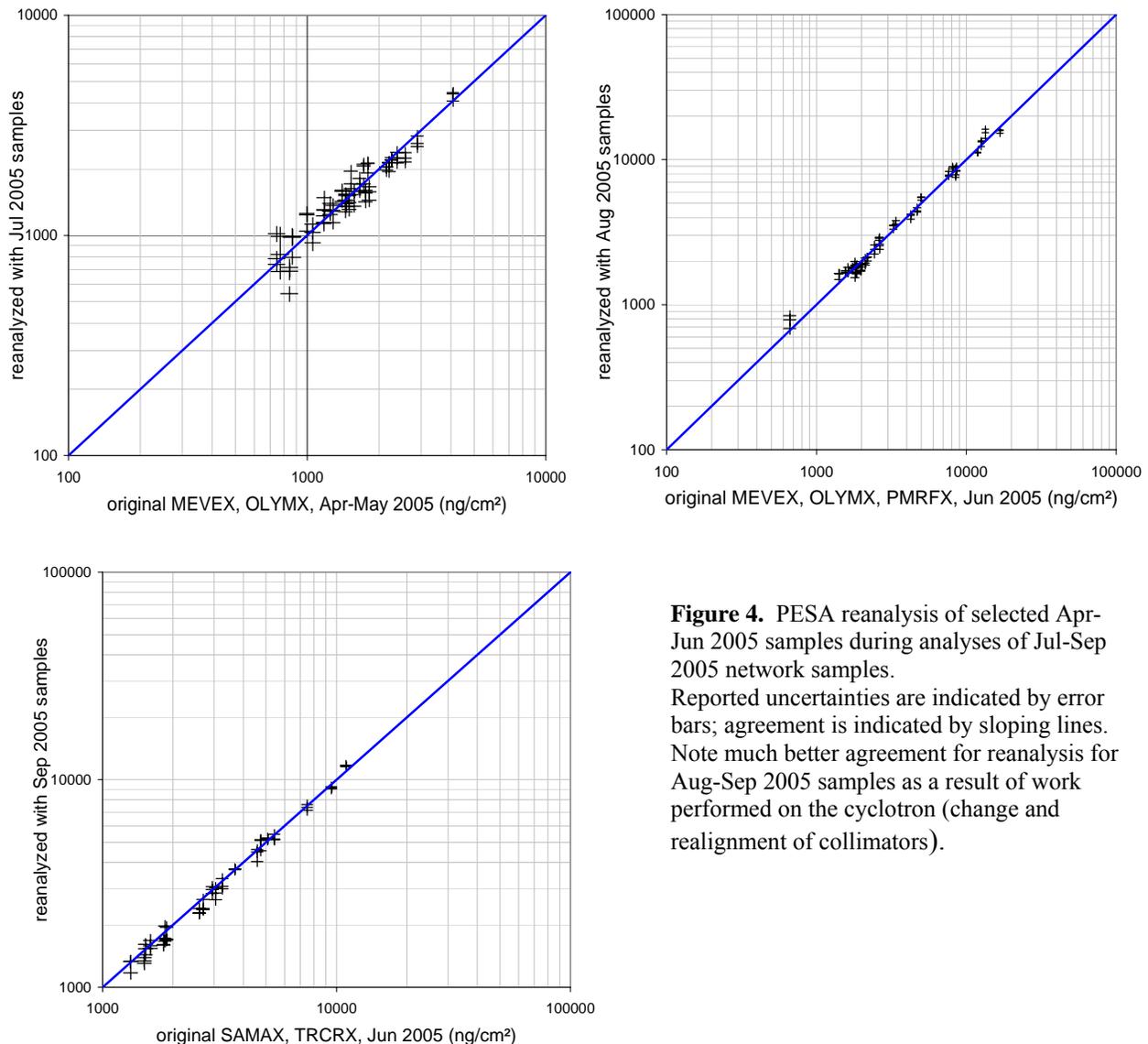
Figure 4. PESA reanalysis of selected Apr-Jun 2005 samples during analyses of Jul-Sep 2005 network samples.
Reported uncertainties are indicated by error bars; agreement is indicated by sloping lines. Note much better agreement for reanalysis for Aug-Sep 2005 samples as a result of work performed on the cyclotron (change and realignment of collimators).

XRF reanalyses are conducted repeatedly on a fixed collection of sample filters. The collection of 72 filters for reanalysis was assembled from January-May 2005 samples that had not been analyzed by PESA. Only samples from collocated A modules were considered, so that routine H data would not be lost when PESA analyses were by-passed. The filters were collected into two trays, designated REANAL1 and REANAL2, each designed to provide a range of compositions representative of the entire network.   These trays were reanalyzed with the XRF-Mo and vacuum XRF-Cu systems approximately monthly during 2006.

The XRF-Mo analyses corresponding to the July-September 2005 samples were performed in January-April 2006, and the reanalyses were done with REANAL1 for July 05 samples and with REANAL1 and REANAL2 for Aug-Sep 2005 samples. The XRF-Cu analyses for July-September 2005 samples were performed in Sep-Dec 2006, with both REANAL1 and REANAL2 trays. The results are summarized in the figures below.

Figures 5-8 show the consistency of reanalysis results from both systems during the analysis of the July-September 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. The development of quantitative criteria for accepting the results will require realistic estimates for the limiting uncertainty in individual analyses. The characterization of XRF uncertainty is under active study at CNL, the accumulated reanalyses providing a good example of the type of data available for this purpose. Development of substantially improved uncertainty estimates is planned during the coming year, and these will make possible a closer review of on-going data quality.
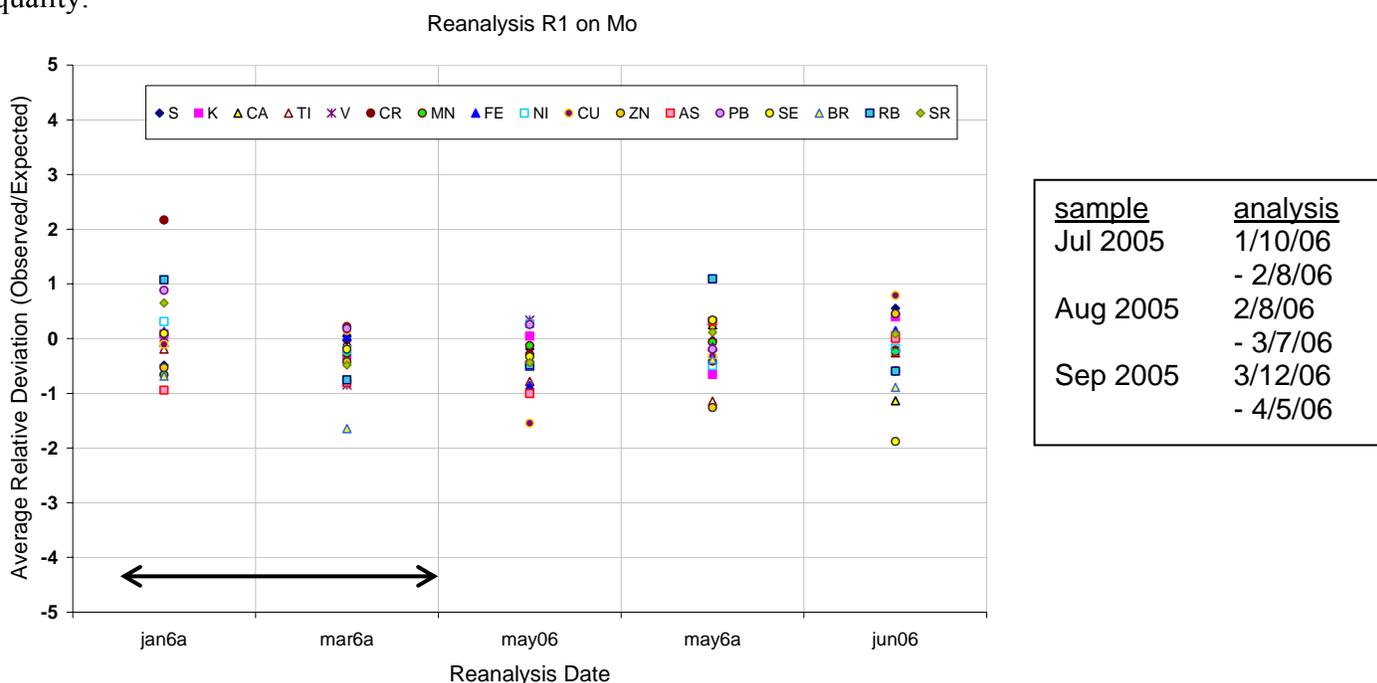

Figure 5.   Reanalyses of REANAL1 samples on XRF-Mo system.   Horizontal arrow indicates when Jul-Sep 2005 network samples were analyzed.
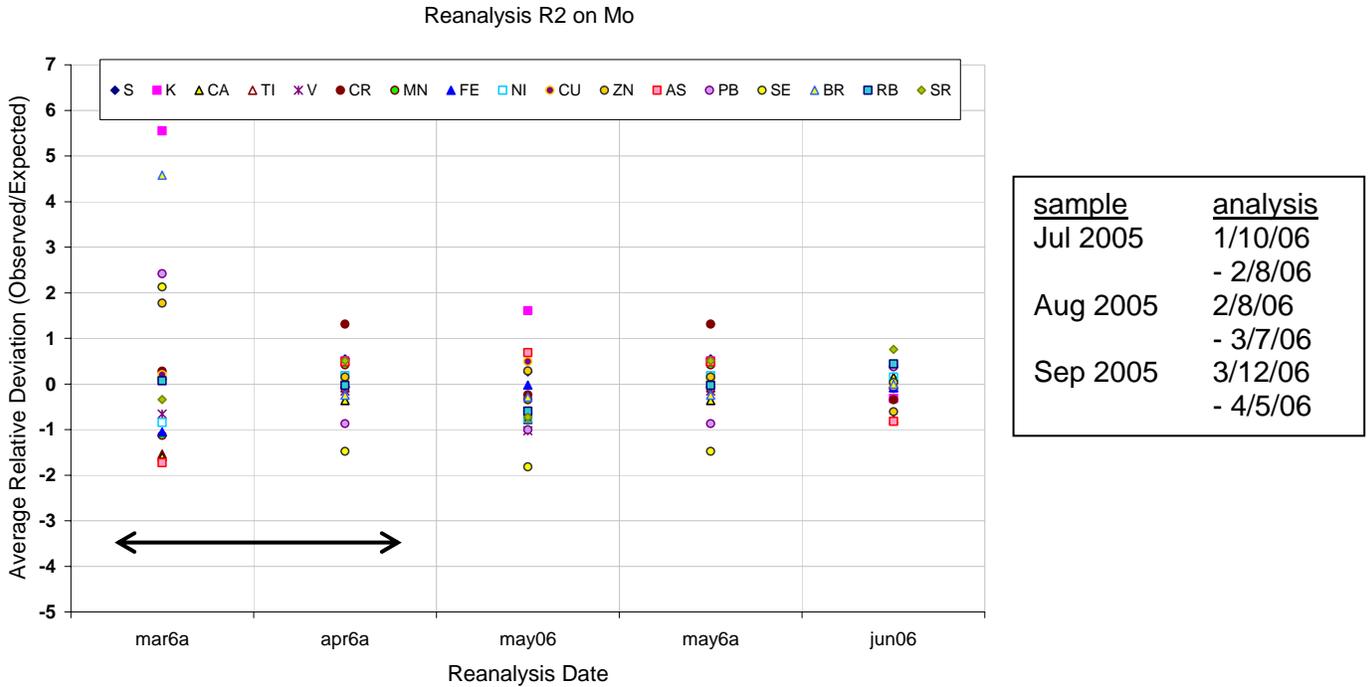
Figure 6. Reanalyses of REANAL2 samples on XRF-Mo system. Horizontal arrow indicates when Jul-Sep 2005 network samples were analyzed.
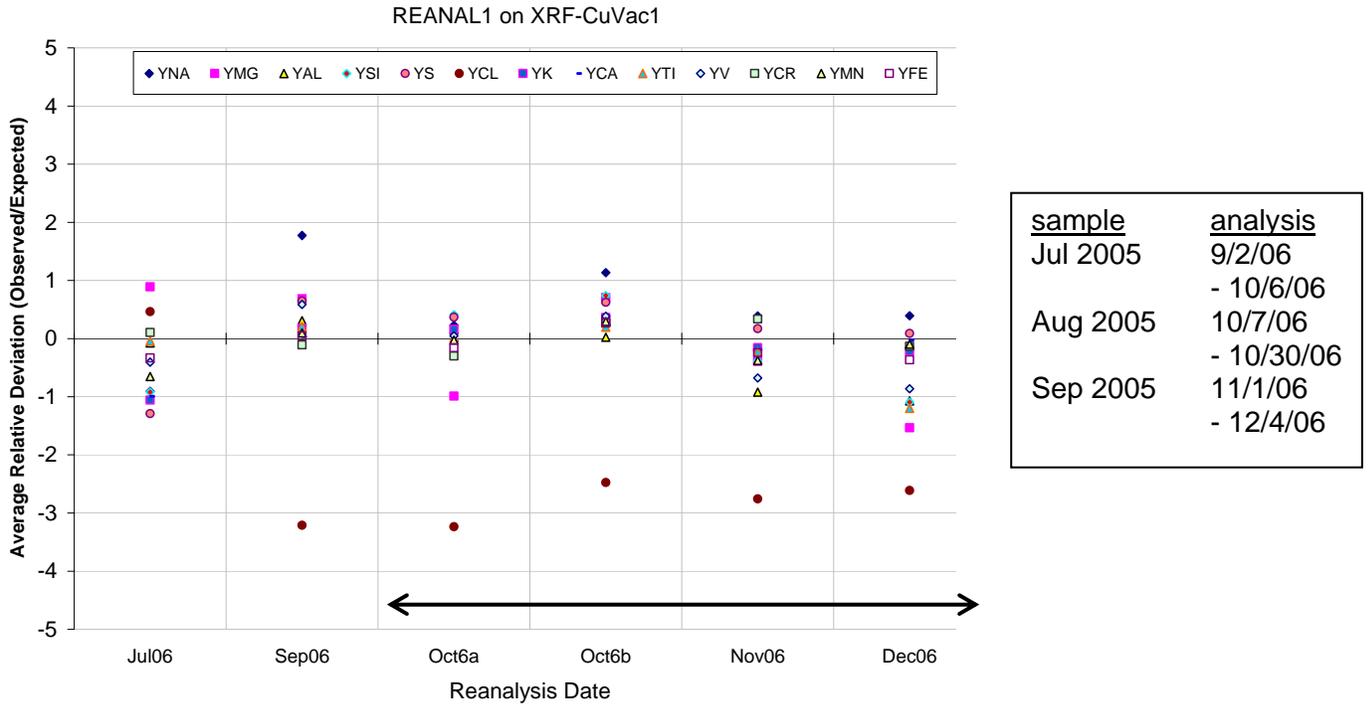

Figure 7. Reanalyses of REANAL1 samples on XRF-Cu system. Horizontal arrow indicates when Jul-Sep 2005 network samples were analyzed.
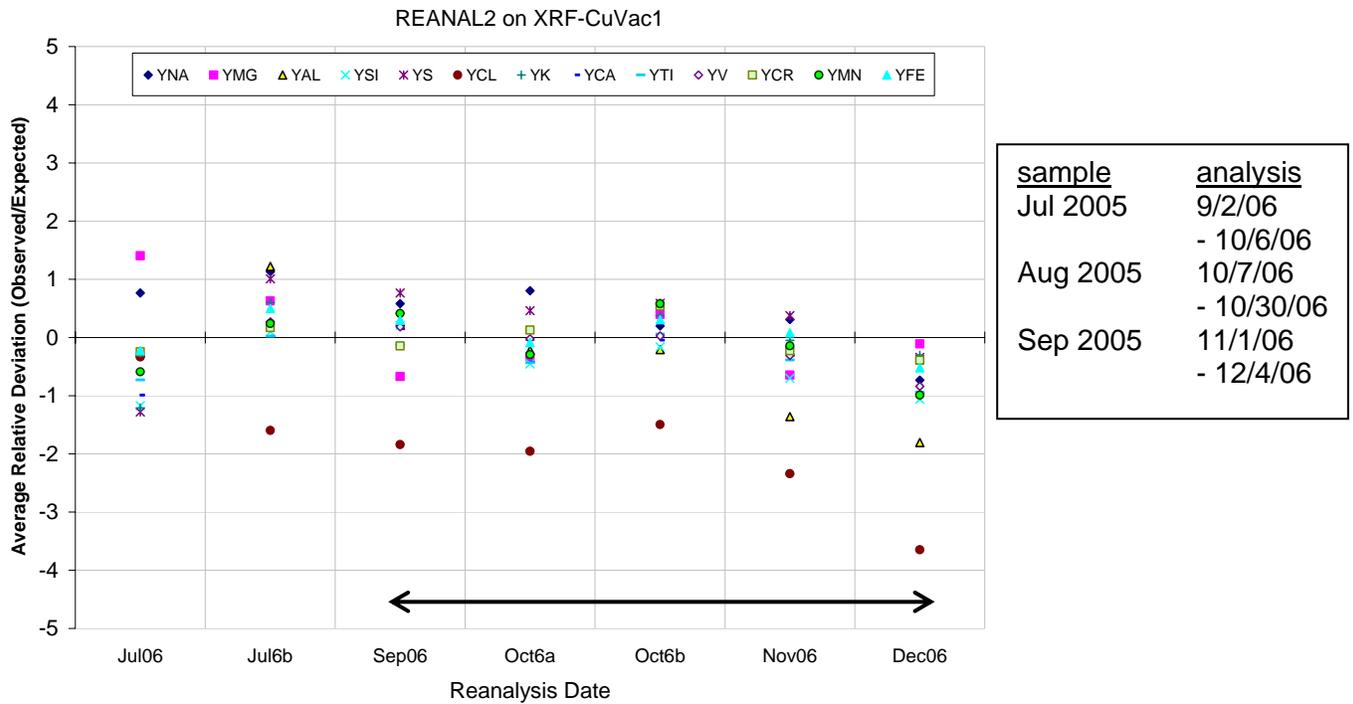
Figure 8. Reanalyses of REANAL2 samples on XRF-Cu system. Horizontal arrow indicates when Jul-Sep 2005 network samples were analyzed.

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 9 and 10 compare the two measurements of these two elements for the samples from July to September 2005. 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.
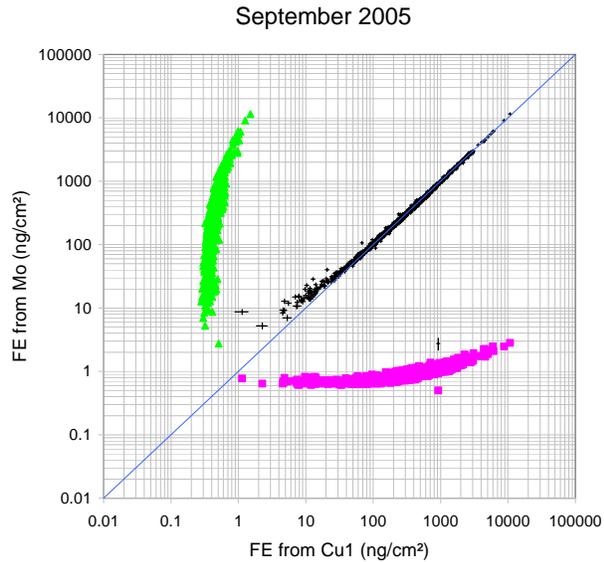
September 2005
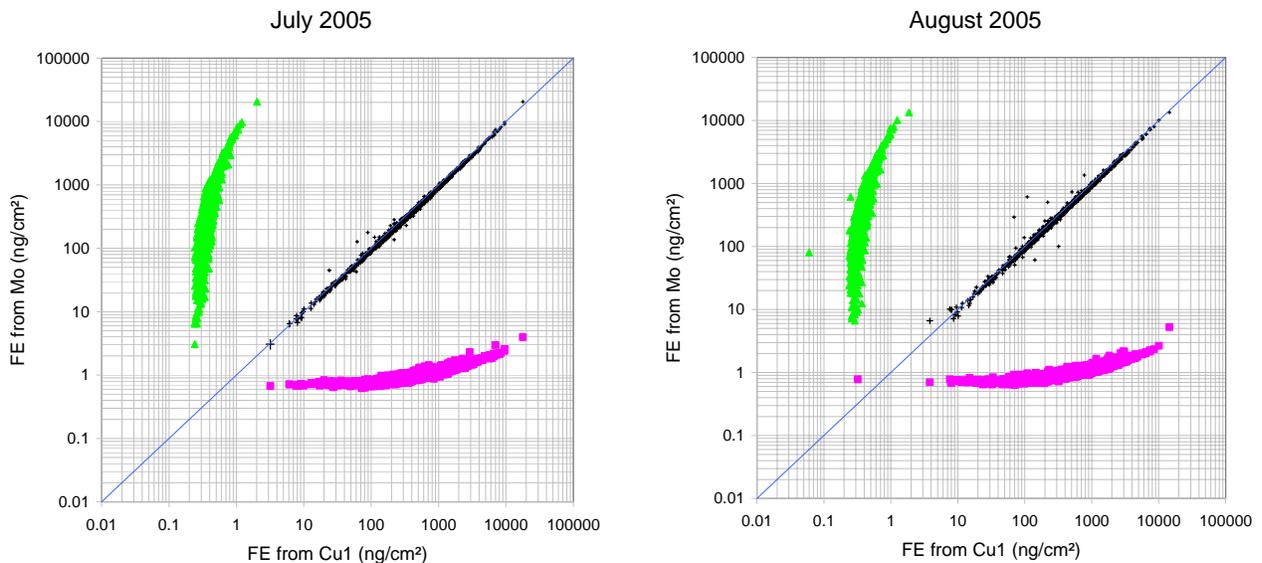
Figure 7. Comparison of Iron data obtained independently from Cu (x-axis) and Mo (y-axis) systems.

July 2005

August 2005
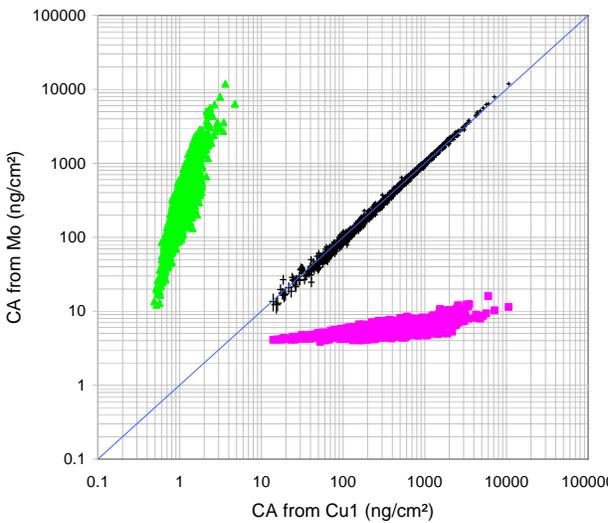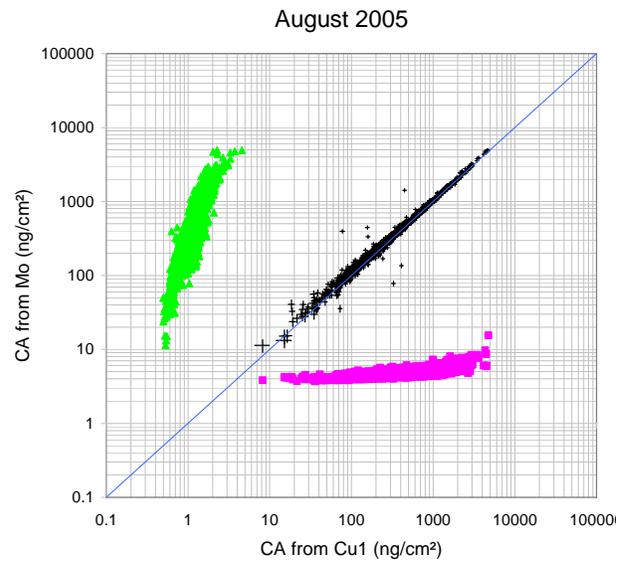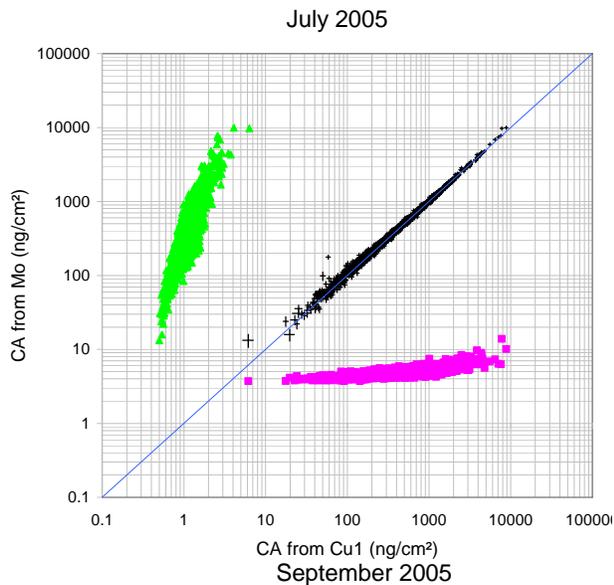

September 2005

Figure 8. 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.