Data report for elemental analysis of IMPROVE samples collected during APRIL MAY AND JUNE 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 April, May and June 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. The following data assessments and quality controls are obtained for all analyses:

- Concentration calibration and verification
- Energy calibration
- Laboratory replicates (reanalysis)
- Systems comparison

These procedures are described below, and their results are presented. The weekly verifications of the calibration of each system were all successful during the period when April - June 2005 samples were analyzed. Two new calibrations (on June 9th and July 28th, 2006) were performed on the XRF-Cu system to account for modifications in this new system. One new calibration of the existing XRF-Mo system was performed on October 11th 2005 to account for detector maintenance and re-installment.

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 April-June 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 April, May and June 2005 data

XRF and PESA analyses were carried out on 1772 samples collected in April 2005, 1943 samples collected in May 2005 and 1758 samples collected in May 2005. All samples collected in the second quarter of 2005 were analyzed between 18 July 2005 and 14 November 2005 on the Mo-anode XRF system, between 5 May 2006 and 31 August 2006 on the Cu-anode XRF system, and between 14 June 2006 and 7 September 2006 on the PESA system. Table 1

summarizes the second-quarter 2005 detection rates on the three systems, with rates for March 2005 included for comparison.

PESA					
Z	**element**	**3-2005**	**4-2005**	**5-2005**	**6-2005**
1	H	98%	99%	99%	98%

Cu-anode XRF					
Z	**element**	**3-2005**	**4-2005**	**5-2005**	**6-2005**
11	Na	44%	47%	37%	50%
12	Mg	21%	40%	31%	33%
13	Al	85%	90%	90%	89%
14	Si	97%	98%	98%	95%
15	P	1%	1%	1%	1%
16	S	99%	99%	99%	98%
17	Cl	14%	13%	9%	10%
19	K	99%	99%	99%	98%
20	Ca	99%	99%	99%	98%
22	Ti	97%	98%	98%	97%
23	V	89%	96%	89%	89%
24	Cr	67%	70%	73%	65%
25	Mn	98%	99%	98%	97%
26	Fe	99%	99%	100%	99%

Mo-anode XRF					
Z	**element**	**3-2005**	**4-2005**	**5-2005**	**6-2005**
28	Ni	49%	57%	54%	60%
29	Cu	88%	84%	81%	91%
30	Zn	99%	100%	100%	98%
33	As	41%	49%	49%	43%
34	Se	90%	90%	92%	86%
35	Br	99%	100%	100%	98%
37	Rb	69%	68%	71%	70%
38	Sr	92%	95%	93%	91%
40	Zr	13%	11%	23%	29%
82	Pb	97%	99%	98%	96%

Table 1. Percentage of cases in which the element was detected on each system. March 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 second quarter of 2005 are listed below in Table 2 (Mo system) and Table 3 (Cu system). 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 all Mo analyses. 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 Cu 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. 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 both XRF systems is monitored by weekly calibration verification checks. 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% 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 March 2005 (for context) and April-June 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.
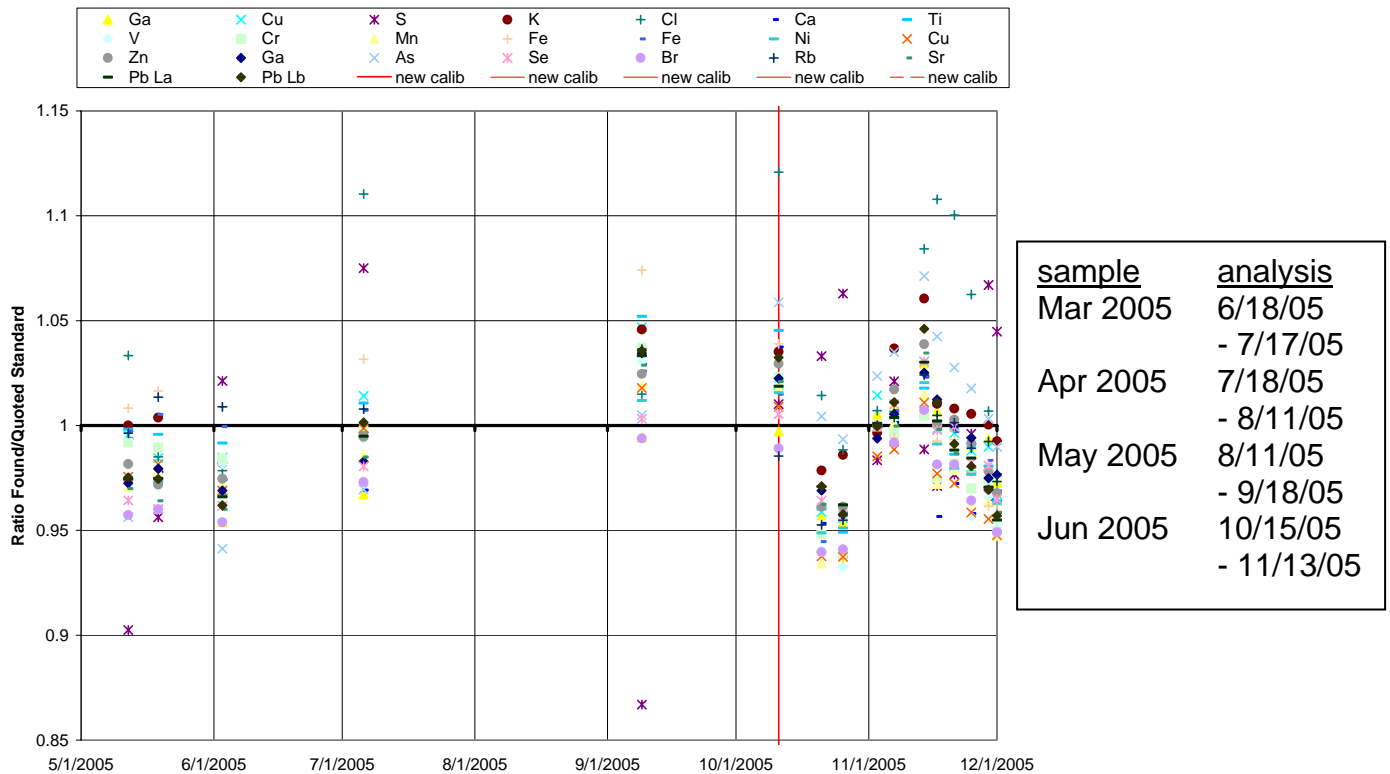

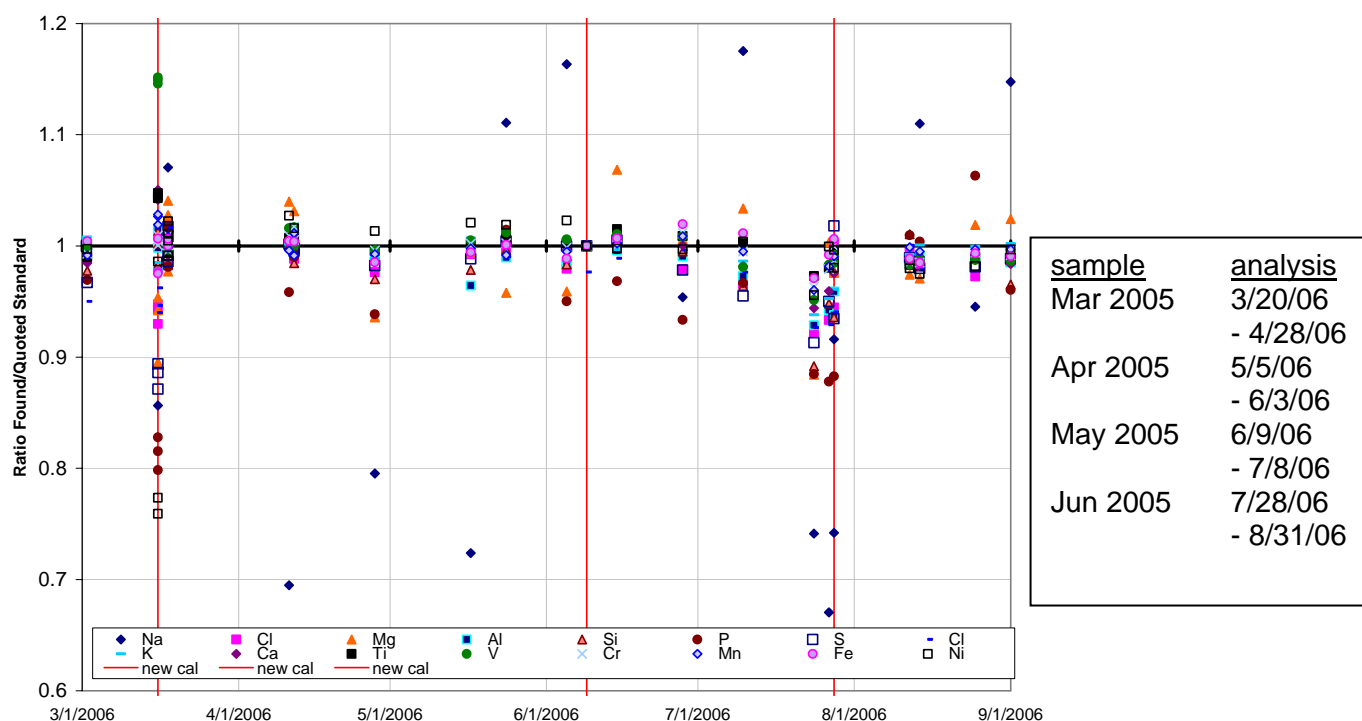**Figure 1.** Mo XRF system performance chart based on standards

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

The XRF-Mo system was reconfigured after detector maintenance and reinstallation on 11 October 2005 and new calibration factors were applied to subsequent analyses. More-frequent calibration checks were also initiated at that time. Values outside criteria were recorded for S on 9 September 2005 (low) and Cl on 17 November 2005 (high). Ambient Ar (atomic number 18) can interfere with neighboring elements in the open air XRF-Mo system, and similar deviations have been observed before for S and Cl (atomic numbers 16 and 17). Because both elements are reported from the vacuum XRF-Cu system, no action was taken and all calibration checks were considered successful.

The XRF-Cu system was recalibrated twice in response to system modifications during the analysis of Apr-Jun 2005 samples, on 9 June and 28 July 2006. Sodium exhibited the highest variability in measured standard values, but was considered acceptable because it is considered qualitative only.

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 $\mu g/cm^2$. 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 March 2005 (for context) and April - June 2005 samples.

1/8 mil Mylar standards
March, April, May and June 2005 samples

Figure 3. PESA standards for March, April, May and June 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 of April, May, and June 2005 samples, respectively:

- for XRF-Cu   intercept= -0.05603950, slope= 0.01692728
  intercept= -0.03073931, slope= 0.01665470
  intercept= -0.03399334, slope= 0.01664978

- for XRF-Mo   intercept= -0.07314897, slope=0.03592077
  intercept=-0.07138395, slope=0.03590873
  intercept=-0.07087657, slope=0.03601250

In addition, the resolution of the Si(Li) detectors in the XRF systems is frequently checked using an Fe-55 source. Results indicating changes of 5% or more in the width of the K-alpha peak for Mn are reported and further investigated.

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 April 2005 samples, 30 SAFOX and SAMAX filters from January-February 2005 were reanalyzed. Similarly, May 2005 and June 2005 reanalyses were performed, respectively, on 16 MEVEX filters from January-February 2005 and 13 SAFOX filters from March-April 2005. Figure 4 compares the original and repeat analyses.
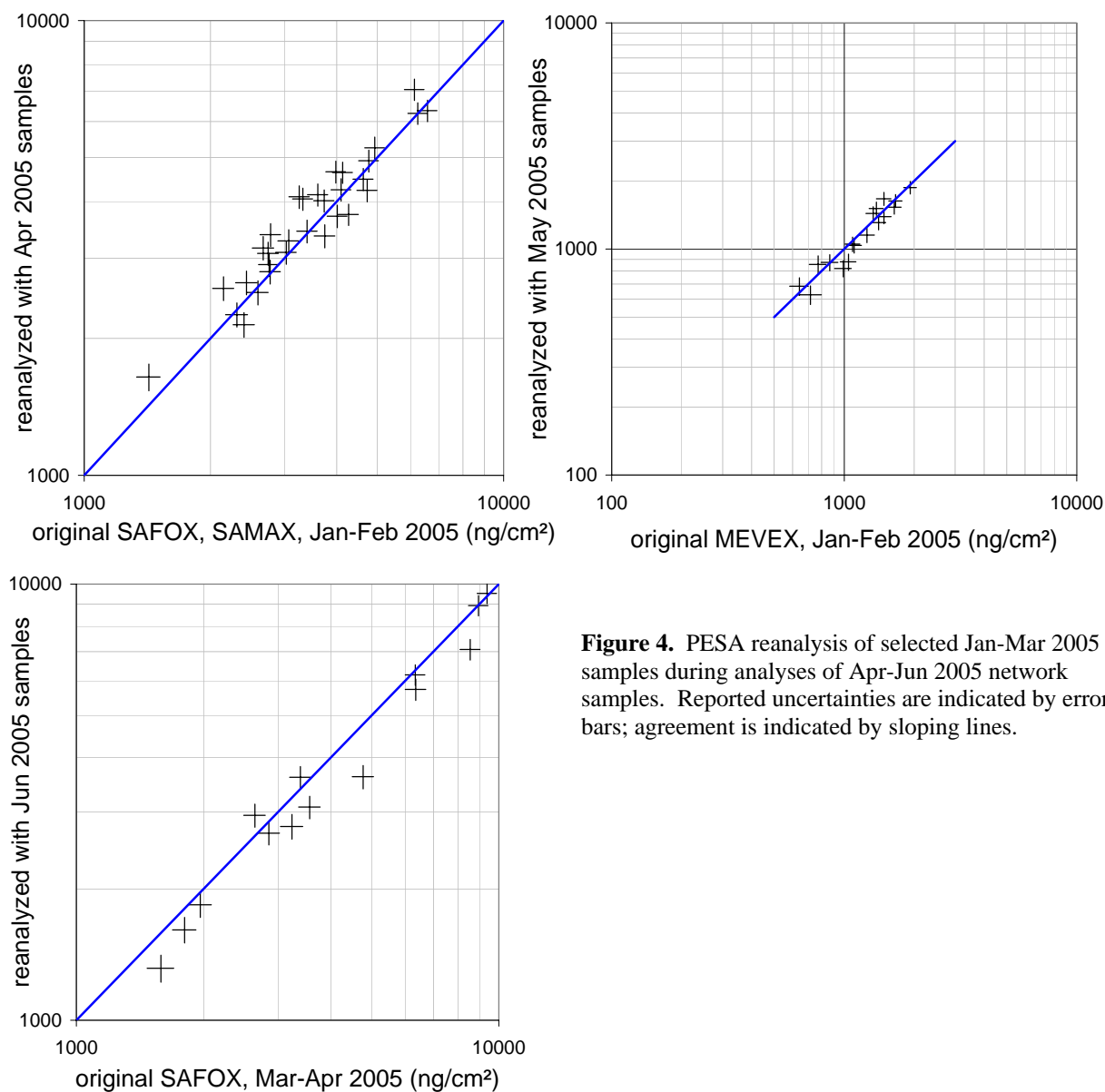
Figure 4. PESA reanalysis of selected Jan-Mar 2005 samples during analyses of Apr-Jun 2005 network samples. Reported uncertainties are indicated by error bars; agreement is indicated by sloping lines.

XRF reanalyses are conducted repeatedly on a fixed collection of sample filters. From late 2004 through 2005, all reanalyses by the XRF-Mo and old helium-flushed XRF-Cu systems used the 28 BIBE1 samples from June-August 2003. Some of these old filters experienced mechanical damage during initial testing of the new vacuum XRF-Cu system at the end of 2005. A new collection of 72 filters for reanalysis was accordingly 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 new 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 April-June 2005 samples were performed in June-November 2005, when reanalyses were still being done on BIBE1 samples. The XRF-Cu analyses for April-June 2005 samples were performed in March-August 2006, after the change to the REANAL1 and REANAL2 trays. The results are summarized in the figures below.

Figures 5-7 show the consistency of reanalysis results from both systems before and during the analysis of the April-June 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.
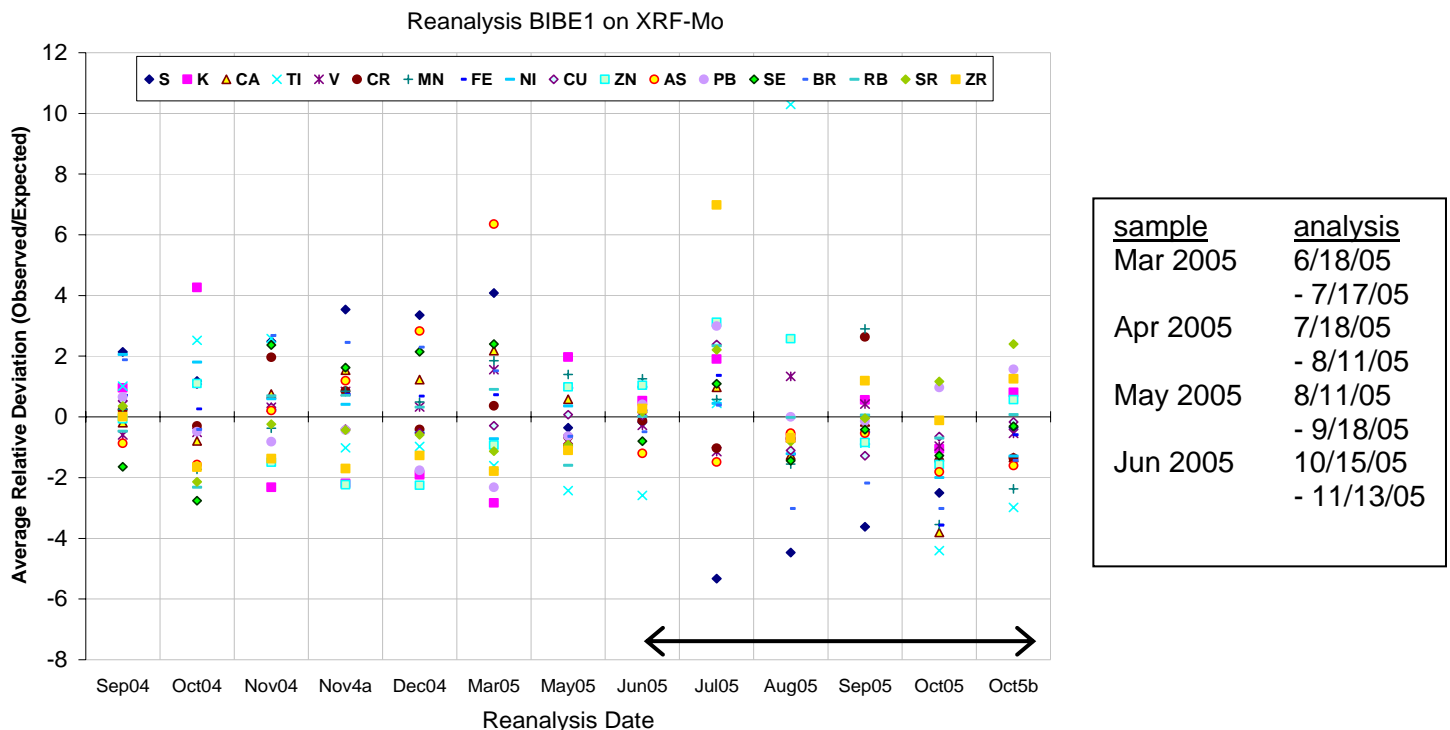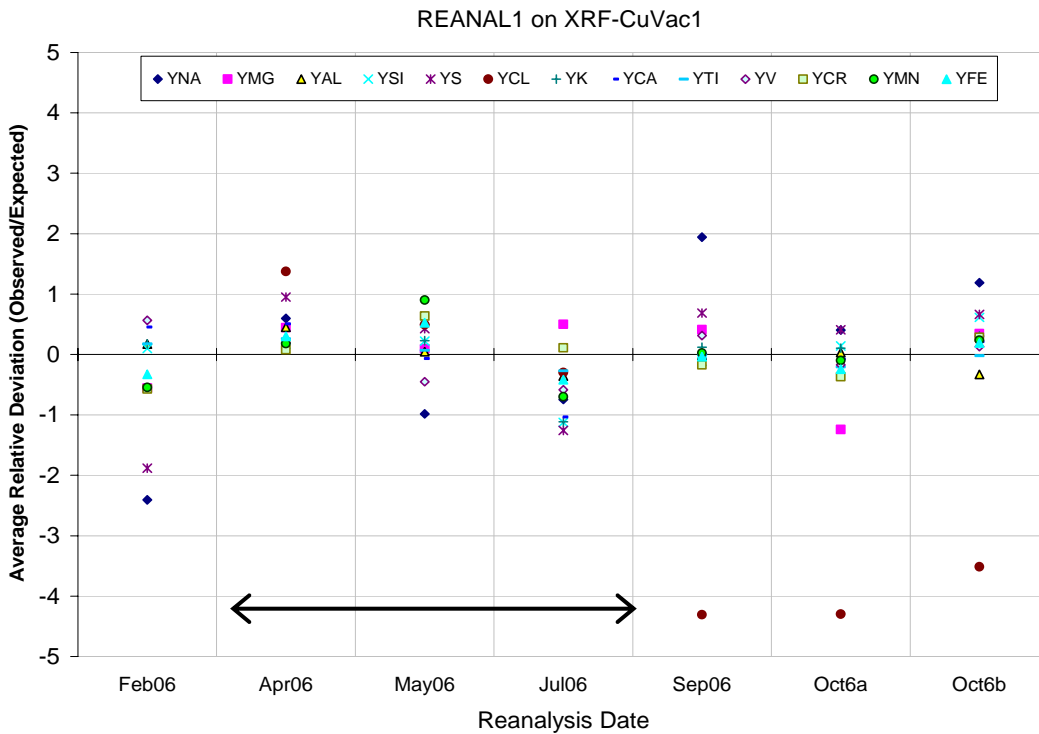

Figure 5. Reanalyses of June-August 2003 BIBE1 samples on XRF-Mo system. Horizontal arrow indicates when April-June 2005 network samples were analyzed. The elements S - Fe are not reported from XRF-Mo.

REANAL1 on XRF-CuVac1

sample	analysis
Mar 2005	3/20/06 - 4/28/06
Apr 2005	5/5/06 - 6/3/06
May 2005	6/9/06 - 7/8/06
Jun 2005	7/28/06 - 8/31/06

Figure 6. Reanalyses of REANAL1 samples on XRF-Cu system. Horizontal arrow indicates when April-June 2005 network samples were analyzed.

REANAL2 on XRF-CuVac1
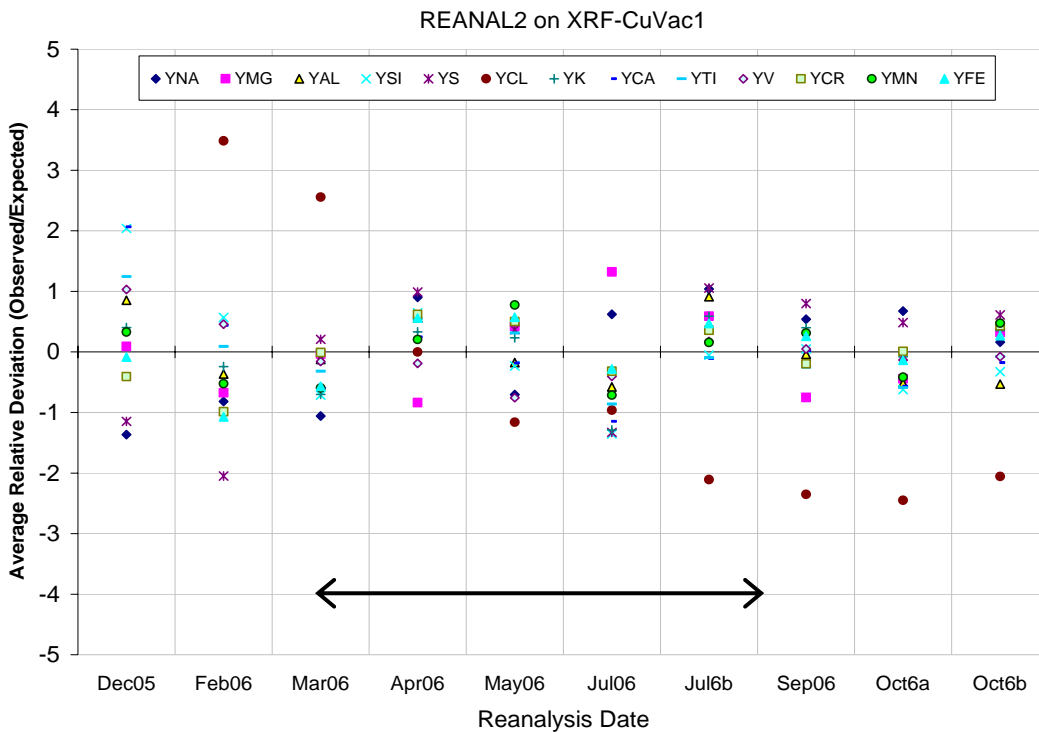
sample	analysis
Mar 2005	3/20/06 - 4/28/06
Apr 2005	5/5/06 - 6/3/06
May 2005	6/9/06 - 7/8/06
Jun 2005	7/28/06 - 8/31/06

Figure 7. Reanalyses of REANAL2 samples on XRF-Cu system. Horizontal arrow indicates when April-June 2005 network samples were analyzed.

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.

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 7 and 8 compare the two measurements of these two elements for the samples from April to June 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.
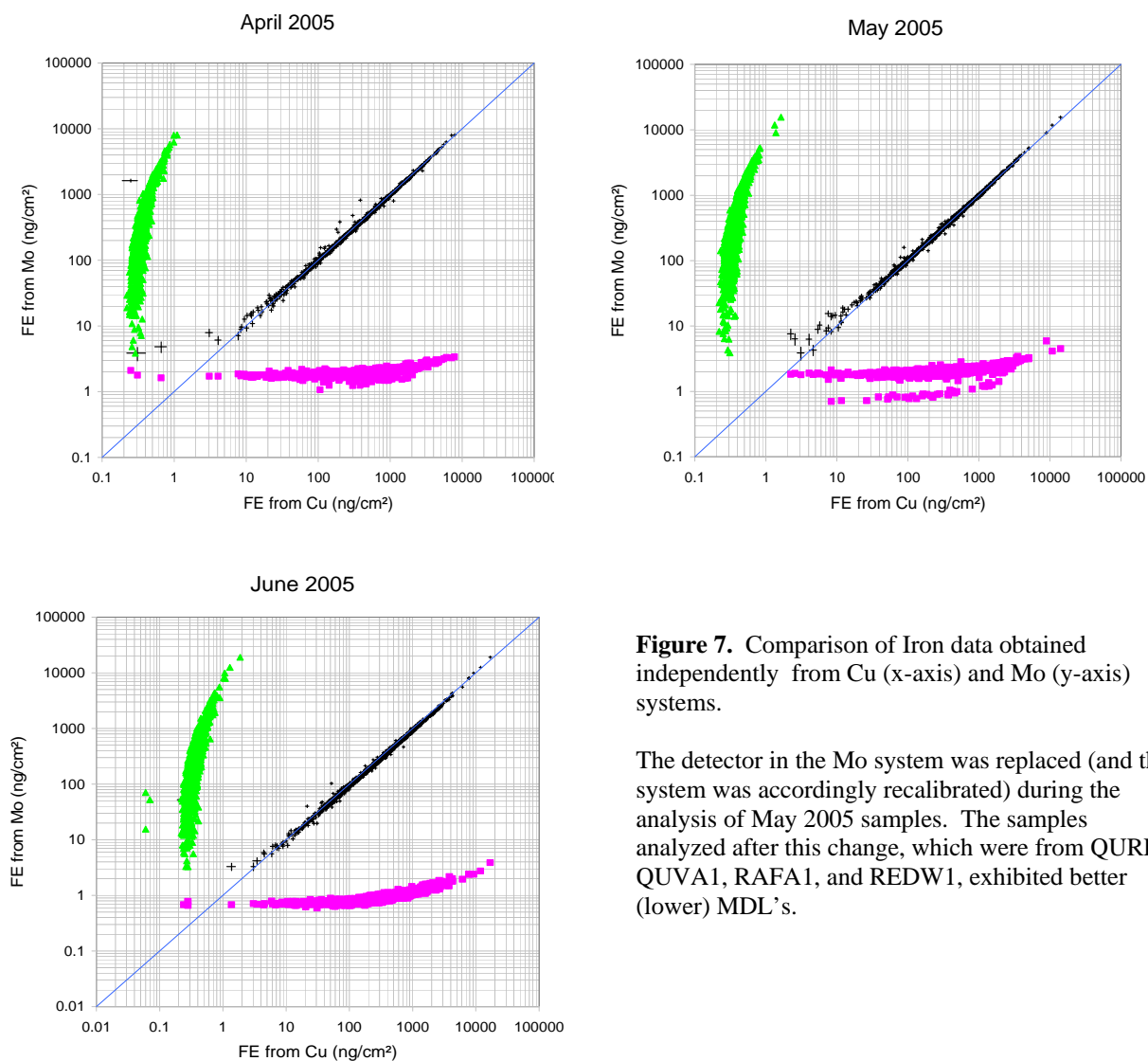

Figure 7. Comparison of Iron data obtained independently from Cu (x-axis) and Mo (y-axis) systems.

The detector in the Mo system was replaced (and the system was accordingly recalibrated) during the analysis of May 2005 samples. The samples analyzed after this change, which were from QURE1, QUVA1, RAFA1, and REDW1, exhibited better (lower) MDL's.
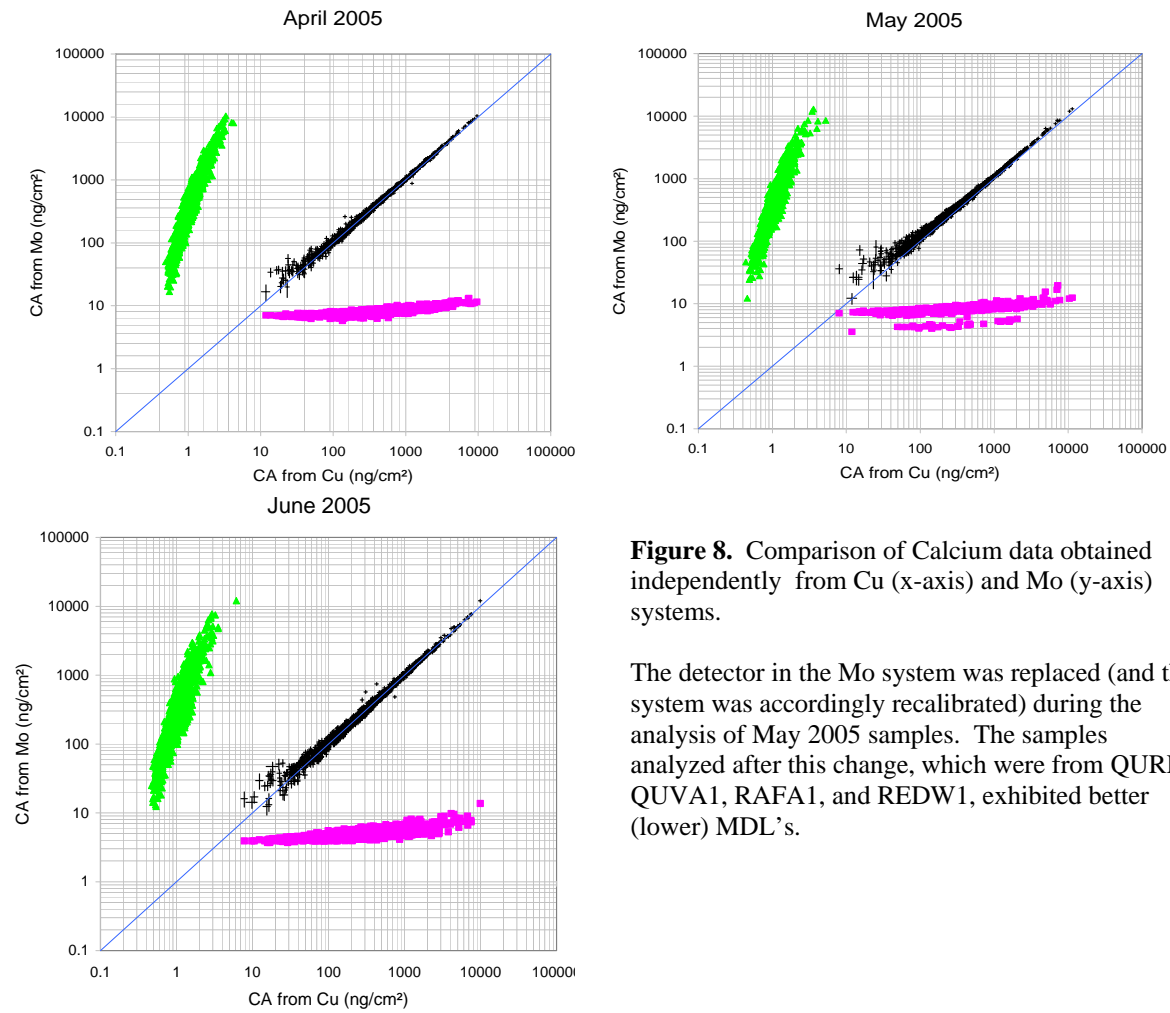
April 2005

May 2005

June 2005

Figure 8. Comparison of Calcium data obtained independently from Cu (x-axis) and Mo (y-axis) systems.

The detector in the Mo system was replaced (and the system was accordingly recalibrated) during the analysis of May 2005 samples. The samples analyzed after this change, which were from QURE1, QUVA1, RAFA1, and REDW1, exhibited better (lower) MDL's.

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 check they provide on both systems' performance. The current check is a qualitative one, but the planned development of improved uncertainty estimates noted above may lead to quantitative acceptance criteria.