

Data report for elemental analysis of IMPROVE samples collected during
January, February, March 2007
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SUMMARY

This report summarizes the quality assurance performed during elemental analysis of the IMPROVE samples collected in January, February and March of 2007. 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.

Jan and Feb 2007 samples were analyzed on Cu-Vac2 and Mar 2007 samples were analyzed on Cu-Vac1. All calibration checks performed on both Cu systems and the Mo system during the analyses of Jan-Mar 2007 samples met criteria.

The procedure for analyzing XRF system calibration data was modified beginning with the January 2007 data. In prior years the calibration for any element has been based upon the quoted concentration of the calibration standard foil for that element, as reported by the Micromatter, the manufacturer of the standard foils. Beginning with the January 2007 data, a standard was analyzed for each element and then a smooth curve was drawn through the resulting instrument responses. The curve fit value for each element was then used as the basis for calibration. This new curve fitting approach was initiated in an attempt to dampen the concentration uncertainty associated with any single standard foil. The result is a shift in the typical concentrations reported for some elements, which will be illustrated in detail in this report.

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 January, February and March 2007 data

XRF and PESA analyses were carried out on 1595 samples collected in January 2007, 1509 samples collected in February 2007 and 1812 samples collected in March 2007. All samples were analyzed between 2 June 2007 and 13 August 2007 on the Mo-anode XRF system, between 17 August 2007 and 10 October 2007 on Cu-Vac2, between 2 October 2007 and 27 October 2007 on Cu-Vac1, and on 10/19-11/1/07 (Jan, Feb 2007 samples), and 11/15-16/07 (Mar 07 samples) on the PESA system.

Table 1 summarizes the first quarter 2007 detection rates on the three systems, with rates for December 2006 included for comparison. Month-to-month differences can result both from seasonal atmospheric variability and from differences in the minimum detectable limits (MDLs) of the analytical systems.

PESA					
Z	element	1-2007	2-2007	3-2007	12-2006
1	H	100%	100%	100%	100%

Cu-anode XRF					
Z	element	1-2007	2-2007	3-2007	12-2006
11	Na	70%	81%	52%	37%
12	Mg	42%	43%	39%	21%
13	Al	81%	84%	91%	63%
14	Si	97%	99%	99%	90%
15	P	3%	3%	1%	1%
16	S	100%	100%	100%	100%
17	Cl	19%	23%	18%	22%
19	K	100%	100%	100%	100%
20	Ca	100%	100%	100%	100%
22	Ti	98%	99%	99%	92%
23	V	88%	87%	91%	75%
24	Cr	66%	64%	69%	46%
25	Mn	97%	97%	99%	90%
26	Fe	100%	100%	100%	100%

Mo-anode XRF					
Z	element	1-2007	2-2007	3-2007	12-2006
28	Ni	40%	43%	66%	52%
29	Cu	89%	83%	88%	90%
30	Zn	99%	97%	100%	100%
33	As	44%	49%	39%	52%
34	Se	78%	78%	88%	77%
35	Br	100%	100%	100%	100%
37	Rb	61%	59%	73%	62%
38	Sr	95%	94%	99%	90%
40	Zr	43%	46%	39%	19%
82	Pb	99%	96%	100%	98%

Table 1. Percentage of cases in which the element was detected on each system. December 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 first quarter of 2007 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. As mentioned in the Summary section of this report, beginning with the January 2007 samples the calibration factors relating spectral counts to elemental concentrations are determined from the ratio of an element's observed peak area to the concentration determined from a smooth curve fit through the available standards.

The change from a single foil calibration approach to a curve fitting approach resulted in a shift in the typical concentrations reported for some elements. These shifts can be seen in Figures 1 through 3 for the Mo, Cu-Vac1, and Cu-Vac2 systems, respectively. During the analyses of Jan-Mar 2007 samples, the performance of each of these systems was monitored approximately weekly. For these calibration checks fifteen standards were analyzed on the Cu systems and 19 on the Mo system, and the ratios of reported to quoted values are calculated. These ratios are illustrated in Figures 1 through 3, shown both before and after the change to the curve fitting calibration procedure. It is evident that the new calibration procedure shifted the reported values for some elements; the magnitude of the shift is represented by the deviation from unity on the y-axis. As an example, in Figure 3 the reported values for sulfur hover around 0.9, indicating that the reported concentrations for sulfur are about 10 percent lower than those that would be calculated from the old single-foil procedure. The effect of this calibration shift on network data is illustrated in Figure 4, which shows the daily IMPROVE network median value, along with upper and lower quartiles for the ratio of 3 times sulfur (from XRF) to sulfate (from

ion chromatography). A drop in this ratio of approximately 10 percent is evident in January 2007, consistent with the change in the calibration approach.

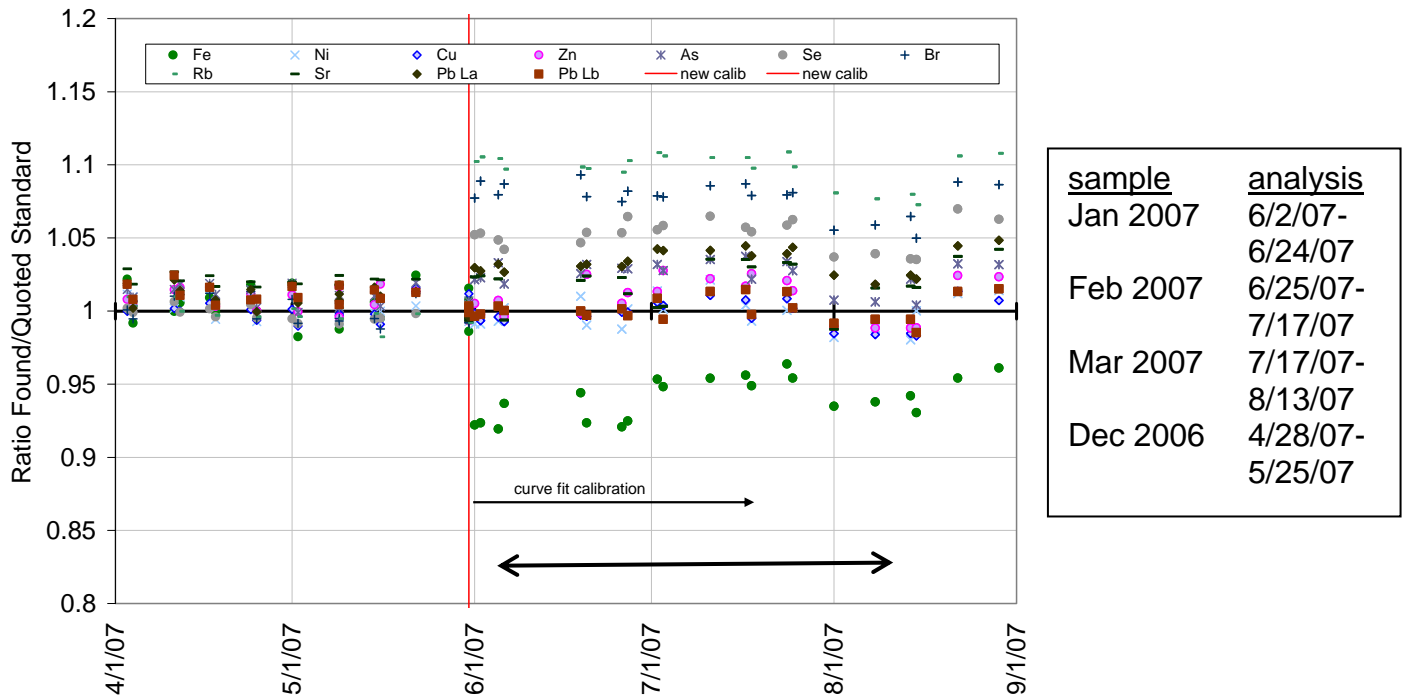


Figure 1. Mo XRF system performance chart based on standards

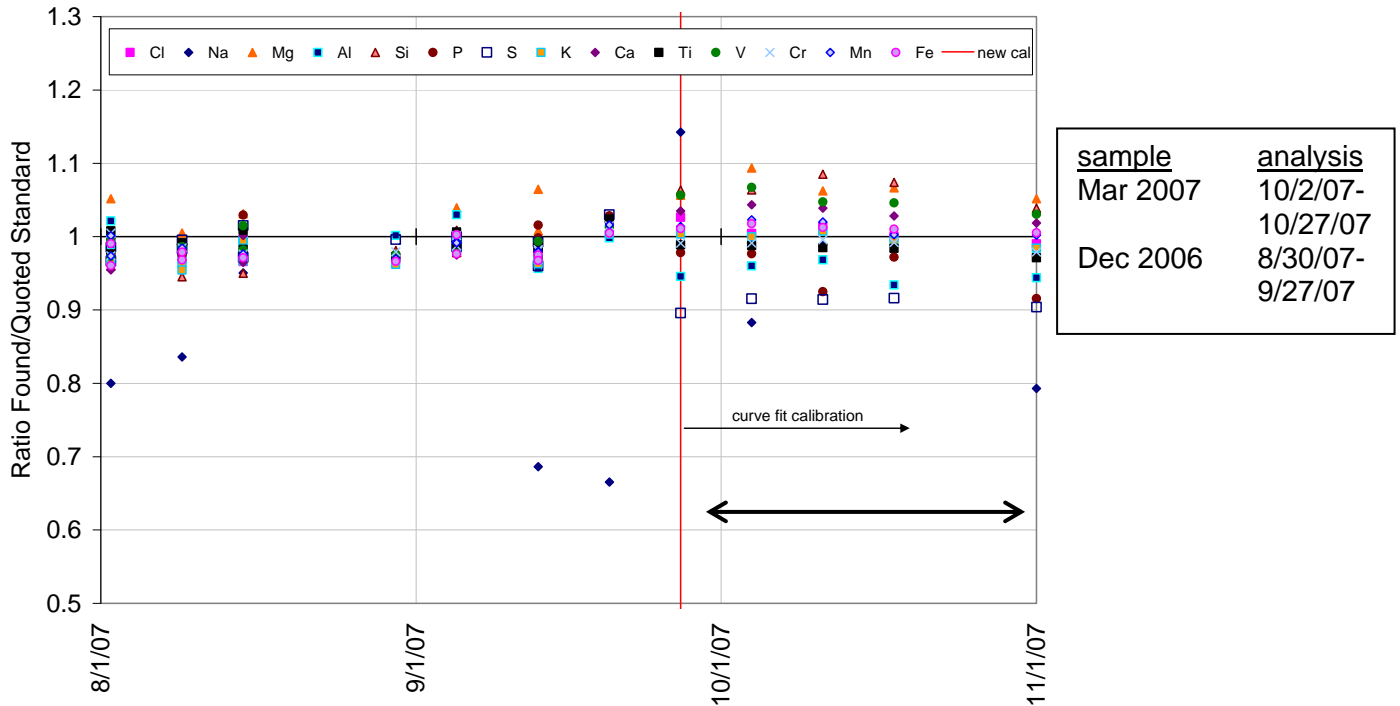


Figure 2. Cu-Vac1 XRF system performance chart based on standards.

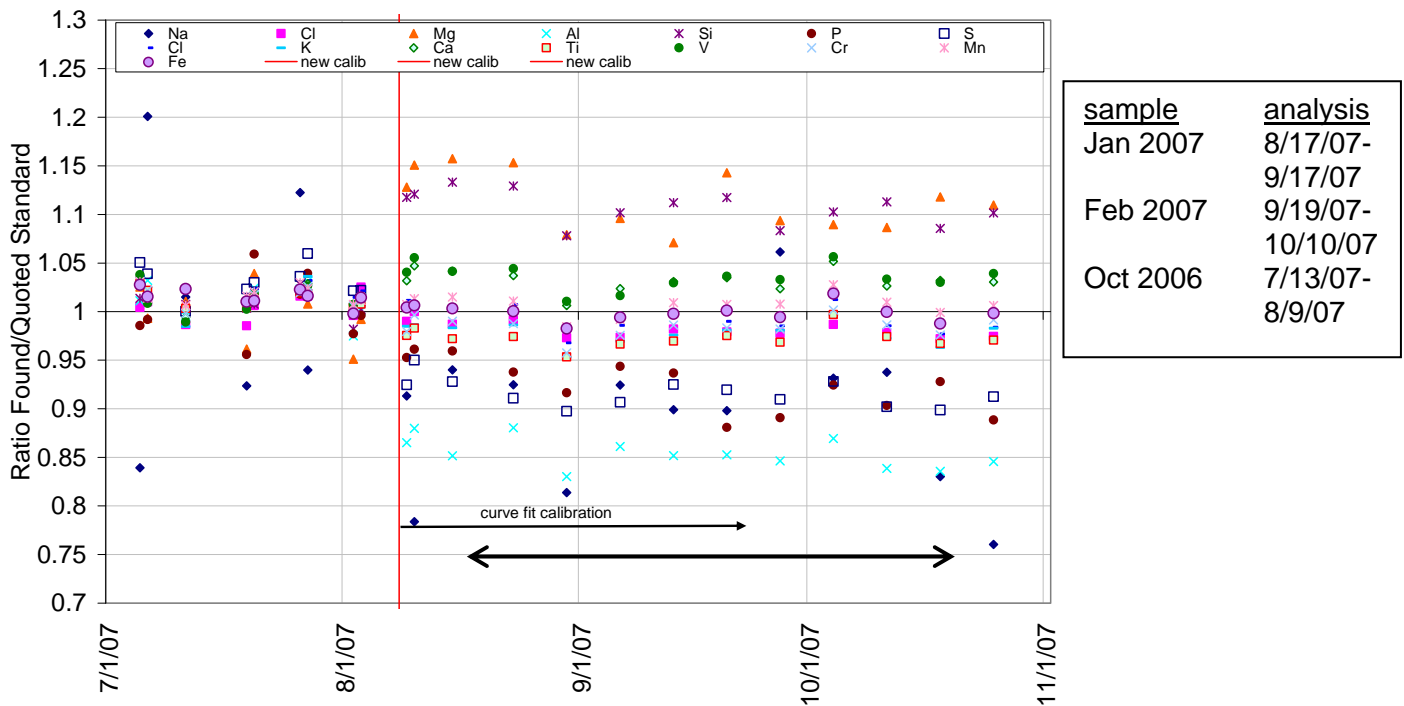


Figure 3. Cu-Vac2 XRF system performance chart based on standards.

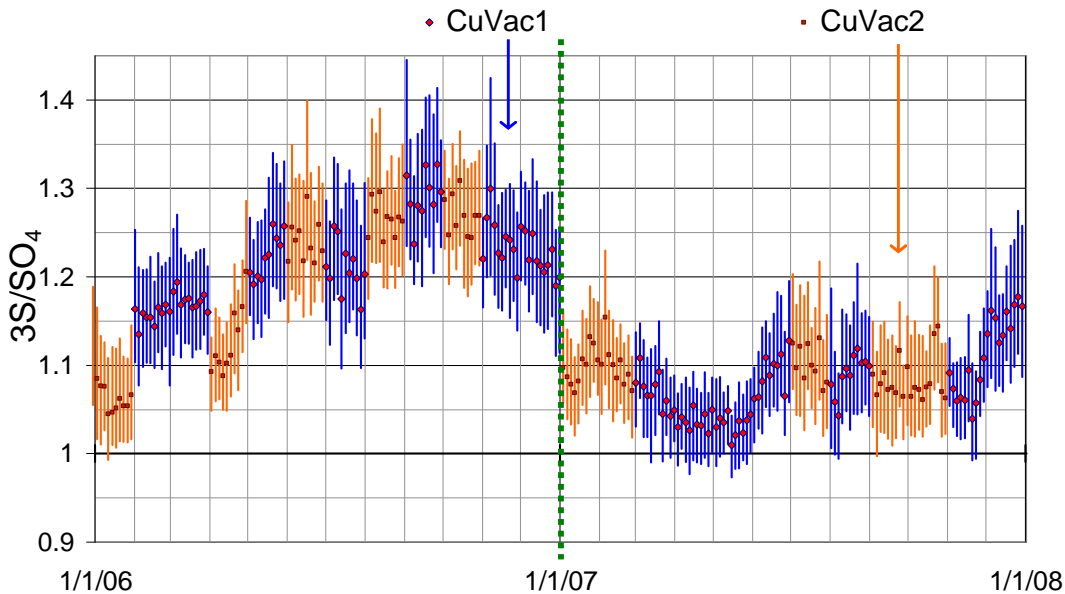
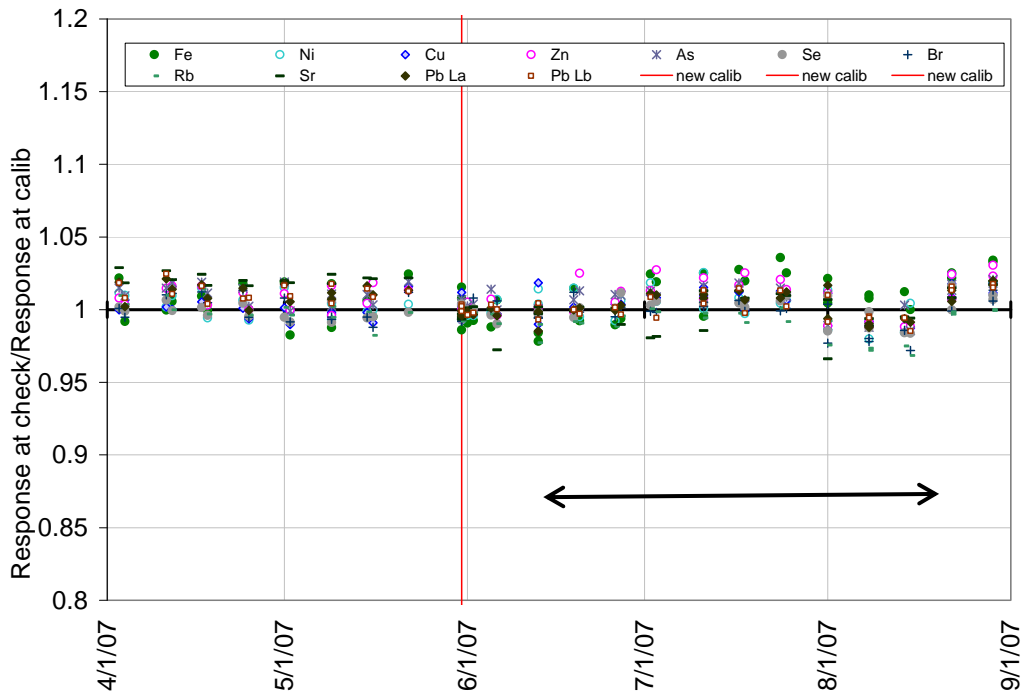


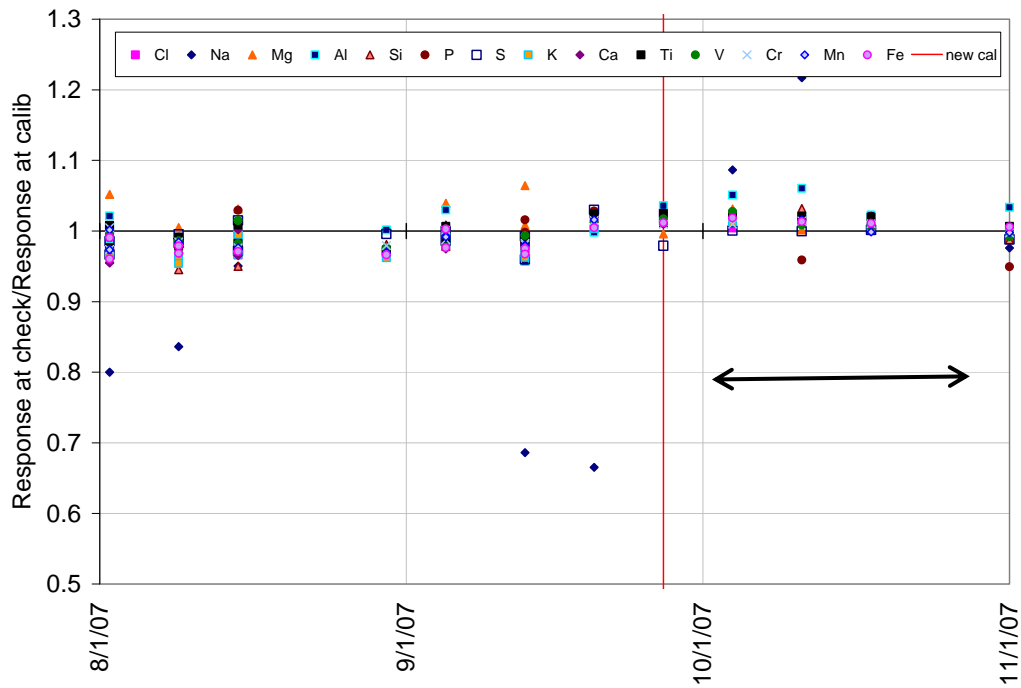
Figure 4. IMPROVE network medians for 3S/SO₄. Sulfur determined by XRF and sulfate by IC.

A principal purpose of the approximately weekly calibration checks is to evaluate the physical stability of each XRF system since its last calibration. Figures 5 through 7 present a modified presentation of Figures 1 through 3, here plotting the ratio of the system response at each check to the response observed at the last calibration. For samples prior to January 2007 both responses are based upon the quoted single-standard values, and beginning with January 2007 both responses are based upon the curve fit. 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.



sample	analysis
Jan 2007	6/2/07-6/24/07
Feb 2007	6/25/07-7/17/07
Mar 2007	7/17/07-8/13/07
Dec 2006	4/28/07-5/25/07

Figure 5. Mo XRF system performance chart referenced to last calibration.



sample	analysis
Mar 2007	10/2/07-10/27/07
Dec 2006	8/30/07-9/27/07

Figure 6. Cu-Vac1 XRF system performance chart referenced to last calibration.

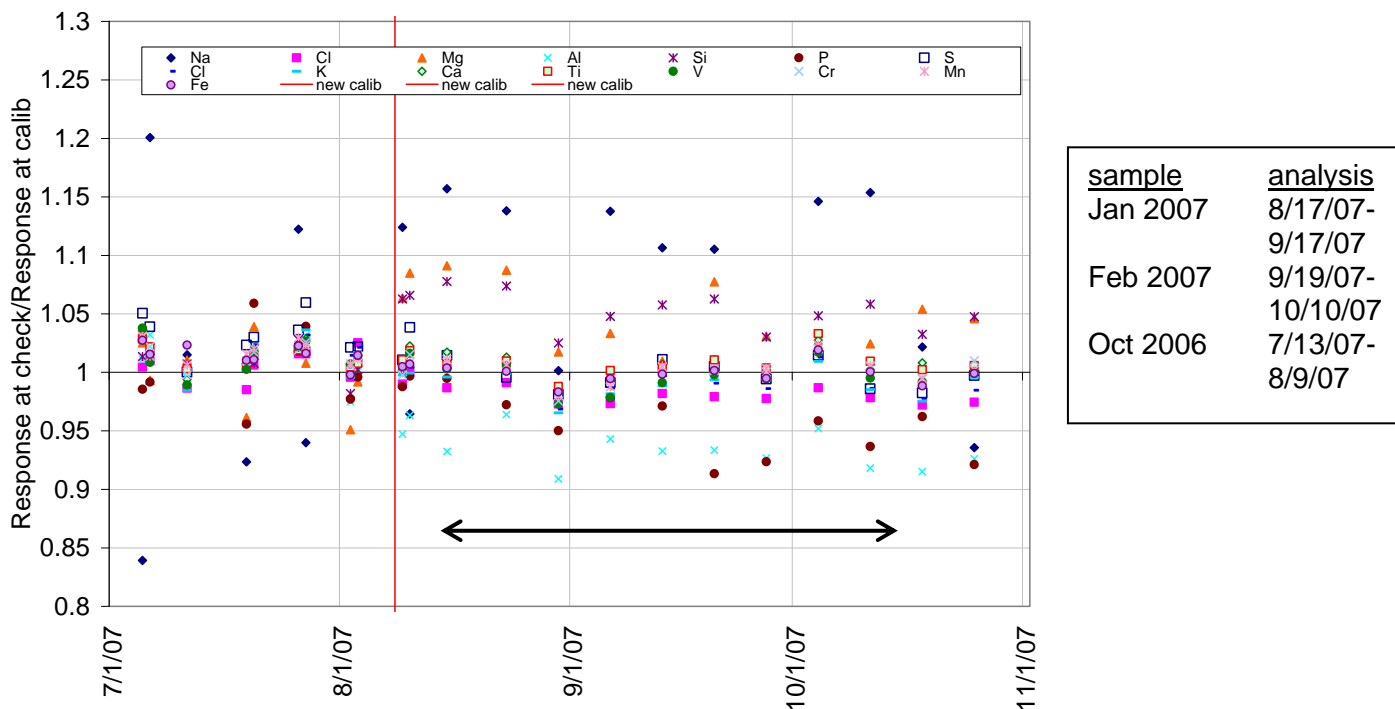


Figure 7. Cu-Vac2 XRF system performance chart referenced to last calibration.

None of the standards ratios exceeded acceptance limits during the analysis of Jan-Mar 2007 samples on the Mo system. All calibration checks were within criteria.

January and February 2007 samples were analyzed on the XRF Cu-Vac2 system and March 2007 samples were analyzed on the XRF Cu-Vac2 system. All weekly calibration checks on both systems were within criteria.

Eight Mylar foils were used for calibrations and calibration checks of the PESA system. Over the time the foil may become damaged and replaced with a new one. The change is recorded and the calculated H concentration for each of the PESA standards is entered in the table. The current H concentrations are listed below:

PESA Standard	1	2	3	4	5	6	7	8
Calculated H amount (ug/cm ²)	18.82	17.12	28.61	32.90	17.34	18.11	12.26	16.70

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 8 shows calibration verifications and calibrations during the analysis of the Jan-Mar 2007 samples.

Mylar PESA standards
January, February, March 2007 samples

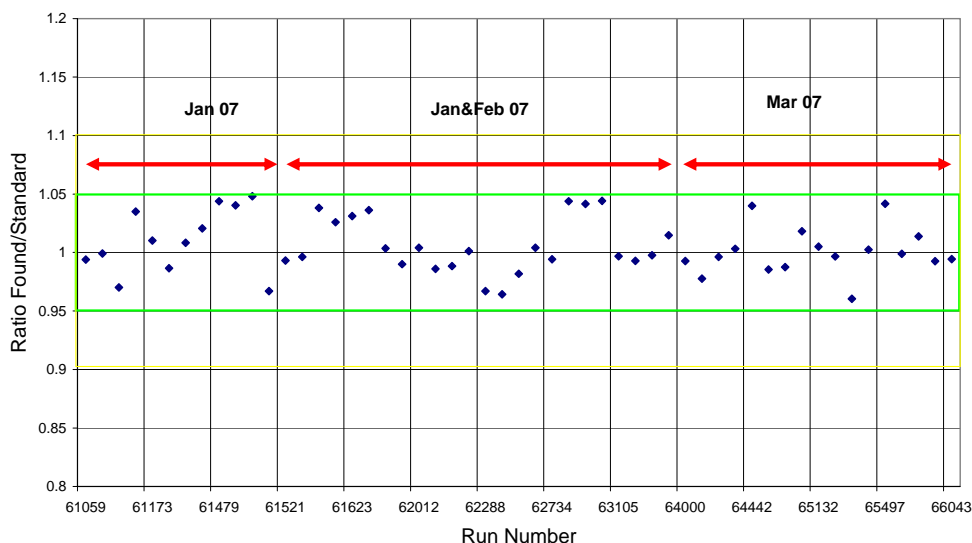


Figure 8. PESA standards for Jan-Mar 2007 samples

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 the Mo system and whenever determined necessary for the Cu systems. The established relationships have a form

$$\text{energy} = \text{intercept} + \text{slope} * \text{channel}$$

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 Jun07	
Jan-07					-4.09E-02	1.72E-02	8.766	0.19%		-7.42E-02	3.69E-02	18.809	0.00%	
Feb-07					-4.09E-02	1.72E-02	8.766	0.19%		-7.75E-02	3.69E-02	18.806	-0.02%	
Mar-07	-3.80E-02	1.67E-02	8.493	0.03%						-7.75E-02	3.69E-02	18.806	-0.02%	

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 Jan 2007 samples, 23 SAFOX, SAMAX, TRCRX filters from August 2006 were reanalyzed multiple times. For Feb 2007 samples, 28 MEVEX, OLYMX, TRCRX from Sep 2006 were reanalyzed, and multiple reanalyses for Mar 2007 samples were performed on 26 SAFOX, SAMAX, TRCRX filters from Oct 2006. Figure 9 compares the original and repeat analyses.

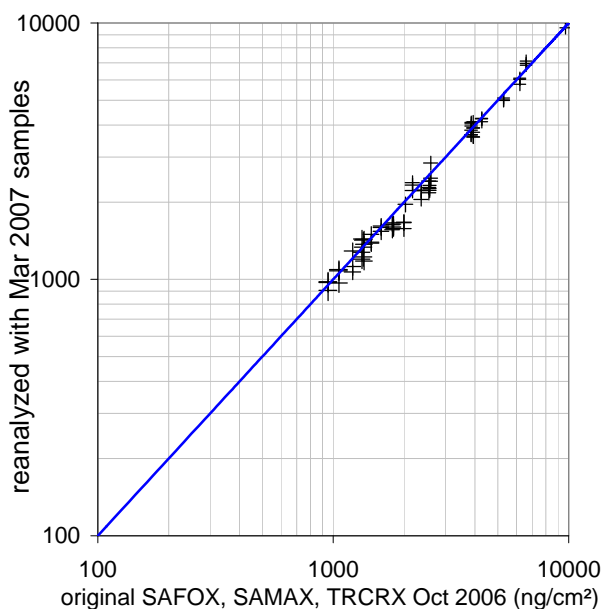
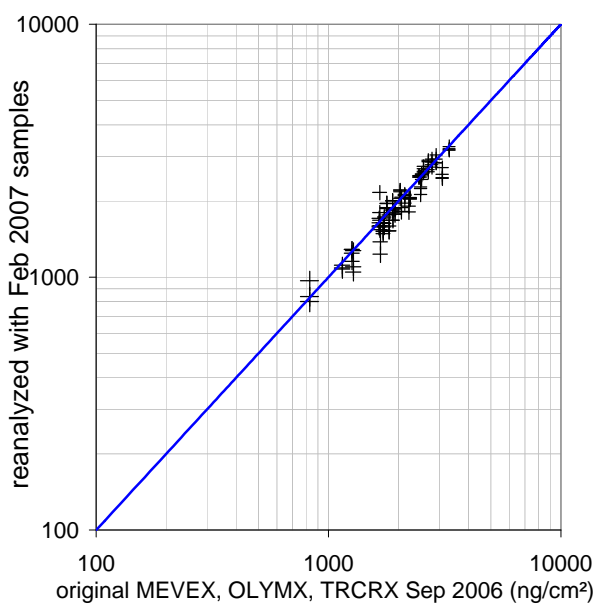
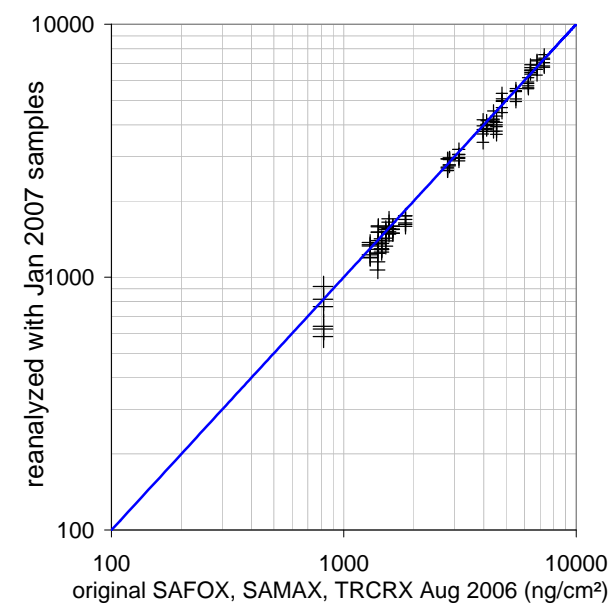


Figure 9. PESA reanalysis of selected August, September and October 2006 samples during analyses of Jan-Mar 2007 network samples. Reported uncertainties are indicated by error bars; agreement is indicated by sloping lines.

Regular 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 on the Mo and Cu-Vac2 systems and less frequently on Cu-Vac1 during analyses of the Jan-Mar 2007 samples. The results are summarized in Figures 10-12, below.

For all the systems, the mean loadings calculated based on approximately 12 consecutive runs (about a year of data during which calibrations have been based on a fixed collection of standard reference foils) are used as a benchmark for comparison. The average ratio of observed deviations from all samples (from the mean) to reported measured uncertainties for each element is calculated and shown on the y-axis. Figures 10-12 highlight the reanalysis results for four elements selected for each system, Fe, Cu, Zn and Br for Mo and Si, S, Ca and Fe for Cu. These major elements serve here as general indicators of system performance. Currently, the reanalysis is used as a qualitative check of the system performance. However, the horizontal continuous and dotted red lines shown are intended to provide proposed action and warning limits, respectively. They are based on historical systems' performance only and may need to be reevaluated if any operational conditions change.

The horizontal black arrows indicate the periods of analysis of the 1st quarter 2007 samples. The shifts in reported values for some elements due to the new curve fitting calibration procedure are evident in the reanalysis results. For example, the downward shift in reported sulfur concentrations is clearly evident in Figure 12 (red circles). Eventually, reanalysis results from 2007 will constitute a new baseline period, and future years will be compared to 2007, all processed with the curve fit calibration approach.

The increased Zn concentrations observed in reanalysis in Aug 07 (Figure 10) are more likely due to temporary contamination of the system or/and selected filters, and not to calibration shifts.

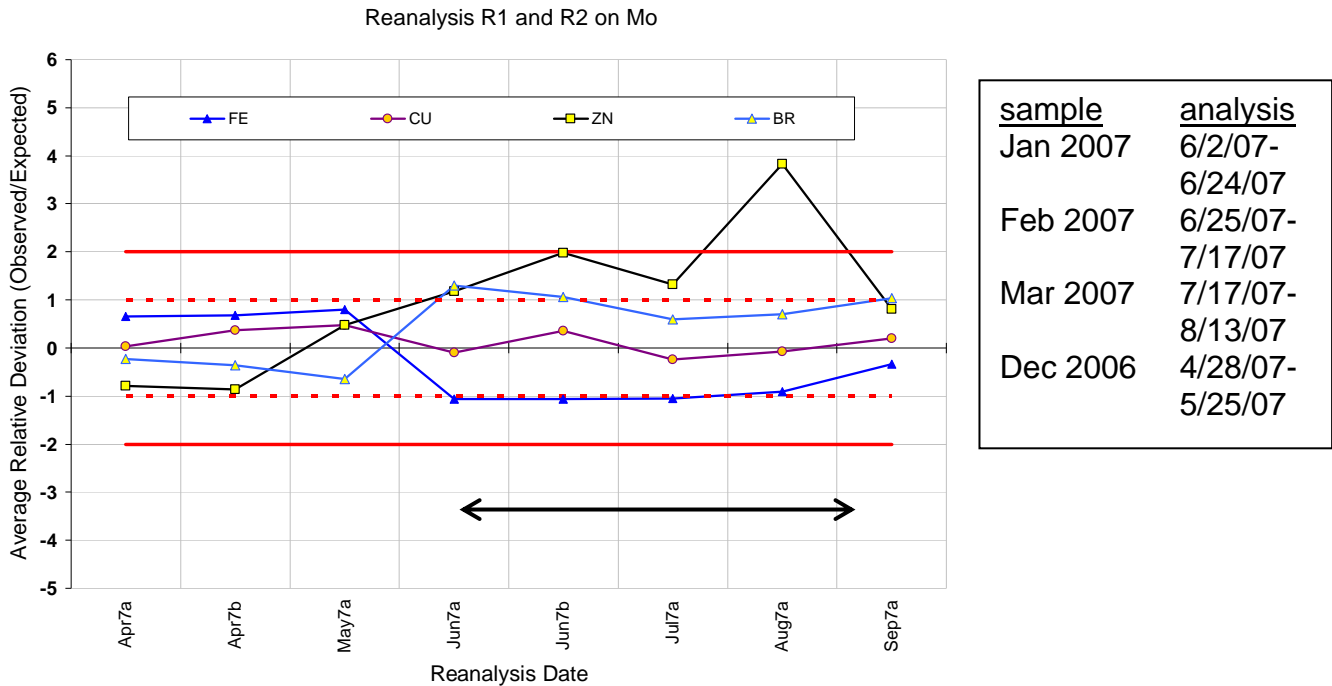


Figure 10. Reanalyses of REANAL1 and REANAL2 samples on XRF-Mo system. Horizontal arrow indicates when Jan-Mar 2007 network samples were analyzed.

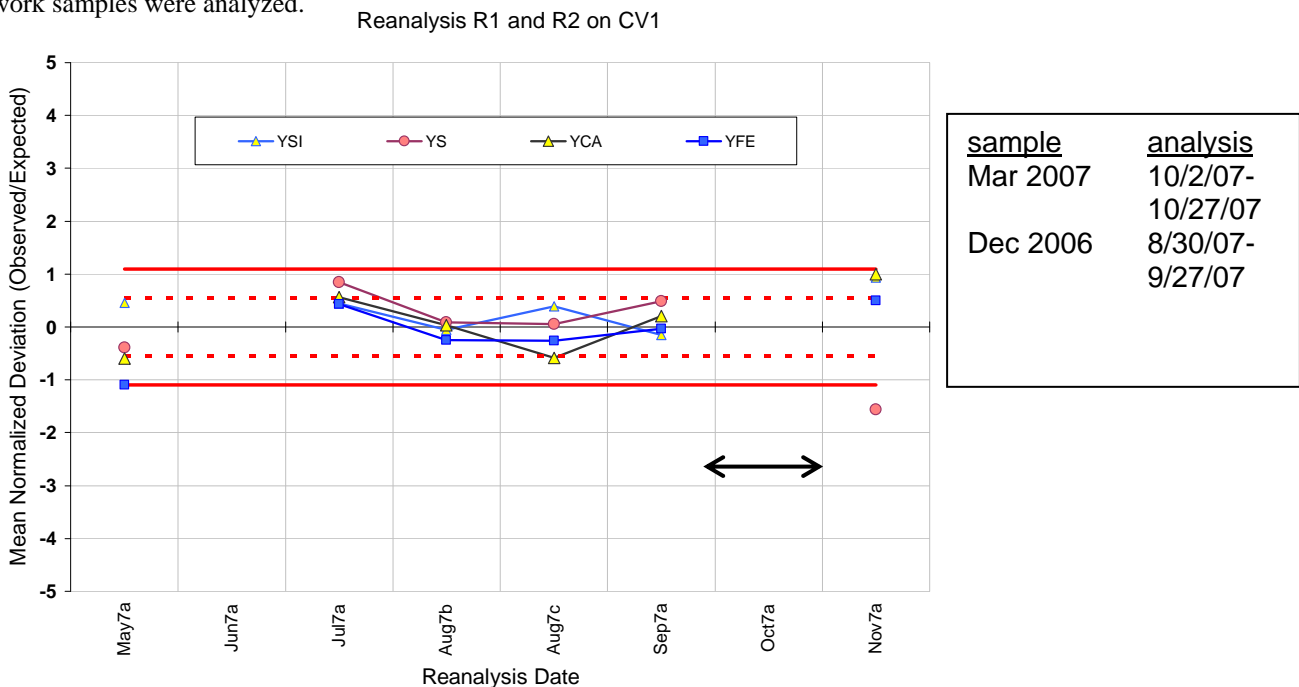


Figure 11. Reanalyses of REANAL1 and REANAL2 samples on XRF-Cu1 system. Horizontal arrow indicates when Mar 2007 network samples were analyzed.

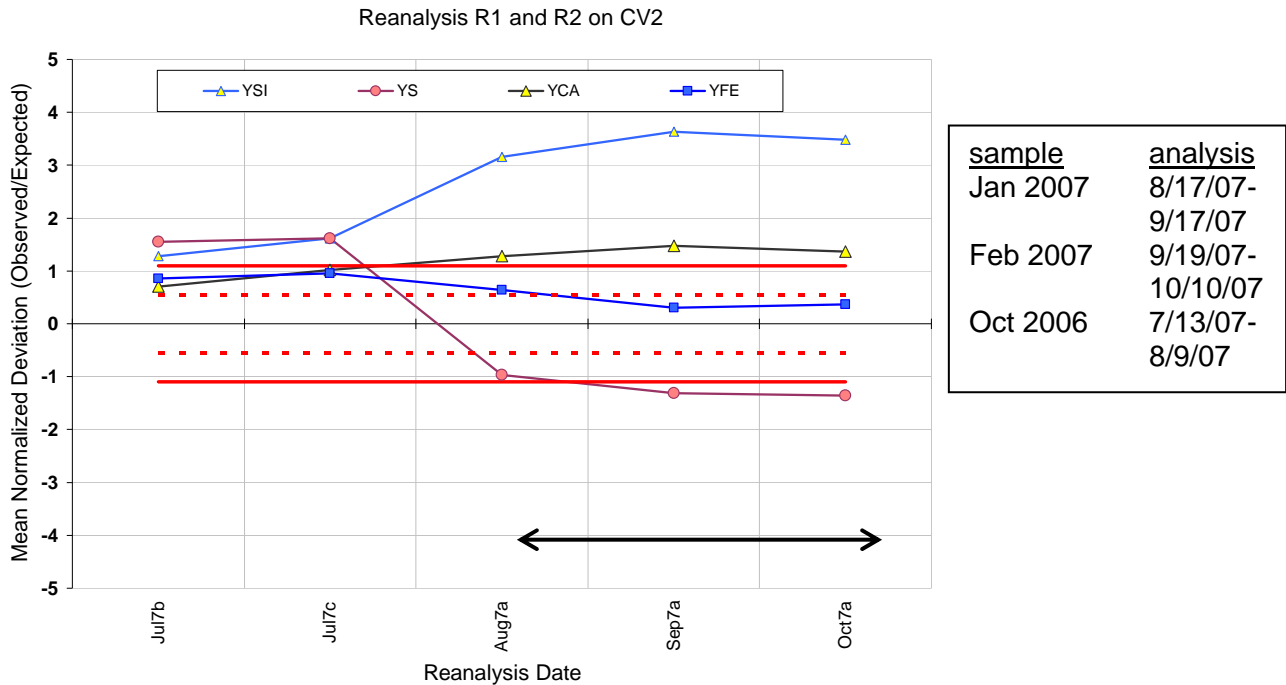


Figure 12. Reanalyses of REANAL1 and REANAL2 samples on XRF-Cu2 system. Horizontal arrow indicates when Jan and Feb 2007 network samples were analyzed.

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 13 and 14 compare the two measurements of these two elements for the samples from Jan-Mar 2007. 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.

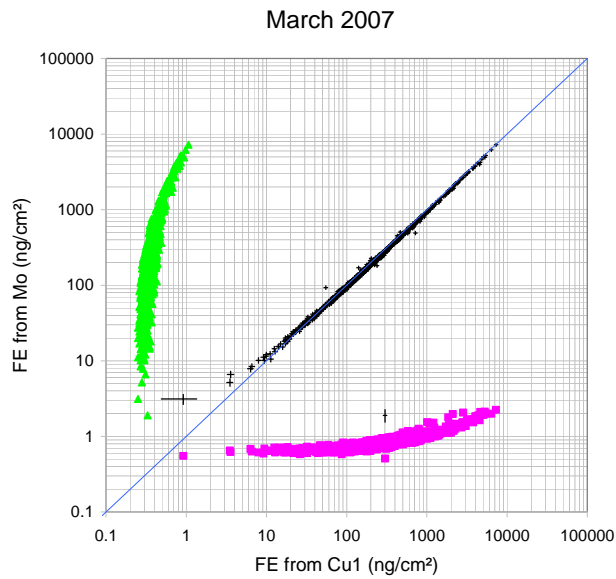
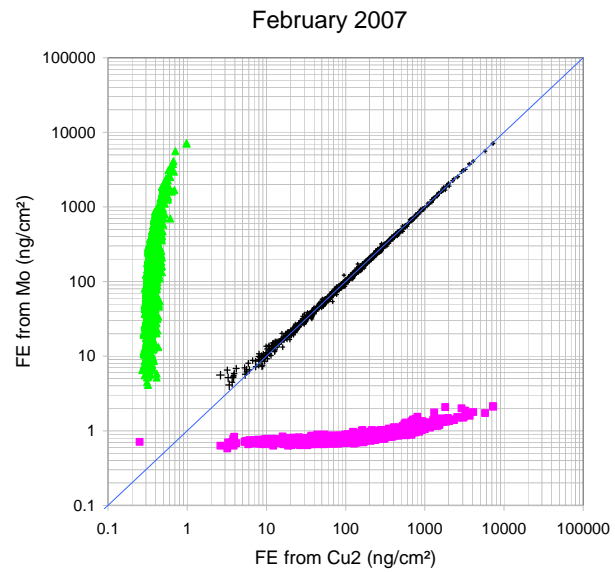
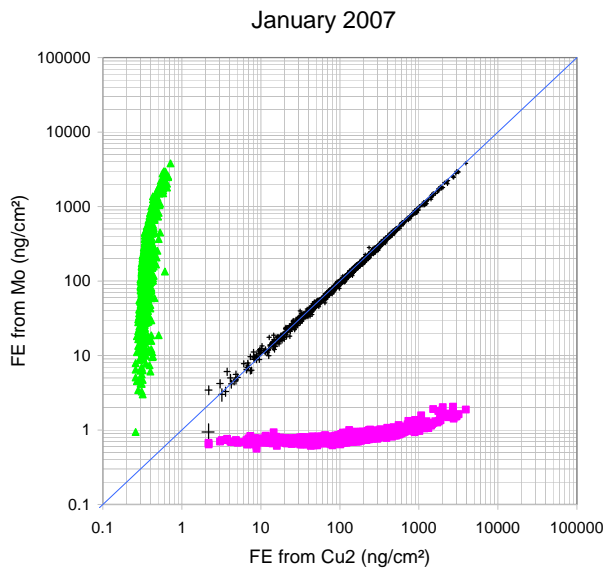


Figure 13. Comparison of Iron data obtained independently from Cu (x-axis) and Mo (y-axis) systems. Cu₁ refers to Cu-Vac1 and Cu₂ to Cu-Vac2.

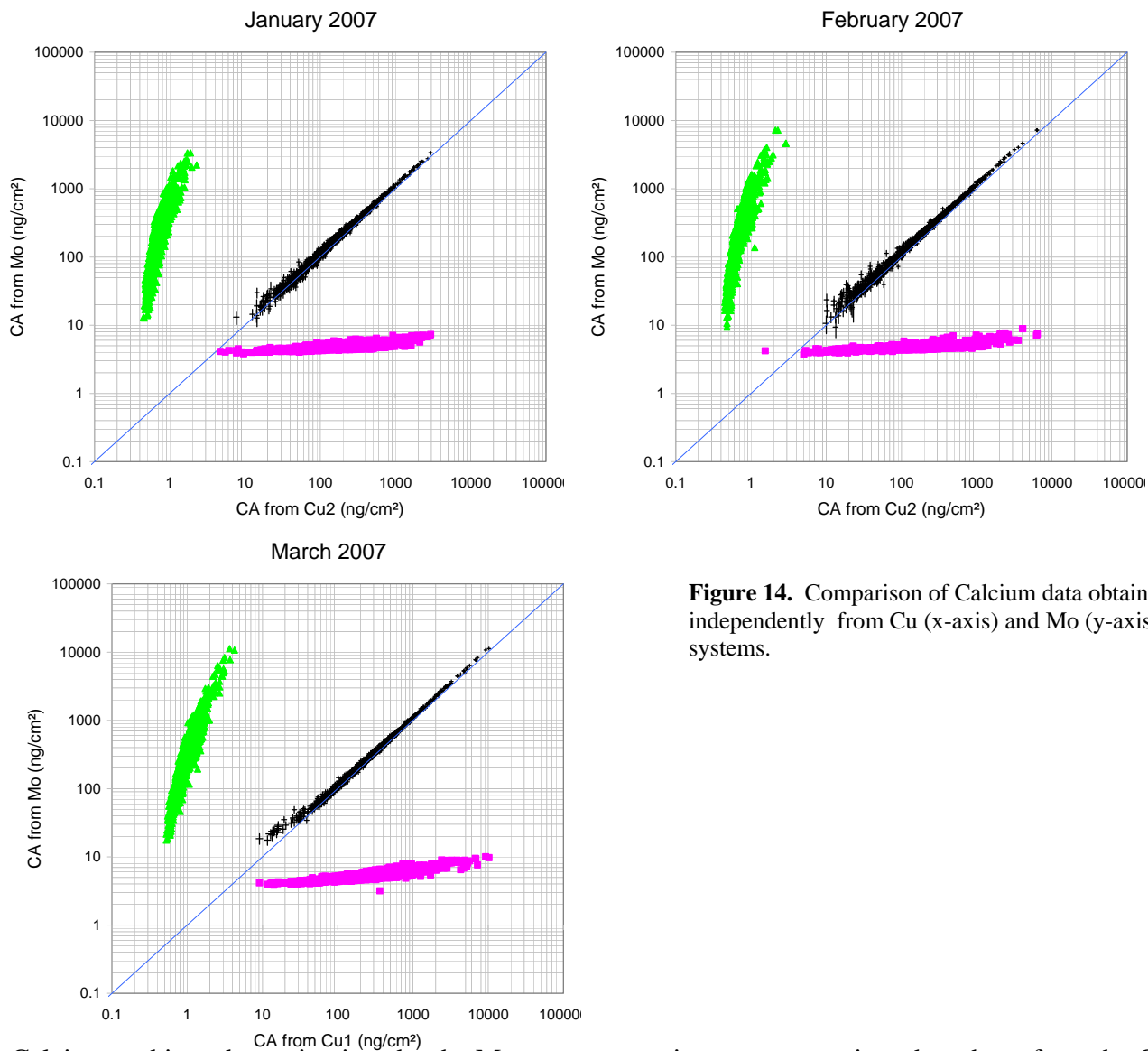


Figure 14. Comparison of Calcium data obtained independently from Cu (x-axis) and Mo (y-axis) systems.

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

Eighteen field blanks for January 2007, 16 field blanks for February 2007 and 19 field blanks for March 2007 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 January, February and March 2007. Loadings are considered well measured when their uncertainties are less than 10%. Thus, the 95th percentile field blank loading for Fe (Jan 2007 samples) was at or above about 6.6% of all well measured sample loadings on Cu system (9.4% on Mo system).

Cu anode

Jan 2007	Na	Mg	Al	Si	P	S	Cl	K	Ca	Ti	V	Cr	Mn	Fe
95 %ile	0.0%	0.0%	0.0%	0.1%	0.0%	0.0%	0.0%	0.4%	0.5%	0.0%	0.0%	0.0%	0.0%	6.6%
90 %ile	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.2%	0.3%	0.0%	0.0%	0.0%	0.0%	1.8%
75 %ile	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.1%	0.0%	0.0%	0.0%	0.0%	0.0%	0.4%
Feb 2007	Na	Mg	Al	Si	P	S	Cl	K	Ca	Ti	V	Cr	Mn	Fe
95 %ile	0.0%	0.0%	0.0%	0.9%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	1.1%
90 %ile	0.0%	0.0%	0.0%	0.2%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.5%
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%
Mar 2007	Na	Mg	Al	Si	P	S	Cl	K	Ca	Ti	V	Cr	Mn	Fe
95 %ile	0.0%	0.0%	0.0%	5.1%	0.0%	0.0%	0.0%	0.1%	0.2%	0.0%	0.0%	0.0%	0.0%	0.9%
90 %ile	0.0%	0.0%	0.0%	1.1%	0.0%	0.0%	0.0%	0.0%	0.1%	0.0%	0.0%	0.0%	0.0%	0.5%
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

Jan 2007	Fe	Ni	Cu	Zn	As	Pb	Se	Br	Rb	Sr	Zr
95 %ile	9.4%	0.0%	3.4%	32.4%	0.0%	0.5%	0.0%	0.0%	0.0%	0.0%	0.0%
90 %ile	1.6%	0.0%	0.0%	21.7%	0.0%	0.3%	0.0%	0.0%	0.0%	0.0%	0.0%
75 %ile	0.0%	0.0%	0.0%	12.7%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%
Feb 2007	Fe	Ni	Cu	Zn	As	Pb	Se	Br	Rb	Sr	Zr
95 %ile	2.4%	0.0%	0.0%	25.9%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%
90 %ile	0.4%	0.0%	0.0%	18.2%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%
75 %ile	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%
Mar 2007	Fe	Ni	Cu	Zn	As	Pb	Se	Br	Rb	Sr	Zr
95 %ile	0.2%	0.0%	0.0%	64.9%	0.0%	1.2%	0.0%	0.0%	0.0%	0.0%	0.0%
90 %ile	0.1%	0.0%	0.0%	61.7%	0.0%	1.2%	0.0%	0.0%	0.0%	0.0%	0.0%
75 %ile	0.0%	0.0%	0.0%	9.2%	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 except for Fe (Jan 2007) and, as observed in previous reports, Zn (Jan, Feb and Mar 2007).