Data report for elemental analysis of IMPROVE samples collected during JANUARY, FEBRUARY AND MARCH 2005
UC Davis, August 7, 2006

SUMMARY

This report provides a short summary of the quality assurance performed during and after elemental analysis of the IMPROVE samples collected during the months of January, February and March of 2005. The elemental analyses include the determination of hydrogen by Proton Elastic Scattering Analysis (PESA) and the determination of most elements with atomic numbers from 11 to 40 and 82 (Na-Zr and Pb) using an energy dispersive X-ray fluorescence systems (XRF). Two XRF systems are employed. The elements Na to Fe are reported from a system with a Cu-anode grounded X-ray tube, and the elements Ni to Zr and Pb are reported from a similar system with a Mo-anode grounded X-ray tube. Argon in ambient air interferes with the determination of some of the light elements reported from the Cu-anode system. The samples reported here are the first to be reported from an upgraded Cu-anode system that operates under vacuum and is described in Attachment 1. Samples collected in December 2004 and earlier were reported from a Cu-anode system that used helium to displace ambient air.

The following data assessments and quality controls are obtained for all analyses:
- Concentration calibration and verification
- Energy calibration
- Laboratory blanks
- Laboratory replicates (reanalysis)
- Systems comparison

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.

Each of these procedures is described below, along with the results obtained for the most recent tests corresponding to the actual analytical periods.

The frequent (weekly) verifications of the calibration of each system were all successful during the period of analysis of the January through March 2005 samples. Three new calibrations were performed on the XRF-Cu system to account for modifications in this new system. No new calibrations of the existing XRF-Mo system were needed.

During the analytical session for these samples the systems were performing according to their specifications (see details in sections below) and the reported data meet our QA criteria.

Section 1.0   General Statistics of January, February and March 2005 data

XRF and PESA analyses were carried out on 1936 samples collected in January 2005, 1615 samples collected in February 2005 and 1777 samples collected in March 2005. All samples collected in the first quarter of 2005 were analyzed between March 28th 2005 and July 17th 2005 on the Mo-anode system and between December 22nd 2005 and April 27th 2006 on the new Cu-anode vacuum system. PESA analysis was performed in three analytical sessions: October 26th to 28th 2005, March 29th to 30th 2006 and May 24th to 26th 2006.
Table 1 summarizes the detection rates on the three systems during this analytical session. The detection rates for December 2004 are included for comparison.

Cu-anode XRF

Z	element	12-2004	1-2005	2-2005	3-2005
11	Na	33%	41%	40%	44%
12	Mg	30%	17%	23%	21%
13	Al	40%	49%	85%	85%
14	Si	87%	88%	94%	97%
15	P	4%	1%	1%	1%
16	S	100%	99%	99%	99%
17	Cl	23%	12%	9%	14%
19	K	100%	99%	99%	99%
20	Ca	100%	99%	99%	99%
22	Ti	86%	95%	97%	97%
23	V	63%	79%	86%	89%
24	Cr	39%	57%	62%	67%
25	Mn	88%	94%	96%	98%
26	Fe	100%	99%	99%	99%

Mo-anode XRF					
Z	element	12-2004	1-2005	2-2005	3-2005
28	Ni	65%	69%	66%	49%
29	Cu	87%	88%	86%	88%
30	Zn	100%	100%	99%	99%
33	As	45%	44%	43%	41%
34	Se	77%	78%	80%	90%
35	Br	100%	100%	98%	99%
37	Rb	34%	37%	35%	69%
38	Sr	87%	87%	88%	92%
40	Zr	10%	12%	10%	13%
82	Pb	96%	96%	96%	97%

PESA					
Z	element	12-2004	1-2005	2-2005	3-2005
1	H	100%	99%	99%	98%

Table 1. Percentage of cases in which the element was detected on each system.
December 2004 data included for reference.

Section 2.0   Overview of Elemental Analysis Systems

The newly completed XRF-Cu system operates under a vacuum environment (< 350 microns Hg) and is used for reporting elements from Na to Fe (the concentrations reported for Na and Mg should be treated as qualitative only). All first quarter 2005 samples were analyzed for 1000 seconds at 10 mA and 20 kV (default settings for sample analysis). Attachment 1 gives a more detailed description of the new system, which was designed and built at CNL, U.C. Davis.

The XRF-Mo system operates in ambient air and is used to report elements from Ni to Pb. First quarter 2005 samples were analyzed for 1000 seconds at 23 mA and 35 kV (default settings for sample analysis).
The PESA system operates under a vacuum environment (< 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 3.0   Quality Control

3.1   Concentration calibration and verification

The calibration factors that relate elemental concentrations to spectral counts are determined based on analyzing and processing spectra from a number of single or double-element thin film Micromatter standards. The foil standards used in the calibration for the first quarter of 2005 samples are listed in Table 2 and Table 3 below. The Table 2 standards were used for all analyses on the Mo system and for analyses of the January and February 2005 samples on the Cu system. The Table 3 standards were used for analyses of the March 2005 samples on the Cu system. The ratios of measured to quoted stoichiometric values for each element are used to establish calibration factors. For elements such as Cl and Fe, which are found in more than one standard, the new calibration factor is determined based on the average of measured to quoted values from each standard. The standard's concentrations are relatively high, and are analyzed at reduced X-ray tube current (2.6 mA) to maintain counting live times comparable with those of actual IMPROVE samples. XRF-Cu and XRF-Mo calibration is conducted after modifications have been made to the instrument set-up (physical or settings), or if the continuing calibration verification ratios (measured standard to quoted standard) have fallen outside of the acceptance limits (0.9-1.1).

Standard	Elemental Concentrations ($\mu g/cm^2$)	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 (stoichiometrically)	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 (stoichiometrically)	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 and for January and February Cu analyses. Some standards (*) have variable stoichiometry; they are not use directly in calibration of the systems but serve only as "indicators".

Standard	Elemental Concentrations ($\mu g/cm^2$)	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 (stoichiometrically)	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 (stoichiometrically)	16511
GaAs*	Ga: 8 As: 8.7 (stoichiometrically)	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 March Cu analyses. Some standards (*) have variable stoichiometry;
they are not use directly in calibration of the systems but serve only as "indicators".

The PESA system is calibrated at the beginning of each analytical session using six 1/8 mil thick Mylar blanks with known areal densities. The average hydrogen concentration for these PESA standards is calculated to be 20 µg/cm^2 (quoted). The calibration factor for the analytical session is established based on the ratio of reported to quoted average H concentration of the six PESA standards. The calibration factor is frequently monitored and is expected to stay within 0.95-1.05 range during an analysis run.

Calibration verification is performed periodically to monitor the performance of the system between calibrations. Fifteen standards are analyzed on the XRF-Cu system and 19 on the XRF-Mo system, and the ratios of reported to quoted Micromatter values are calculated. If the ratio lies within ±10% of the quoted value for each element, then the system is considered stable and the existing calibration factors continue to be used. Deviations beyond ±10% merit 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 recalibration performed for XRF-Cu and XRF-Mo, respectively. The dates shown correspond to the actual period of analysis on each system. The y-axis indicates the ratio of reported values to the Micromatter standard values.
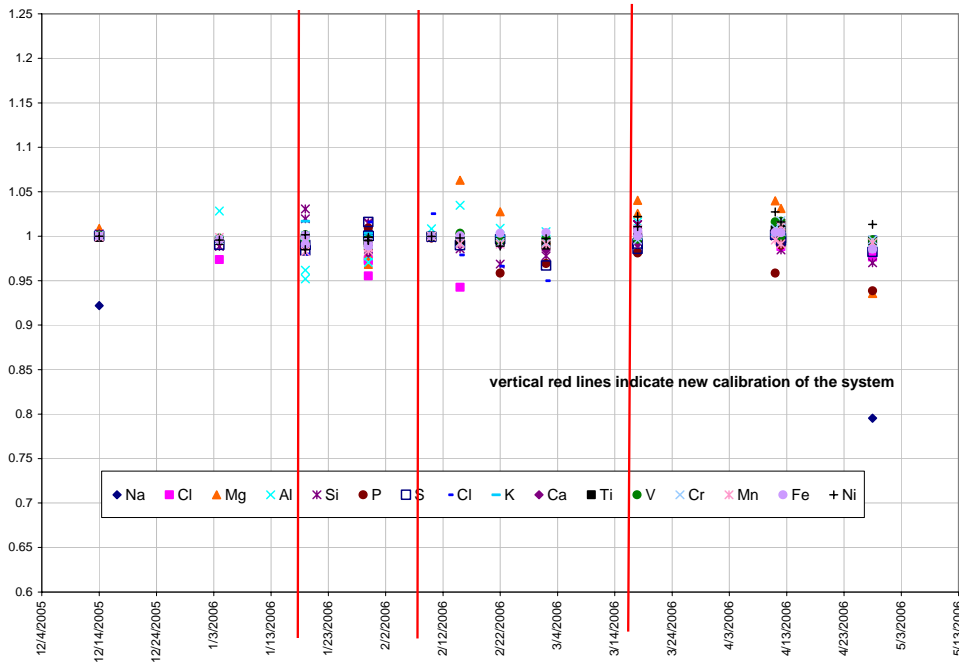
Figure 1. XRF-Cu system performance chart based on standards.

All calibration verifications were successful and new calibrations of the XRF-Cu system were performed on January 19th, February 10th and March 16th 2005 due to some modifications to the system. The single deviant point (Na) present during last calibration verification in April (Figure 1 above) was considered acceptable because Na concentrations determined by XRF are considered qualitative.
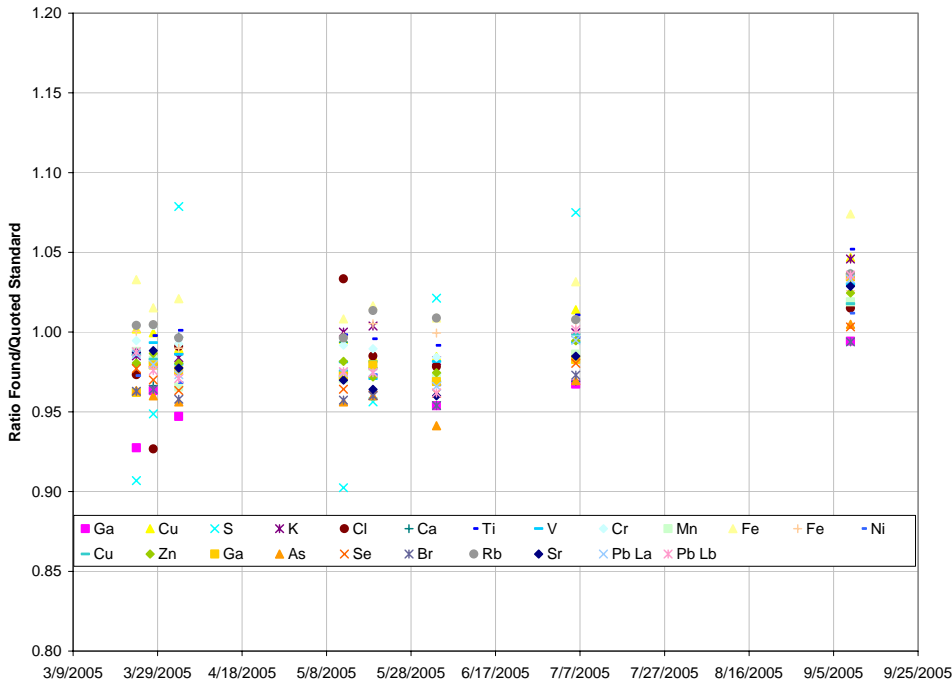

Figure 2. Mo XRF system performance chart based on standards

The XRF-Mo system was not reconfigured or adjusted, but was monitored by continuous calibration verification with standards (all successful).

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 repeatedly reanalyzed to verify the calibration throughout the session (every 400 samples). If the system drifts by more than 5% during an analytical session, the system is re-tuned, recalibrated, and samples reanalyzed. Figure 3 shows the calibration verification and calibration of the PESA system. The run numbers correspond to the dates (indicated above) when analysis for Jan-Mar 2005 samples were performed. The y-axis indicates the ratio of averaged hydrogen concentrations from 6 foils (represented by each point) reported values to the calculated concentration of 20 $\mu g/cm^2$.
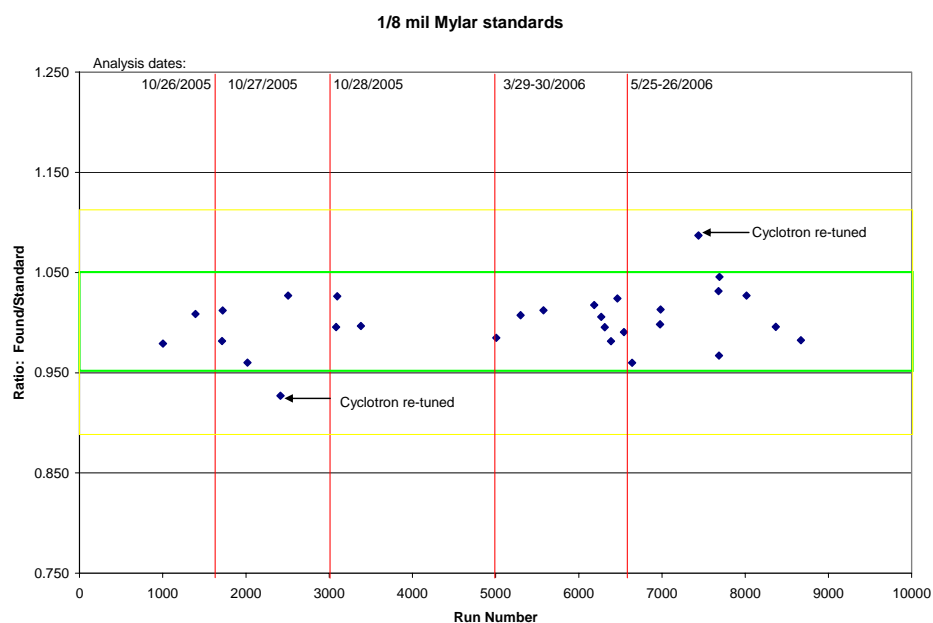

Figure 3. PESA standards for January, February and March 2005 samples

3.2   X-ray energy calibration

In order to identify the elements associated with specific peaks in the spectrum it is necessary to accurately determine the energies of the x-rays in those peaks. The multi channel analyzer records the x-ray spectrum in 512 discrete channels, within the window of interest set by the amplifier. The relationship between x-ray energies and the 512 channels has the form energy = intercept + slope * channel. The choice of the two constant coefficients, "intercept" and "slope", determines the energy calibration of the system.

The energy calibration is done at the beginning of the analytical session by choosing a sample filter from that session. A moderately loaded filter is chosen that has a normal status. The characteristic x-ray energy spectrum from the filter is analyzed by RACE using previous energy calibration coefficients. Four distinct and unambiguously identifiable energy peaks are chosen, and the known energy lines of their elements are compared with the peak energies determined from the previous energy calibration table. A new x-ray energy calibration equation is then determined using a least squares technique. If the change from the previous x-ray energy calibration to the new calibration is more than 20 channels, this may indicate a problem with the electronics, such as the amplifier or pre-amp. Routine analysis is halted for the investigation to locate the problem and determine a resolution. This equation is used to process all samples for a given analytical period.

The following energy calibration equations were used for the analysis of January, February, and March 2005 samples, respectively:

- for XRF-Cu   intercept=-0.07217002, slope=0.01691298
                   intercept=-0.07217002, slope=0.01691298
                   intercept=-0.06250992, slope=0.01693000

- for XRF-Mo   intercept= -0.09010490, slope=0.03605580

All x-ray energy calibrations met the acceptance criteria (did not differ from previous by more than 20 channels).

3.3   System blank

X-ray spectral analysis requires a system blank to estimate the incremental addition to the spectrum due to the presence of the filter substrate (i.e. Teflon). At the beginning of each analytical session, several laboratory blank filters from the same lot used to collect samples are analyzed in each of the XRF systems. One filter is selected to become a blank for subtraction from the spectra of subsequent analyses. The filter is selected as representative of the lot of filters that show no sign of visual or spectral contamination.

3.4   Reanalysis

Precision of both XRF systems (independently) is tracked by monitoring the reproducibility of the data obtained by analyzing a selected set of filters over an extended period of time. For this purpose, two sets of filters were selected which were not previously analyzed by PESA. (PESA weakens the Teflon membrane, increasing the likelihood of damage in subsequent reanalyses.) The filters are from collocated X modules in the IMPROVE network, sampled between January and May of 2005. The first tray, called REANAL1 contains 34 filters and the second tray, REANAL2 contains 38 filters. Filters were selected based on the elemental composition to provide a broad spectrum of samples being representative of the whole IMPROVE network. Previously, the BIBE1 B03 (samples collected at Big Band in June, July and August of 2003) samples were used to monitor the reproducibility of the data on Cu and Mo systems.

For the analysis corresponding to the January-March 2005 samples, the precision of the Cu-Vac XRF system was monitored with new samples, REANAL2, and the precision of the Mo XRF system was monitored with BIBE1 B03 samples.

Typically, the variability of observed concentrations is for most elements consistent with the uncertainties reported for these elements. Figures 4 and 5 below show examples of the results for the Cu and Mo systems, respectively. The dates indicated in the figures are those of the actual reanalyses.
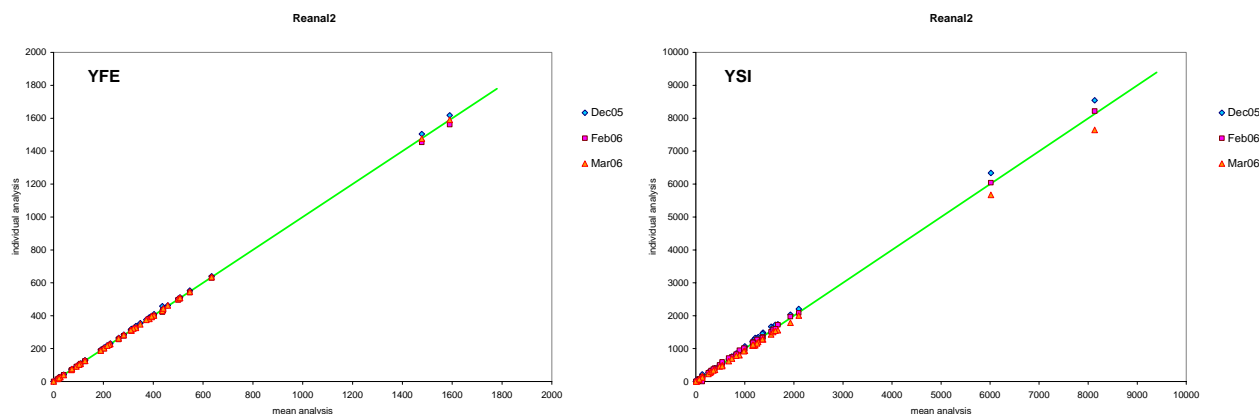

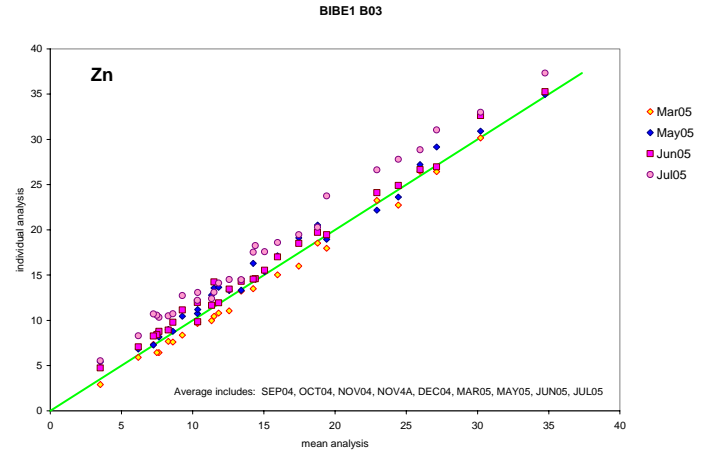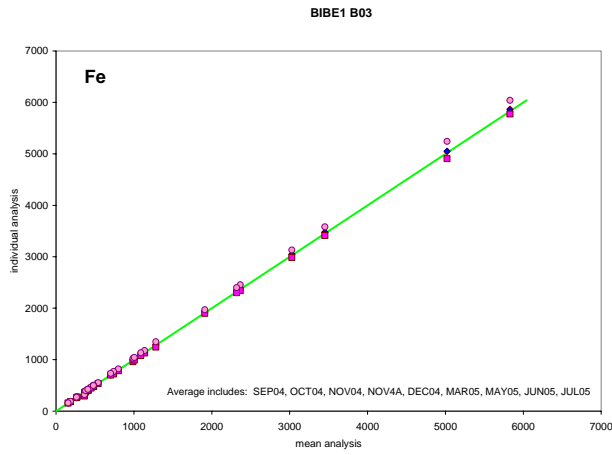**Figure 4.** Precision of Cu-Vac XRF system monitored with REANAL2.

**Figure 5.** Precision of Mo XRF system monitored with BIBE1 B03.

A set of samples from a previous analysis run is also reanalyzed by PESA to determine the continuity of that system. Samples are limited to a cumulative PESA exposure of 60 seconds due to the proton beam interaction with the Teflon substrate noted above. For this reason, a new set of reanalysis samples is taken from the previous quarter's sample analysis run or runs. The reanalysis data is renormalized based on the standard and compared to the previous analysis. The results for the January-March 2005 samples are below.

January 2005

Date of Reanalysis	Slope	Intercept	Precision	Goodness of fit (χ^2)
10/26/05	0.95+/-0.03	51+/-62	5%	0.7
10/27/05	0.97+/-0.03	-5+/57	5%	0.6

REANAL, N = 30, R = 0.989, R² = 0.979
Y = 0.9475*X + (51.1860), Slope error = 0.037, Intcpt. error = 62.306
Mean X = 1531.26Mean Y = 1502.00Mean Y/Mean X = 0.981
Precision = 0.05, Chi-Square = 0.69

REANAL, N = 29, R = 0.992, R² = 0.984
Y = 0.9685*X + (-5.2093), Slope error = 0.034, Intcpt. error = 57.561
Mean X = 1555.85Mean Y = 1501.70Mean Y/Mean X = 0.965
Precision = 0.05, Chi-Square = 0.59
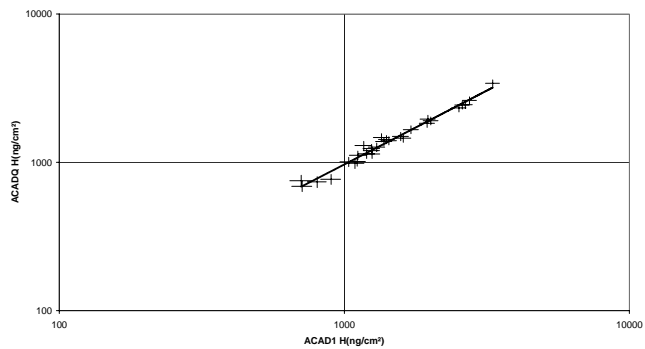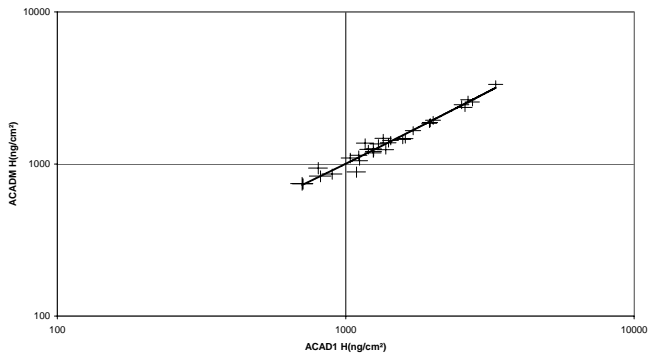
February 2005

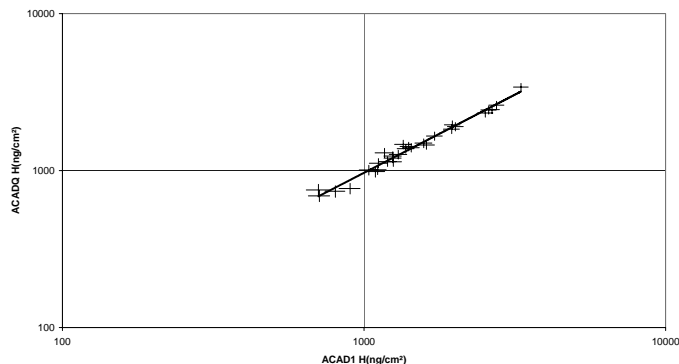| Date of Reanalysis	Slope	Intercept	Precision	Goodness of fit (χ^2)
3/29/06	0.96+/-0.03	-5.21+/-57.56	5%	0.59

REANAL, N = 29, R = 0.992, R² = 0.984
Y = 0.9685*X + (-5.2093), Slope error = 0.034, Intcpt. error = 57.561
Mean X = 1555.85 Mean Y = 1501.70 Mean Y/Mean X = 0.965
Precision = 0.05, Chi-Square = 0.59

March 2005

Date of Reanalysis	Slope	Intercept	Precision	Goodness of fit (χ^2)
5/26/06	1.03+/-0.08	-47.88+/-298	6%	1.6

REANALG05, N = 29, R = 0.965, R² = 0.931
Y = 1.0315*X + (-47.8847), Slope error = 0.077, Intcpt. error = 298.400
Mean X = 3688.62 Mean Y = 3756.94 Mean Y/Mean X = 1.019
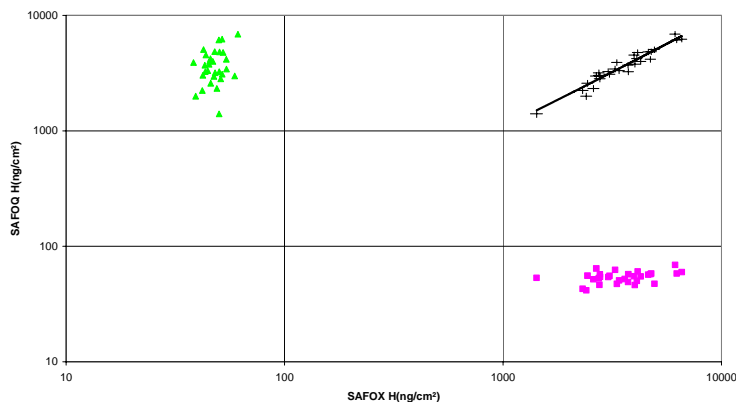Precision = 0.06, Chi-Square = 1.60

Figure 6. Precision of PESA system for Jan-Mar 2005 data. Reported uncertainties are shown as bars for each sample, and reported MDL's are indicated by green and pink points for original and reanalysis samples (for March data).

3.5   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 January, February and March 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.
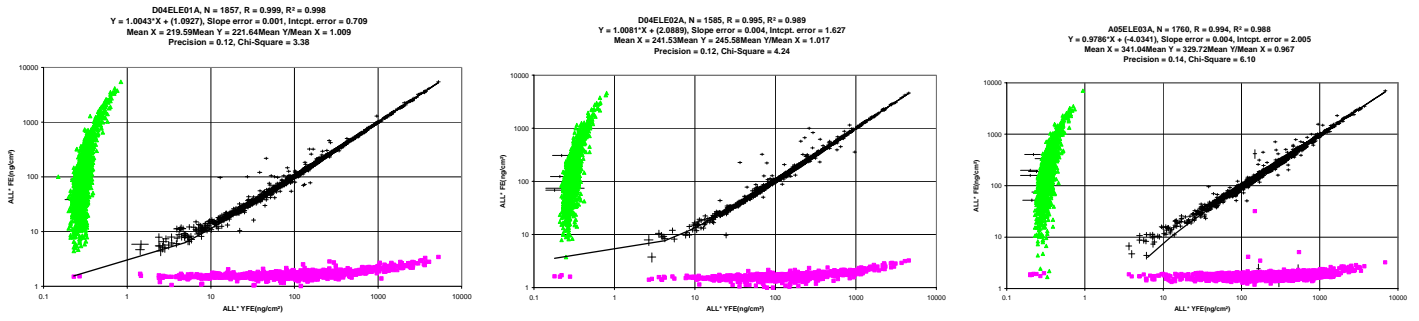
D04ELE01A, N = 1857, R = 0.999, R² = 0.998
Y = 1.0043*X + (1.0927), Slope error = 0.001, Intcpt. error = 0.709
Mean X = 219.59Mean Y = 221.64Mean Y/Mean X = 1.009
Precision = 0.12, Chi-Square = 3.38

D04ELE02A, N = 1585, R = 0.995, R² = 0.989
Y = 1.0081*X + (2.0889), Slope error = 0.004, Intcpt. error = 1.627
Mean X = 241.53Mean Y = 245.58Mean Y/Mean X = 1.017
Precision = 0.12, Chi-Square = 4.24

A05ELE03A, N = 1760, R = 0.994, R² = 0.988
Y = 0.9786*X + (-4.0341), Slope error = 0.004, Intcpt. error = 2.005
Mean X = 341.04Mean Y = 329.72Mean Y/Mean X = 0.967
Precision = 0.14, Chi-Square = 6.10

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

D04ELE01A, N = 1803, R = 0.999, R² = 0.997
Y = 0.9820*X + (1.5180), Slope error = 0.002, Intcpt. error = 0.829
Mean X = 234.99Mean Y = 232.27Mean Y/Mean X = 0.988
Precision = 0.14, Chi-Square = 2.10

D04ELE02A, N = 1562, R = 0.993, R² = 0.985
Y = 0.9907*X + (0.7755), Slope error = 0.004, Intcpt. error = 1.491
Mean X = 220.45Mean Y = 219.18Mean Y/Mean X = 0.994
Precision = 0.11, Chi-Square = 2.17

A05ELE03A, N = 1739, R = 0.986, R² = 0.973
Y = 1.0351*X + (-13.4601), Slope error = 0.006, Intcpt. error = 3.751
Mean X = 375.36Mean Y = 375.07Mean Y/Mean X = 0.999
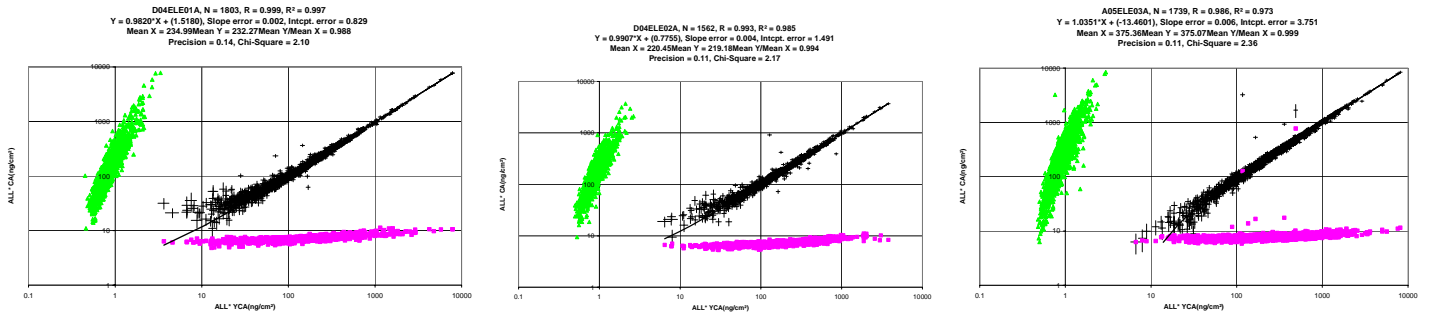Precision = 0.11, Chi-Square = 2.36

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

It was established that a small percentage of the analyzed samples lie out of acceptable ranges. These happened to be filters damaged during analysis under vacuum or filters showing post sampling contamination due to filter handling. However, they are a small percentage of the whole IMPROVE network.

Generally, more than 98 percent of the samples were in the expected ranges and as shown by calibration verification and reanalysis, the systems were performing according to specified criteria during the analytical session.

ATTACHMENT 1

Overview of the Copper Vacuum (Cu-Vac) XRF System

IMPROVE aerosol samples taken on or after 1/1/05 are analyzed for light elements with a Cu-Vacuum XRF system built at CNL, UCDavis. The following elements are reported based on the data obtained with this system: Na, Mg, Al, Si, P, S, Cl, K, Ca, Ti, V, Cr, Mn and Fe.

- o The XRF system uses a General Electric CA8-L grounded anode diffraction type X-ray tube with:
  - Copper anode
  - 0.01 inches thick beryllium window
  - Operating at 2.6 mA and 10 mA current
  - Operating at 20 kV voltage
- o The primary x-rays produced by the tube (primary radiation) are filtered and collimated (custom made 0.002 inch thick integrated Cu collimator attached to the X-ray tube exit window; see XRF-3894 document for details) and projected onto an aerosol sample. The geometry used in this direct mode is (both angles relative to the sample):
  - $35°$ incidence angle
  - $55°$ take-off angle (detection angle)
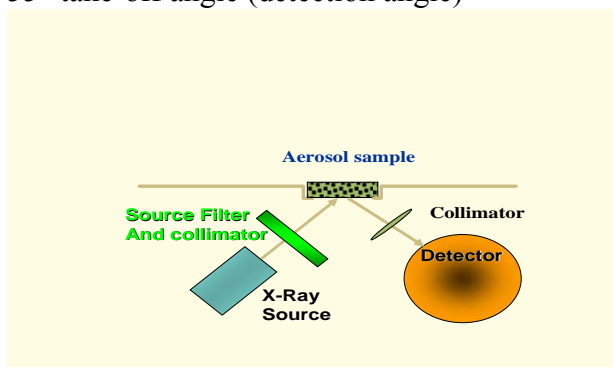
- o A sample chamber (one slide at a time enters the chamber) is evacuated using single stage vacuum pump. The vacuum gauge with electronic readout is installed. The vacuum is preset to be at least 350 microns Hg (=350 millitorr; atmospheric pressure standard = 760 mm Hg=760 torr) in order to initiate data collection by the system.
- o The system uses a Si(Li) detector, Canberra SL30165 SN05041067 with 0.008 mm thick Be window, cooled with liquid nitrogen (LN). The detector has an energy resolution of 165 eV FWHM for 5.9 keV (Mn Kalpha) at 1000 counts per seconds (based on Fe-55 source test established by the manufacturer). The detector is collimated with silver collimator placed securely at 0.75 cm distance from the detector window.
- o Preamplifier attached to the detector is Canberra 2008B
- o Canberra fast spectroscopy amplifier Model 2024 operates under the following settings:
  coarse gain: 1000
  fine gain: 0.72
  input polarity: +
  shaping time: 8μsec
  restorer mode: asymmetric (asym)
  restorer threshold: variable (var)
  PUR(Pile-Up Rejection): unipolar (uni): ON
- o The power supply for the detector is currently a Canberra™ Model 3102D providing a bias voltage of -500 V.

- The X-ray tube power supply Spellman DF3 is wired directly to the X-ray tube. For XRF sample analysis, the power supply is generally set to provide the tube with 20 kV and 10 mA. For standards, the settings are 20kV and 2.6 mA. The preset limits for the filament are: 3.99 A and 1 kW.
- Voltage to Frequency converter (V to F) is wired directly to the X-ray tube power supply. It monitors the voltage use by the x-ray tube, processes that value to a frequency measurement, and outputs its signal to the computer room. The voltage use by the tube correlates to the charge exposure of each filter sample while undergoing XRF analysis.
- Automatic sample changer in XY geometry, equipped with load-lock device, allows load of 6 trays (240 samples) at one time.
- Sample manipulation controller (diagram below) is wired directly to power and is mounted onto the XRF system. The sample manipulation controller in Command Mode (automatic) is controlled by the data acquisition program ACE, through the slide position changer and vacuum controllers in the computer room. It allows to insert or remove slide (sample) from the vacuum chamber and to reposition tray of samples when needed. To perform all the sample manipulations using sample manipulation controller one has to be in Local mode.
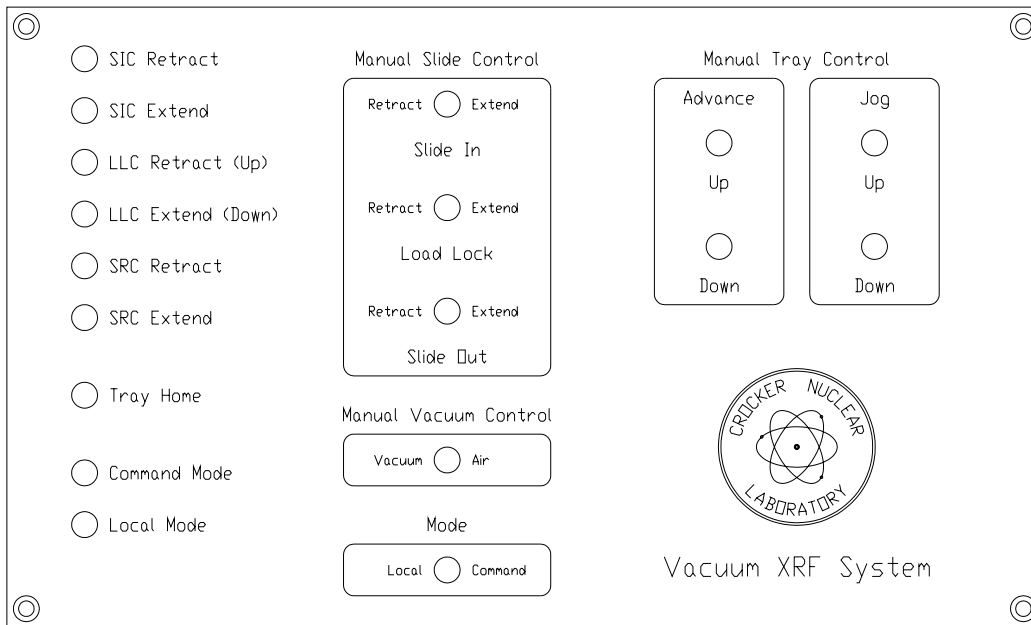
- ADC Canberra 9635 - Analog to Digital Converter that processes the raw spectrum produced by the XRF system into digital format. Operates in a preset real-time acquisition mode and ranges from 0.65 to 8.46 keV.
- AIM - acquisition interface module; connects the ADC to the local Ethernet.
- MicroVAX - TONY is the System controller. It runs data acquisition program ACE and data processing program RACE.
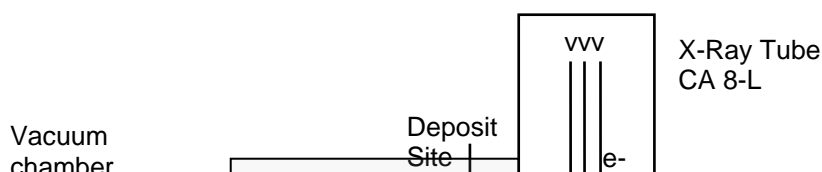
Figure 1. Schematic of the XRF system with Cu anode under vacuum environment.

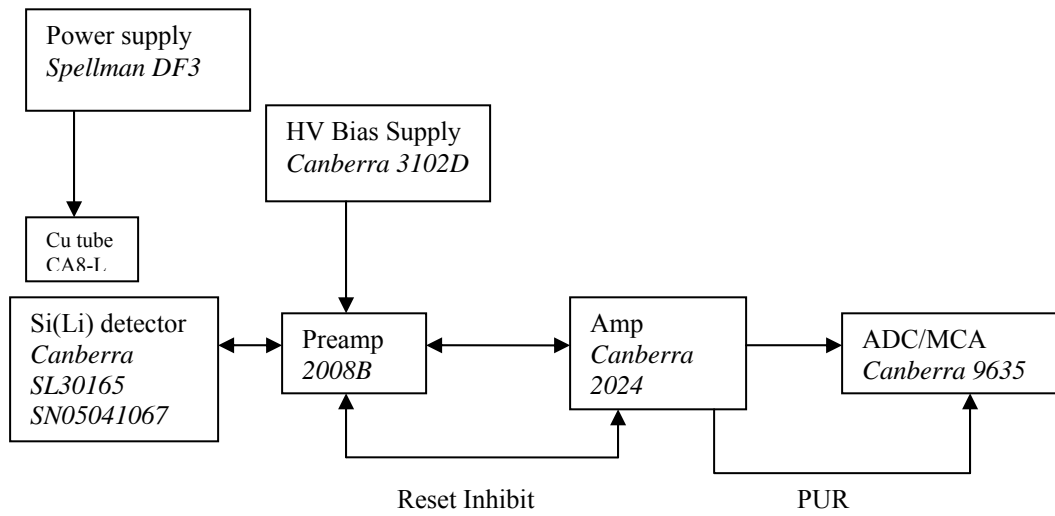| Power supply *Spellman DF3* |
| HV Bias Supply *Canberra 3102D* |
| Cu tube CA8-L |
| Si(Li) detector *Canberra SL30165 SN05041067* | Preamp *2008B* | Amp *Canberra 2024* | ADC/MCA *Canberra 9635* |

Reset Inhibit   PUR

Figure 2. Block diagram of Si(Li) setup for Cu-XRF system.