Semi-Annual Data Summary Report for the Chemical Speciation of PM2.5 Filter Samples Project

January 1, 2004 through June 30, 2004

Prepared for:
U.S. Environmental Protection Agency
Office of Air Quality Planning and Standards
Research Triangle Park, NC 27711

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RTI INTERNATIONAL

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1.0 Introduction

1.1 Program Overview

In 1997, the U.S. Environmental Protection Agency (EPA) promulgated the new National Ambient Air Quality Standards (NAAQS) for particulate matter. The regulations (given in 40 CFR Parts 50, 53, and 58) apply to the mass concentrations (μg/cubic meter of air) of particles with aerodynamic diameters less than 10 micrometers (the PM10 standard) and less than 2.5 micrometers (the PM2.5 standard). Currently, a 1500-site mass measurements network and a 240-site chemical speciation monitoring network have been established.

The ambient air data from the first network, which measures solely the mass of particulate matter, will be used principally for NAAQS comparison purposes in identifying areas that meet or do not meet the NAAQS criteria and in supporting designation of an area as attainment or non-attainment.

The smaller chemical Speciation Trends Network (STN) consists of a core set of 54 trends analysis sites and some 186 other sites. Chemically speciated data will be used to serve the needs associated with development of emission mitigation approaches to reduce ambient PM2.5 concentration levels. Such needs include emission inventory establishment, air quality model evaluations, and source attribution analysis. Other uses of the data sets will be regional haze assessments, estimating personal exposure to PM2.5 and its components, and evaluating potential linkages to health effects.

RTI is assisting in the PM2.5 STN by shipping ready-to-use filter packs and denuders to the field sites and by conducting gravimetric and chemical analyses of the several types of filters used in the samplers. The details of the quality assurance (QA) activities being performed are described in the RTI QA Project Plan (QAPP) for this project. The QAPP focuses on the QA activities associated with RTI's role in performing these analyses, as well as in validating and reporting the data, and should be considered a companion document to this annual QA report.

Prior to operation of the core and additional sites, EPA ran a prototype network informally known as the "mini-trends" network. This network was composed of approximately 13 monitoring stations at sites throughout the U.S. Each site had two or more PM2.5 chemical speciation monitors to enable various sampler intercomparisons. The mini-trends network ran from February 2000 to July 31, 2000. Subsequently, the network sites have been increased and as of June 30, 2004, RTI is providing support for 240 sites which include the 54 trends analysis sites under the STN.

1.2 Project/Task Description

The STN laboratory contract involves four broad areas:

1. Supplying each site or state with sample collection media (loaded filter packs, denuders, and absorbent cartridges) and field data documentation forms. RTI ships the collection media to monitoring agencies on a schedule specified by the Delivery Order Project Officer (DOPO).

2. Receiving the samples from the field sites and analyzing the sample media for mass and for an array of chemical constituents including elements (by EDXRF), soluble anions and cations (by ion chromatography), and carbonaceous species (using the Sunset thermal degradation/laser transmittance system). Analysis of semi-volatile organic compounds and examination of particles by electron or optical microscopy have been performed on a very limited basis.

3. Assembling validated sets of data from the analyses, preparing data reports for EPA management and the states, and entering data to the Aerometric Information Retrieval System (AIRS) data bank 60 days after initial data reports are first submitted to the DOPO and the states.

4. Establishing and applying a comprehensive quality assurance/quality control (QA/QC) system. RTI's Quality Management Plan, QAPP, and associated Standard Operating Procedures (SOPs) provide the documentation for RTI's quality system.

1.3 Schedule

The initial portion of the STN program was a six-month pilot project at 13 different sites. This "mini-trends" project was conducted from February 2000 to July 2000. This period gave all participants an opportunity to work out technical and logistical problems. Additional sites have been added. As of June 30, 2004, we were providing support to 240 sites which include the 54 STN sites. This QA report covers the collection and analysis of samples from January 1 through June 30, 2004.

1.4 Major Laboratory Operational Areas

This report addresses the operation of the Sample Handling and Archiving Laboratory (SHAL) and QA/QC for the four major analytical areas active during the time period of this request. These analytical areas are the: (1) gravimetric determination of particulate mass on Teflon® filters; (2) determination of 48 elements on Teflon® filters using X-ray fluorescence spectrometry; (3) determination of nitrate, sulfate, sodium, ammonium and potassium on nylon or Teflon filters using ion chromatography; and (4) determination of organic carbon, elemental carbon, total carbon, and five new peaks (PK1C, PK2C, PK3C, PK4C, and PyrolC) on quartz filters using thermal optical transmittance. Also addressed is denuder refurbishment, data processing, and QA and data validation.

1.5 Significant Corrective Actions Taken

Any significant problems and corrective actions taken during this period under each analytical laboratory are described in this section. A detailed description of the problems encountered and corrective actions taken are given in Section 2.0.

- Gravimetric Mass – No significant corrective actions have been taken.
- Elemental Analysis – Currently four XRF instruments are used for elemental analysis. Corrective actions taken for the RTI XRF instruments are described in Section 2.4.3.3.
- Ion Analysis – No significant corrective actions have been taken.
- OE/EC Analysis – No significant corrective actions have been taken.
- Sample Handling and Archiving Laboratory (SHAL) – No significant corrective actions have been taken; however, the problem of late shipments is discussed.
- Data Processing – A problem with blank reporting in the text files used by some states for their monthly review is discussed in Section 2.7.3.

2.0 Laboratory Quality Control Summaries

2.1 Gravimetric Laboratory

The laboratory's two weigh chambers were used to tare 12,522 filters between November 2003 and June 2004 (7,578 in Chamber 1, 4,944 in Chamber 2).

2.1.1 Personnel and Facilities

One Gravimetric Laboratory technician took a three-month leave of absence at the beginning of calendar year 2004. The technician has since returned to the laboratory. In his absence, an employee from another RTI department was cross-trained in Gravimetric Laboratory tasks to provide temporary assistance. A second technician left RTI in June 2004. As of this writing, the Gravimetric Laboratory Supervisor is interviewing prospective replacements to fill the vacant position.

No changes in facilities have occurred since the previous QA report. Corrective actions in response to facilities problems are summarized in **Table 1**.

2.1.2 Description of QC Checks Applied

QC data for the laboratory (types and frequency as recommended in Guidance Document 2.12) are summarized in **Table 2**. PM2.5 STN sample throughput data for the Gravimetry Laboratory are summarized in **Table 3**.

2.1.3 Statistical Summary of QC Results

QC data for the laboratory (types and frequency as recommended in Guidance Document 2.12) are summarized in **Table 2**. PM2.5 STN sample throughput data for the Gravimetric Laboratory are summarized in **Table 3**.

2.1.4 Data Validity Discussion

A session flag was applied to 183 filters from one initial weighing session for which the assigned laboratory blank displayed a net eight loss of 32 μg in its subsequent reweighing. The decrease in weight is probably attributable to contamination during the initial weighing session that was dislodged prior to subsequent reweighings. In response, the laboratory's SOP was modified to provide clarification for technicians in the designation of laboratory blanks and to more clearly require a laboratory blank for every weighing session. Laboratory personnel were also reminded of the importance of adhering to the regular chamber cleaning schedule.

Table 1. Gravimetry Laboratory - Corrective Actions in Response to Facility Problems RTI HVAC Reference Chamber 1

NOTE: Began to routinely utilize Chamber 1 for Chemical Speciation project in February 2002.

Chamber	Duration of Problem	Nature of Problem	Corrective Action
2	2/11-27/04	Actuator Failure	Chilled water valve actuator failed on 2/11/04. RTI HVAC personnel responded immediately to temperature alarm and adapted a spare chilled water valve actuator to keep the chamber within spec to allow staff to keep working. Replacement actuator was installed on Saturday, 2/27/04, to minimize disruption to the laboratory work schedule. RTI HVAC reported that the valve was inactive for less than 90 seconds during the change-out; highest temperature deviation noted during this time was + 0.5° C. Note: No filter samples were lost due to the actuator failure. RTI HVAC personnel also left the temporary actuator on top of the chamber as an emergency replacement for future use.
1	5/5-15/04	Fan motor failure	Fans failed on 5/5/04. RTI HVAC personnel responded immediately and found three of the six fans for chamber 1 inoperable. They were able to repair one fan motor, but two were beyond repair and a third sounded like it was in the process of losing an inboard bearing. The chamber functioned adequately with four fans. Replacement motors were installed on Saturday, 5/15/04, to minimize disruption to the laboratory work schedule. Note: No filter samples were lost due to the fan motor failure. Chamber temp exceeded acceptance range by 1° C for approximately 1.5 hours on 5/5/04 (max recorded temp on 05/05/04 = 24° C). RH did not exceed upper limit of acceptance range on 5/5/04 (max recorded RH = 40%). Mean and std dev for temp and RH for 24-hour period were within acceptance range. Also, RTI Electrical Department personnel repaired and returned the one repairable blower motor for use as a replacement for either chamber as needed in the future.
1	5/10-11/04	Campus-wide power failure	A power surge associated with a campus-wide power outage destroyed the control board for Chamber 1 the afternoon of 5/10/04. The problem was discovered by laboratory personnel the morning of 5/11/04. The board controls all chamber systems (electrical, temperature, humidity, air circulation, etc). RTI HVAC personnel located a control board locally, installed it the afternoon of 05/11/04, and had the chamber up and running by close of business 05/11/04. Note: No filter samples were lost due to the destruction of the control board. The chamber and the samples conditioning in the chamber were to stabilize before weighing.

Table 2. Summary of QC Checks Applied in the Gravimetry Laboratory

QC Check	Requirements	QC Checks Applied to RTI Laboratory	Lab Mean and Standard Deviation	Comments
Working standard reference weights (mass reference standards)	Verified value ± 3 µg (Standard reference weights initially calibrated by Troemner and verified by North Carolina Department of Agriculture and Consumer Services (NCDA&CS) Standards Laboratory)	100-mg S/N 41145 (Chamber 1) 10/25/02 Class 1 Calibration: 100.0008 mg ± 0.0024 Lab Tolerance Interval: 99.995-100.006 mg	Mean = 99.997 mg Std Dev = 0.0016 for 1558 weighings	Lab mean falls within tolerance interval. Rotated with 100-mg S/N 12936.
		100-mg S/N 12936 (Chamber 1) 6/22/04 Class 1 Calibration: 99.95525 mg ± 0.00082 Lab Tolerance Interval: 99.951-99.959 mg	N/A	Were not returned from NCDA&CS Standards Lab in time to be included in this report.
		200-mg S/N 41147 (Chamber 1) 10/25/02 Class 1 Calibration: 200.0066 mg ± 0.0024 Lab Tolerance Interval: 200.001-200.012 mg	Mean = 200.007 mg Std Dev = 0.0018 for 1522 weighings	Lab mean falls within tolerance interval. Rotated w/ 200-mg S/N 12935.
		200-mg S/N 12935 (Chamber 1) 6/22/04 Class 1 Calibration: 199.99054 mg ± 0.00079 Lab Tolerance Interval: 199.987-199.994 mg	N/A	Were not returned from NCDA&CS Standards Lab in time to be included in this report.
		100-mg S/N 41144 (Chamber 2) 10/25/02 Class 1 Calibration: 100.0068 mg ± 0.0024 Lab Tolerance Interval: 100.001-100.012 mg	Mean = 100.001 mg Std Dev = 0.0097 for 401 weighings	Lab mean falls within tolerance interval. Rotated with 100-mg S/N 58097.
		100-mg S/N 58097 (Chamber 2) 8/12/03 Class 1 Calibration: 100.0035 mg ± 0.0024 Lab Tolerance Interval: 99.998-100.009 mg	Mean = 100.004 mg Std Dev = 0.0021 for 513 weighings	Lab mean falls within range.
		200-mg S/N 41148 (Chamber 2) 10/25/02 Class 1 Calibration: 200.0076 mg ± 0.0024 Lab Tolerance Interval: 200.002-200.013 mg	Mean = 200.007 mg Std Dev = 0.0011 for 325 weighings	Lab mean falls within tolerance interval. Rotated with 200-mg S/N 58099
		200-mg S/N 58099 (Chamber 2) 8/12/03 Class 1 Calibration: 200.0053 mg ± 0.0024	Mean = 200.006 mg Std Dev = 0.0016 for 523 weighings	Lab mean falls within tolerance interval.

Table 2. (Continued.)

QC Check	Requirements	QC Checks Applied to RTI Laboratory	Lab Mean and Standard Deviation	Comments
		Lab Tolerance Interval: 200.000-200.011 mg		
Laboratory (Filter) Blanks	Initial weight ± 15 µg	578 total replicate weighings of 74 lab blanks	Mean difference between final and initial weight = 0.005 mg (5 µg) Std Dev = 0.0049 Min wt change = 0 µg Max wt change = 32 µg	183 filters flagged from initial weigh session due to possible contamination of lab blank during initial weighing; subsequent reweighings had negative weight changes exceeding 15 µg. SOP clarified in April 2004 to address lab blanks. Lab blanks from 4/21/04 and 6/23/04 weigh sessions had net mass loadings ≥ 15 µg. Filters weighed in these weigh sessions were also flagged.
Replicates	Initial weight ± 15 µg	1231 Pre-sampled (Tared) Replicates (11/19/03-6/15/03) 1243 Post-sampled Replicates (1/1/04-6/30/04)	Mean = 0.001 mg (1 µg) Std Dev = 0.0009 Mean = 0.001 mg (1 µg) Std Dev = 0.0029	Max = 6µg; within required range Max = 95 µg; This outlier was attributed to analyst error. All other replicates were within required range
Polonium Strips	Each filter placed near strips for minimum of 60 seconds to minimum electrostatic charge	Replace strips every six months	N/A	Strips were replaced Oct 2003 and April 2004.

Table 2. (Continued.)

QC Check	Requirements	QC Checks Applied to RTI Laboratory	Lab Mean and Standard Deviation	Comments
Lot Blanks (Lot Stability Filters)	24-hour weight change < ± 5 µg	Whatman Lot 3182001 - 6 filters weighed (2 randomly selected from each of 3 randomly selected boxes)	24 hours = 0 µg 48 hours = -1 µg 72 hours = 0 µg 96 hours = 0 µg	Fall well within required range.
		Whatman Lot 3213005 - 6 filters weighed (2 randomly selected from each of 3 randomly selected boxes)	24 hours = -1 µg 48 hours = 1 µg 72 hours = 1 µg 96 hours = 0 µg	
		Whatman Lot 3148691 - 6 filters weighed (2 randomly selected from each of 3 randomly selected boxes)	24 hours = -3 µg 48 hours = -1 µg 72 hours = -1 µg 96 hours = 1 µg	
		Whatman Lot 2207003 - 6 filters weighed (2 randomly selected from each of 3 randomly selected boxes)	24 hours = -3 µg 48 hours = -1 µg 72 hours = 1µg 96 hours = -2 µg	
		Whatman Lot 3308007 - 6 filters weighed (2 randomly selected from each of 3 randomly selected boxes)	24 hours = 0 µg 48 hours = 1 µg 72 hours = 1 µg 96 hours = 2 µg	
		Whatman Lot 4049007 - 6 filters weighed (2 randomly selected from each of 3 randomly selected boxes)	24 hours = 0 µg 48 hours = 1 µg 72 hours = 0 µg 96 hours = 0 µg	
		Whatman Lot 4051002 - 6 filters weighed (2 randomly selected from each of 3 randomly selected boxes)	24 hours = -3 µg 48 hours = -3 µg 72 hours = -3 µg 96 hours = 3 µg	

Table 2. (Continued.)

QC Check	Requirements	QC Checks Applied to RTI Laboratory	Lab Mean and Standard Deviation	Comments
Calibrations				
• Balances (Chamber 2 Balance B- S/N 1118311244 and Chamber 1 Balance C - S/N 1118252777)	Auto (internal) calibration daily	Daily	N/A	
	External calibration annually or as needed	Balance B last inspected and calibrated by Mettler Toledo on August 11, 2003 using NIST-traceable weights. Balance C last inspected and calibrated by Mettler Toledo on July 16, 2003 using NIST-traceable weights.	N/A	Inspection and calibration scheduled for July 2004

Table 3. Sample Throughput for the Gravimetry Laboratory

Number of Filters	Previous QA Report	This QA Report
Tared	11477 (5/28/03-11/18/03)	12522 (11/19/03-6/15/04)
Tared in Weigh Chamber 1	6181	7578
Tared in Weigh Chamber 2	5296	4944
Retained by Grav Lab for use as Lab Blanks	45 (0.39%)	68 (0.55%)
Not Transferred to SHAL; does not include lab blanks	0	0
Total Transferred to and Retained by SHAL for Sampler Modules	11432	12454
Returned to Grav Lab by SHAL for Final Weighing	11000 (96.2% return rate) (6/23/03-12/31/03)	10572 (84.9% return rate) (1/1/04-6/30/04)
Voided by SHAL and Grav Lab (% of samples returned)	6 (0.05%)	13 (0.12%)
Flagged by Grav Lab for Exceeding 10-day Holding Time in Lab (% of samples returned)	0	17(0.16 %)
Flagged by Grav Lab for Laboratory Environmental Criteria Being Out of Limits (% of samples returned)	0	0
Filters reweighed at request of SHAL (% of samples returned)	6 (0.05%)	6 (0.06%)

2.1.5 Audits, Performance Evaluations, Training, and Accreditations

On January 8, 2004, RTI's FRM Quality Assurance Officer performed an internal systems audit of the laboratory. She made the following recommendations:

- The laboratory should train additional staff in its procedures to ensure coverage during times of illness, vacation, holidays, etc.
- Due to staff leave of absence and the recent holidays, the chamber cleaning schedule had slipped at the time of the audit. The laboratory must adhere to its schedules for cleaning, calibration, etc.

On April 20, 2004, a quality systems (QS) audit of the Gravimetry Laboratory was performed by personnel from Louisiana Department of Environmental Quality's (LDEQ's) Louisiana Environmental Laboratory Accreditation Program (LELAP). The LELAP audit was performed to the standards of National Environmental Laboratory Accreditation Conference (NELAC) and Louisiana administrative code. No findings were presented to the laboratory in

the exit interview. As of this writing, the audit report has not been delivered to RTI. Gravimetric Laboratory staff have contacted the LELAP auditor, who has promised to follow up and track the status of the audit report. The laboratory's audit performance was adequate; the laboratory's renewed LELAP Accreditation Certificate was received on July 6, 2004. The laboratory is accredited by LELAP for the performance of the Federal Reference Method for the determination of PM2.5 in ambient air.

On June 4, 2004, RTI's STN Quality Assurance Officer performed an internal systems audit of the laboratory. He made three recommendations, as follows:

- Staff from different departments borrow weighing chamber space to conduct weighings of exposure assessment filters. It is recommended that chamber users at the program level agree on a common set of facility requirements that apply to all personnel. This could take the form of a short facilities manual. Potential topics might include cleaning and inspection procedures, personnel clothing requirements, and rules regarding entering and leaving the chamber.
- Temperature, RH, and airflow measurements should be made at various points in the chamber, particularly between shelves and near walls where filters are allowed to equilibrate. This will help ensure that equilibration conditions are reasonably uniform throughout the chamber.
- RTI is investigating the potential of having HEPA and charcoal filtration added to the two weighing chambers in Building 11. The purpose of the charcoal filtration is primarily to reduce nuisance chemical odors from other work being done in Bay 6, but it will reduce the (remote) possibility of chemical sample contamination from external vapors. The installation plan should be thought out very carefully to avoid long downtime for the project and to avoid potential for filter contamination. Consistency of environmental conditions throughout the chamber (T, RH, and air flow) should be checked after installation.

2.1.4.2 EPA Performance Evaluation – Performance Evaluation (PE) samples consisting of Teflon filters and metallic reference weights were provided to the RTI Gravimetry Laboratory by EPA NAREL. The filters were tared at RTI, sent to NAREL in Montgomery, Alabama, re-tared at the NAREL facility, and used for sampling in Montgomery. The sampled filters were reweighed at the NAREL facility and then returned to RTI for reweighing. RTI's final PE sample results were submitted to NAREL for evaluation in the fall of 2003. The report issued by NAREL in December 2003 showed good performance by the laboratory.

2.2 Ion Analysis Laboratory

2.2.1 Facilities

Ion chromatographic analyses are performed by personnel from RTI's Environmental Chemistry Department (ECD). Four of our six ion chromatographic systems (Systems 3, 4, 5, and 6) were used for performance of the measurements. These are described in **Table 4**. The use of these four systems was determined by the workload.

Table 4. Description of Ion Chromatographic Systems used for Analysis of PM2.5 Filter Samples

System No.	Dionex IC Model	Ions Measured
1	Model 500 (S1A)	SO_4, NO_3
2	Model 500 (S2A)	SO_4, NO_3
3	Model 500 (S3A)	SO_4, NO_3
4	DX-600 (D6A)	SO_4, NO_3
5	Model 500 (D5C)	Na, NH_4, K
6	DX-600 (D6C)	Na, NH_4, K

2.2.2 Description of QA/QC Checks Applied

QA/QC checks for ion analyses are summarized in **Table 5**. For ion analyses, a daily multipoint calibration (7 points for cations; 8 points for anions) is performed over the range 0.05 to 25.0 ppm for each ion (Na^+, NH_4^+, and K^+ for cation analyses; NO_3^- and SO_4^{2-} for anion analyses) followed by QA/QC samples including (1) an RTI-prepared QC sample containing concentrations of each ion in the mid- to high-range of the calibration standard concentrations, (2) an RTI-prepared QC sample containing concentrations of each ion at the lower end of the calibration standard concentrations, and (3) a commercially-prepared, NIST-traceable QA sample containing known concentrations of each ion.

The regression parameters (a,b,c and correlation coefficient, r) for the standard curve for each ion are compared with those obtained in the past. Typically, a correlation coefficient of 0.999 or better is obtained for each curve. If the correlation coefficient is <0.999, the analyst carefully examines the individual chromatograms for the calibration standards and reruns any standard that is judged to be out of line with respect to the other standards or to values (peak area and/or height) obtained in the past for the same standard. Possible causes for an invalid standard run include instrumental problems such as incomplete sampling by the autosampler. If necessary, a complete recalibration is performed.

Table 5. Ion Analysis of PM2.5 - Quality Control/ Quality Assurance Checks

QA/QC Check	Frequency	Requirements
Calibration Regression Parameters	Daily	$r \geq 0.999$
Initial QA/QC Checks:		
- QC sample at mid to high range concentration	Daily, immediately after calibration	Measured concentrations within 10% of known values
- QC sample at lower end concentration	Daily, immediately after calibration	Measured concentrations within 10% of known values
- Commercially prepared, NIST traceable QA sample	Daily, immediately after calibration	Measured concentrations within 10% of known values
Periodic QA/QC Checks:		
- Replicate sample	Every 20 samples	RPD = 5% at 100x MDL* RPD = 10% at 10x MDL* RPD = 100% at MDL*
- QA/QC sample	Every 20 samples	Measured concentrations within 10% of known values
- Matrix spiked sample extract	Every 20 samples	Recoveries within 90 to 100% of target values

* MDL = Minimum Detectable Limit RPD = Relative Percent Difference

When all individual calibrations have been judged acceptable, the results for the QA/QC samples are carefully examined. If the observed value for any ion being measured differs by more than 10 percent from the known value, the problem is identified and corrected. Any field samples are then analyzed.

During an analysis run, a duplicate sample, a QA/QC sample, and a spiked sample are analyzed at the rate of at least one every 20 field samples. Precision objectives for duplicate analyses are ±5 percent for concentrations that equal or exceed 100 times the minimum detectable limit (MDL), ±10 percent for concentrations at 10 times the MDL, and ±100 percent for concentrations at the MDL. The observed value for any ion being measured must be within 10 percent of the known value for the QA/QC samples, and ion recoveries for the spiked samples must be within 90 to 110 percent of the target value. If these acceptance criteria are not met for any QA/QC or spiked sample, the problem is identified and corrected. All field samples analyzed since the last acceptable check sample are then reanalyzed.

2.2.3 Summary of QC Results

2.2.3.1 Anions – QC checks performed included:

- Percent recovery for QC samples (standards prepared by RTI)
- Percent recovery for QA samples (commercial standards)
- Relative percent difference (RPD) for replicates
- Spike recovery
- Reagent blank (elution solution and DI water)

Table 6 shows recoveries for NO_3^- with low, medium, and high concentration QC samples (prepared by RTI) and with low and medium-high QA samples (commercially prepared and NIST-traceable) for the instrument used for anion analysis. Average recoveries for the six QC samples ranged from 99.1 to 102.1% over the six month period; average recoveries for the four QA samples ranged from 99.1% to 101.2%.

Table 7 shows recoveries for SO_4^{2-} with low, medium, and high QC samples and with low and medium-high QA samples for the instrument used for anion analysis. Average recoveries for the six QC samples ranged from 100.1% to 102.1% over the six month period; average recoveries for the four QA samples ranged from 98.7% to 101.2%.

Figure 1 shows a plot of the original nitrate concentration vs. the duplicate nitrate concentration for replicate measurements of the filter extracts. The plot shows excellent agreement for the duplicate measurements over the entire concentration range.

Figure 2 shows a plot of the original sulfate concentration vs. the duplicate sulfate concentration for replicate measurements of the filter extracts. Again, the plot shows excellent agreement for the duplicate measurements over the entire concentration range.

Table 8 shows percent recovery for nitrate and sulfate spikes for the six month period. The average recoveries of nitrate for ranged from 97.9% to 101.3%, while the average recoveries for sulfate ranged from 99.5% to 101.0%.

Table 9 presents filter blank (N BLANK) and reagent blank values for nitrate and sulfate over the six month period. The highest average value for filter blanks was 0.014 ppm (25 mL extract) for nitrate and 0.005 ppm for sulfate; the highest average reagent blank was 0.002 ppm for nitrate and 0.009 ppm for sulfate.

Table 6. Average Percent Recovery for Nitrate QA and QC Samples

Inst	Sample ID	Count	NO_3 Conc., ug/mL	Av NO_3 Rec	SD NO_3	Min NO_3	Max NO_3
D6A	QA-CPI_LOW	110	0.6	99.1%	0.8%	0.583	0.607
D6A	QA-CPI_MED-HI	86	3	101.1%	0.6%	2.988	3.081
D6A	RTI QC-HIGH	95	6	102.1%	0.5%	6.035	6.206
D6A	RTI QC-LOW	156	0.6	99.5%	1.1%	0.578	0.624
D6A	RTI QC-MED	197	1.5	99.1%	0.8%	1.457	1.539
S3A	QA-CPI_LOW	127	0.6	99.8%	1.1%	0.582	0.623
S3A	QA-CPI_MED-HI	104	3	101.2%	0.8%	2.986	3.088
S3A	RTI QC-HIGH	116	6	102.1%	0.7%	6.035	6.304
S3A	RTI QC-LOW	189	0.6	100.5%	4.5%	0.561	0.955
S3A	RTI QC-MED	239	1.5	99.8%	1.3%	1.439	1.687

Table 7. Average Percent Recovery for Sulfate QA and QC Samples

Inst	Sample ID	Count	SO_4 Conc., ug/mL	Av SO4 Rec	SD SO_4	Min SO_4	Max SO_4
D6A	QA-CPI_LOW	110	1.2	98.7%	0.7%	1.167	1.204
D6A	QA-CPI_MED-HI	86	6	101.2%	0.5%	5.984	6.155
D6A	RTI QC-HIGH	95	12	102.0%	0.9%	11.771	12.378
D6A	RTI QC-LOW	156	1.2	100.1%	0.8%	1.167	1.227
D6A	RTI QC-MED	197	3	100.6%	0.7%	2.968	3.180
S3A	QA-CPI_LOW	127	1.2	99.0%	1.2%	1.138	1.238
S3A	QA-CPI_MED-HI	104	6	101.2%	0.7%	5.962	6.149
S3A	RTI QC-HIGH	116	12	102.1%	1.0%	11.817	12.577
S3A	RTI QC-LOW	189	1.2	100.4%	1.3%	1.105	1.256
S3A	RTI QC-MED	239	3	100.9%	0.8%	2.936	3.113

Figure 1. Nitrate Duplicate Analyses

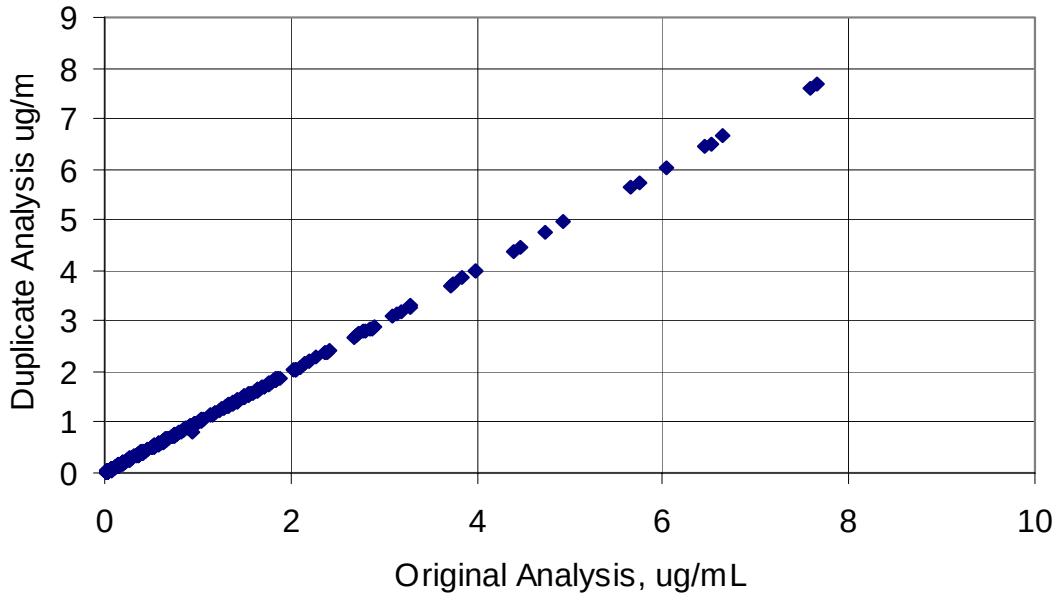


Figure 2. Sulfate Duplicate Analyses

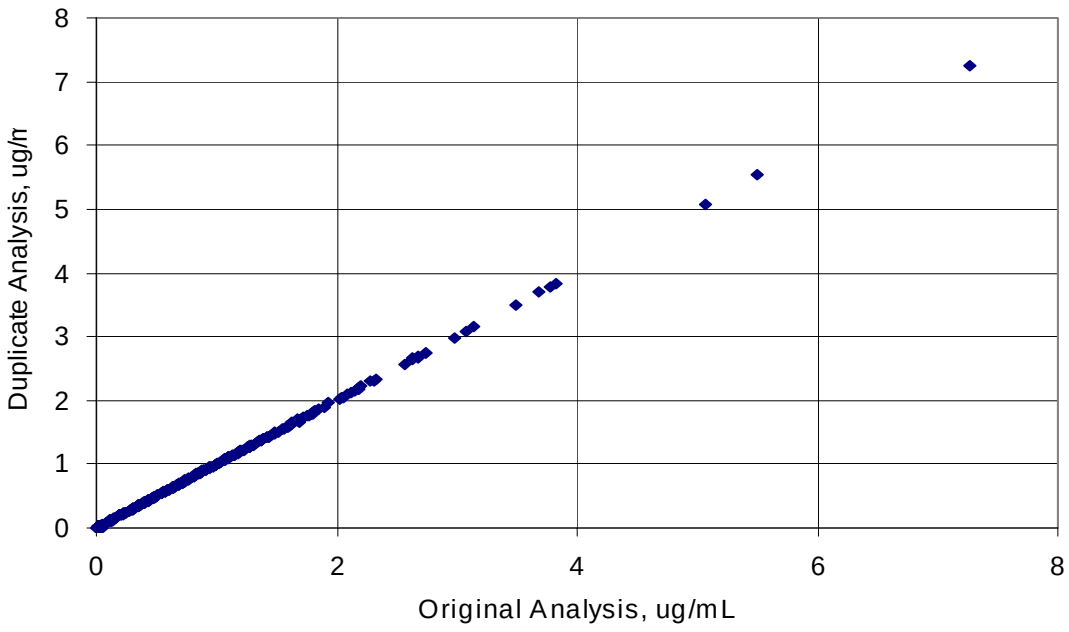


Table 8. Average Percent Recovery for Nitrate and Sulfate Spikes

Inst	D6A					
Analyte	Nitrate					
Date:	Jan-04	Feb-04	Mar-04	Apr-04	May-04	Jun-04
Avg Recovery:	97.9%	99.5%	101.3%	99.1%	99.2%	
St Dev:	12.3%	1.5%	1.9%	2.3%	2.0%	
Count:	42	46	37	31	7	
Min Recovery:	21.1%	95.6%	97.5%	88.8%	95.6%	
Max Recovery:	104.4%	102.8%	109.4%	102.4%	100.7%	
Inst	S3A					
Analyte	Nitrate					
Date:	Jan-04	Feb-04	Mar-04	Apr-04	May-04	Jun-04
Avg Recovery:	99.5%	100.3%	100.0%	99.6%	99.9%	
St Dev:	1.1%	1.6%	2.0%	1.6%	1.3%	
Count:	44	56	33	47	6	
Min Recovery:	97.3%	95.0%	94.4%	93.9%	98.0%	
Max Recovery:	101.9%	103.7%	105.2%	102.1%	102.0%	
Inst	D6A					
Analyte	Sulfate					
Date:	Jan-04	Feb-04	Mar-04	Apr-04	May-04	Jun-04
Avg Recovery:	98.7%	99.7%	101.0%	99.7%	100.0%	
St Dev:	9.3%	1.4%	1.3%	1.8%	1.0%	
Count:	42	46	37	31	7	
Min Recovery:	40.8%	96.9%	97.3%	92.4%	98.2%	
Max Recovery:	104.4%	105.2%	105.2%	103.1%	101.1%	
Inst	S3A					
Analyte	Sulfate					
Date:	Jan-04	Feb-04	Mar-04	Apr-04	May-04	Jun-04
Avg Recovery:	99.5%	99.6%	100.0%	99.9%	100.5%	
St Dev:	1.2%	1.6%	1.9%	1.7%	1.2%	
Count:	44	56	33	47	6	
Min Recovery:	96.3%	93.6%	93.1%	94.4%	98.6%	
Max Recovery:	102.1%	102.2%	104.8%	103.7%	101.7%	

Table 9. Filter Blank (N) and Reagent Blank Values (ppm) for Nitrate and Sulfate

Inst	Blank Type	Count	Av NO_3	STD NO_3	Min NO_3	Max NO_3
D6A	N QC	55	0.014	0.013	0	0.040
D6A	REAG	202	0.002	0.007	0	0.034
S1A	N QC	6	0.005	0.009	0	0.021
S3A	N QC	186	0.013	0.012	0	0.039
S3A	REAG	216	0.001	0.005	0	0.035

Highest Filter blank (N QC) is: 0.014
Highest REAG blank is: 0.002

Inst	Blank Type	Count	Av SO_4	STD SO_4	Min SO_4	Max SO_4
D6A	N QC	55	0.002	0.005	0	0.022
D6A	REAG	202	0.003	0.008	0	0.038
S1A	N QC	6	0.003	0.007	0	0.018
S3A	N QC	186	0.005	0.007	0	0.035
S3A	REAG	216	0.009	0.011	0	0.039

Highest Filter blank (N QC) is: 0.005
Highest REAG blank is: 0.009

2.2.3.2 Cations – QC checks performed included:

- Percent recovery for QC samples
- Percent recovery for QA samples
- RPD for replicates
- Spike recovery tests
- Reagent and filter blank tests

Table 10 presents the average percent recovery value for sodium for both QA and QC samples for the instruments used for these measurements. The average recovery for the QA samples over the six month period ranged from 99.6% to 107.2%. The average recovery for the QC samples ranged from 100.2% to 102.2%.

Table 11 presents the average percent recovery value for ammonium for both QA and QC samples for the instrument used for these measurements. The average recovery for the QA samples over the six month period ranged from 99.6% to 107.4%. The average recovery for the QC samples ranged from 100.3% to 101.6%.

Table 12 presents the average percent recovery value for potassium for both QA and QC samples for the instrument used for these measurements. The average recovery for the QA samples over the six month period ranged from 99.7% to 106.6%. The average recovery for the QC samples ranged from 99.4% to 101.3%.

Table 10. Average Percent Recovery for Sodium QA and QC Samples

Inst	Sample	Count	Conc., ug/mL	Av Na rec	SD Na	Min Na Rec	Max Na Rec
D5C	GFS 0.4 PPM QA	205	0.400	102.0%	2.8%	0.382	0.451
D5C	GFS 4.0 PPM QA	206	4.000	99.6%	1.0%	3.874	4.113
D5C	RTI 2.0 PPM QC	152	2.000	102.2%	12.2%	1.952	5.079
D5C	RTI 5.0 PPM QC	139	5.000	100.2%	6.6%	1.205	5.203
D6C	GFS 0.4 PPM QA	146	0.400	107.2%	69.0%	0.303	3.976
D6C	GFS 4.0 PPM QA	152	4.000	99.7%	0.6%	3.926	4.088
D6C	RTI 2.0 PPM QC	109	2.000	100.9%	1.1%	1.971	2.085
D6C	RTI 5.0 PPM QC	98	5.000	100.7%	0.7%	4.980	5.176

Table 11. Average Percent Recovery for Ammonium QA and QC Samples

Inst	Sample	Count	Conc., ug/mL	Av NH_4 rec	SD NH_4	Min NH_4 Rec	Max NH_4 Rec
D5C	GFS 0.4 PPM QA	205	0.400	101.9%	3.8%	0.361	0.541
D5C	GFS 4.0 PPM QA	206	4.000	99.9%	1.4%	3.711	4.278
D5C	RTI 2.0 PPM QC	152	2.000	101.6%	12.3%	1.823	5.053
D5C	RTI 5.0 PPM QC	139	5.000	100.3%	8.0%	0.374	5.255
D6C	GFS 0.4 PPM QA	146	0.400	107.4%	68.6%	0.317	3.967
D6C	GFS 4.0 PPM QA	152	4.000	99.6%	0.6%	3.940	4.061
D6C	RTI 2.0 PPM QC	109	2.000	100.6%	0.7%	1.974	2.054
D6C	RTI 5.0 PPM QC	98	5.000	100.6%	0.7%	4.963	5.148

Table 12. Average Percent Recovery for Potassium QA and QC Samples

Inst	Sample	Count	Conc., ug/mL	Av K rec	SD K	Min K Rec	Max K Rec
D5C	GFS 0.4 PPM QA	205	0.400	99.9%	3.2%	0.365	0.461
D5C	GFS 4.0 PPM QA	206	4.000	100.2%	1.0%	3.900	4.131
D5C	RTI 2.0 PPM QC	152	2.000	101.3%	12.4%	1.920	5.078
D5C	RTI 5.0 PPM QC	139	5.000	99.6%	8.6%	0.000	5.149
D6C	GFS 0.4 PPM QA	146	0.400	106.6%	69.8%	0.317	3.994
D6C	GFS 4.0 PPM QA	152	4.000	99.7%	0.5%	3.941	4.091
D6C	RTI 2.0 PPM QC	109	2.000	99.8%	0.7%	1.959	2.027
D6C	RTI 5.0 PPM QC	98	5.000	99.4%	0.6%	4.921	5.090

Figure 3 shows a plot of the original sodium concentration vs. the duplicate sodium concentration for replicate measurements of the filter extracts. The plot shows good agreement for the duplicate measurements with a small amount of scatter at the lower concentration range. RTI continues to look for sources of contamination and methods to reduce the scatter.

Figure 4 shows a plot of the original ammonium concentration vs. the duplicate ammonium concentration for replicate measurements of the filter extracts. This plot also shows excellent agreement for the duplicate measurements over the entire concentration range.

Figure 3. Sodium Duplicate Analyses

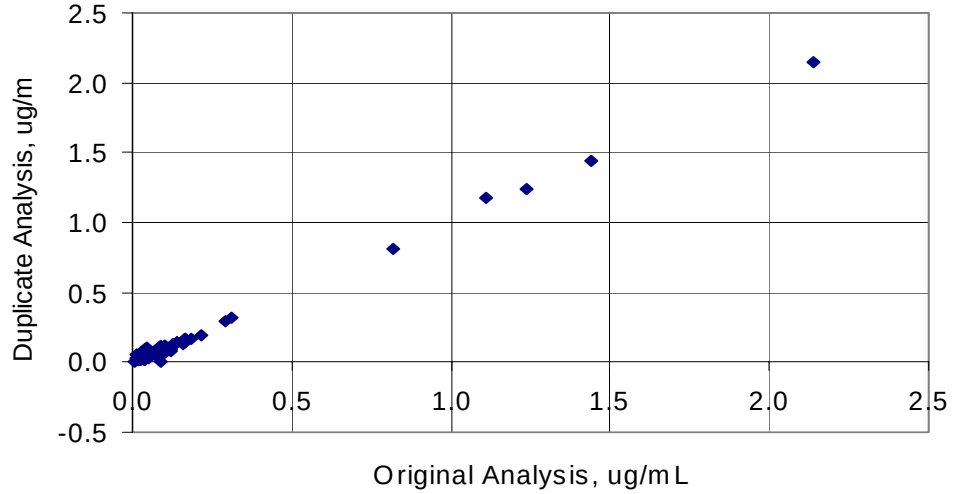


Figure 4. Ammonium Duplicate Analyses

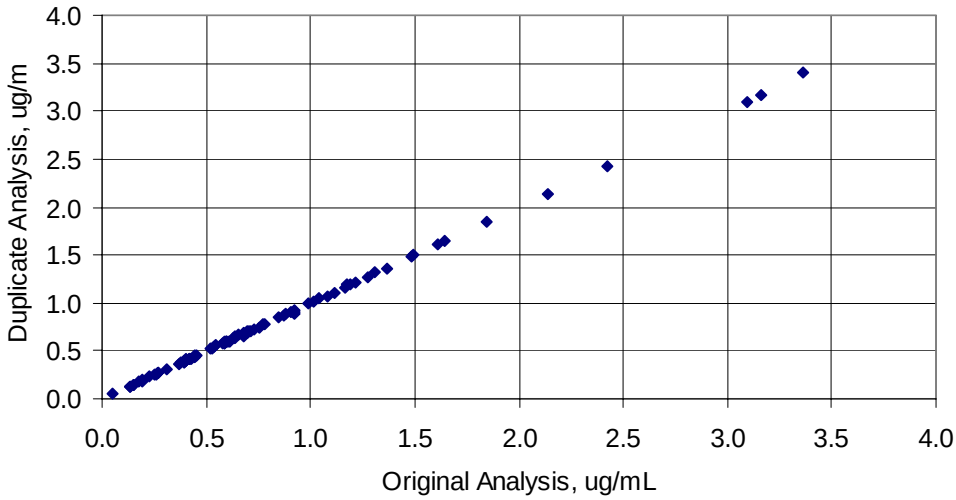


Figure 5 shows a plot of the original potassium concentration vs. the duplicate potassium concentration for replicate measurements of the filter extracts. Again, the plot shows good agreement for the duplicate measurements with a small amount of scatter at the lower concentration range.

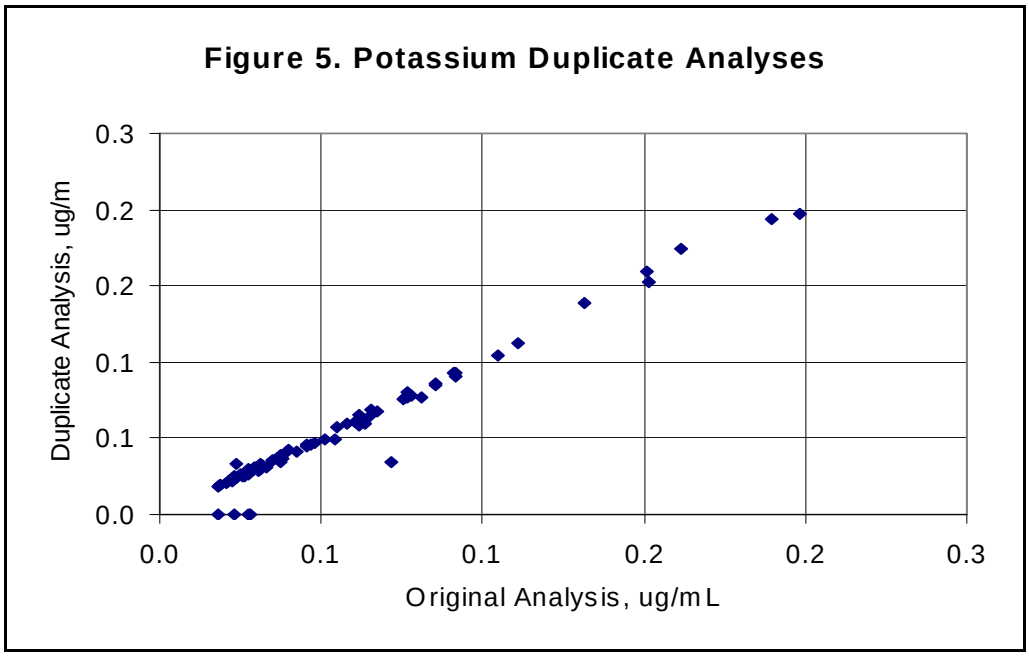


Table 13 shows average percent recovery for spikes of sodium, ammonium, and potassium over the six month period. The average recovery values for ranged from 99.6% to 104.0% for sodium, 98.4% to 102.2% for ammonium, and 97.2% to 101.9% for potassium.

Table 14 presents filter (N BLANK) and reagent blank values for sodium, ammonium, and potassium for the instruments used for these measurements. The highest average sodium values over the six month period were 0.001 ppm for the nylon filter blanks (25 mL extract) and 0.000 ppm for the reagent blank. The highest average ammonium values were 0.000 ppm (25 mL extract) for the nylon filter blanks and 0.000 ppm for the reagent blanks. The highest average potassium value was 0.000 ppm for nylon filter blanks (25 mL extract) and the highest average value was 0.000 ppm for the reagent blank.

2.2.4 Data Validity Discussion

During this period, no data were invalidated as a result of errors in the ion chromatography (IC) laboratory. Any inconsistencies that were observed in the filter samples were flagged on the IC data report when it is submitted for entry into the database. For example, on a few occasions, two or more filters were found in one petri dish. The filters were extracted and analyzed as one, and this was noted on the data report for that batch of samples.

Table 13. Average Percent Recovery for Sodium, Ammonium, and Potassium Spikes

Inst	D5C					
Analyte	Sodium					
Date:	Jan-04	Feb-04	Mar-04	Apr-04	May-04	Jun-04
Avg Recovery:	100.6%	100.7%	102.1%	101.5%	99.9%	
St Dev:	1.5%	3.1%	3.1%	2.6%	1.1%	
Count:	48	52	39	40	7	
Min Recovery:	97.7%	91.9%	97.1%	97.3%	98.5%	
Max Recovery:	104.8%	110.7%	112.8%	106.8%	101.5%	
Inst	D5C					
Analyte	Ammonium					
Date:	Jan-04	Feb-04	Mar-04	Apr-04	May-04	Jun-04
Avg Recovery:	98.7%	98.4%	100.4%	99.9%	99.6%	
St Dev:	3.3%	3.2%	2.8%	3.2%	5.5%	
Count:	48	52	39	40	7	
Min Recovery:	89.1%	87.8%	91.4%	89.9%	88.2%	
Max Recovery:	103.9%	104.1%	107.7%	104.6%	104.2%	
Inst	D5C					
Analyte	Potassium					
Date:	Jan-04	Feb-04	Mar-04	Apr-04	May-04	Jun-04
Avg Recovery:	98.5%	97.7%	99.0%	99.2%	97.2%	
St Dev:	2.1%	2.8%	3.9%	3.0%	2.9%	
Count:	48	52	39	40	7	
Min Recovery:	94.1%	88.8%	90.4%	93.3%	93.7%	
Max Recovery:	102.9%	104.0%	109.7%	106.3%	100.6%	
Inst	D6C					
Analyte	Sodium					
Date:	Jan-04	Feb-04	Mar-04	Apr-04	May-04	Jun-04
Avg Recovery:	99.6%	100.9%	104.0%	100.0%	100.8%	
St Dev:	1.7%	3.1%	5.6%	1.8%	1.6%	
Count:	22	41	31	37	6	
Min Recovery:	97.5%	96.7%	98.1%	95.5%	99.0%	
Max Recovery:	104.8%	115.1%	117.4%	104.3%	103.1%	
Inst	D6C					
Analyte	Ammonium					
Date:	Jan-04	Feb-04	Mar-04	Apr-04	May-04	Jun-04
Avg Recovery:	98.6%	99.8%	102.2%	99.1%	99.9%	
St Dev:	2.1%	2.0%	4.0%	2.3%	0.5%	
Count:	22	41	31	37	6	
Min Recovery:	91.9%	92.9%	94.0%	91.4%	99.5%	
Max Recovery:	100.5%	105.4%	112.2%	102.6%	100.7%	
Inst	D6C					
Analyte	Potassium					
Date:	Jan-04	Feb-04	Mar-04	Apr-04	May-04	Jun-04
Avg Recovery:	98.6%	98.9%	101.9%	98.9%	99.4%	
St Dev:	1.0%	2.1%	4.9%	1.4%	0.8%	
Count:	22	41	31	37	6	
Min Recovery:	96.8%	95.8%	94.5%	95.7%	98.1%	
Max Recovery:	100.3%	107.6%	115.1%	102.6%	100.6%	

Table 14. Filter Blank and Reagent Blank Values (ppm) for Sodium, Ammonium, and Potassium

Inst	TYPE	Count	Av Na	STD Na	Min Na	Max Na
D5C	N QC	204	0.0008	0.0046	-0.0100	0.0317
D5C	Reagent Blank	175	0.0004	0.0031	-0.0082	0.0317
D6C	N QC	54	0.0001	0.0023	-0.0066	0.0138
D6C	Reagent Blank	120	-0.0003	0.0063	-0.0266	0.0329

Inst	TYPE	Count	Avg NH4	STD NH4	Min NH4	Max NH4
D5C	N QC	204	0	0	0	0
D5C	Reagent Blank	175	0	0	0	0
D6C	N QC	54	0	0	0	0
D6C	Reagent Blank	120	0.00002	0.00044	-0.00127	0.00434

Inst	TYPE	Count	Avg K	STD K	Min K	Max K
D5C	N QC	204	0	0	0	0
D5C	Reagent Blank	175	0	0	0	0
D6C	N QC	54	0	0	0	0
D6C	Reagent Blank	120	0	0	0	0

2.2.5 Corrective Actions Taken

There were no corrective actions necessary for IC analysis during this reporting period.

2.3 OC/EC Laboratory

The RTI OC/EC Laboratory analyzed 11,231 quartz filter samples by the STN method during the period January 1, 2004, through June 30, 2004, and reported the results of those analyses to the main STN database.

A fourth Sunset Laboratory Thermal-Optical Carbon Aerosol analyzer, a dual function (transmittance and reflectance) instrument, was validated by analyzing 140 quartz filters on both the Third and Fourth analyzers (the latter in transmittance mode) using the standard STN heating profile and comparing the results. Only 3 of 140 replicate analyses (or about 2.14%) run on both analyzers failed to meet the criteria used to evaluate duplicate analyses run on the same analyzer. The percentage of failures (2.14%) was found to be in the range of the percentages of duplicate analyses that had failed the duplicate criteria on the Retrofit (1.36%), Second (2.26%), and Third (1.68%) analyzers that had been run as of the analysis date of the last validation samples using the current analysis and calculation software versions. The Fourth analyzer was considered validated by these results, and the first samples reported for the instrument were analyzed on June 3, 2004.

2.3.1 Description of QC Checks Applied

Quality control (QC) checks, acceptance criteria, and corrective actions for the OC/EC Laboratory are summarized in **Table 15** below.

2.3.2 Statistical Summary of QC Results

The method detection limit for total carbon (TC) is determined annually or when the oven in an analyzer is replaced, whichever comes sooner. **Table 16** provides a summary on MDLs in effect during the reporting period for all four OC/EC analyzers.

All four OC/EC carbon analyzers met the required limit of ≤ 0.5 μg C/cm^2 for all MDLs determined during the period.

Calibration peak area, which is the response of the FID to the internal standard, is plotted for every analysis run on a given day. Any filter analysis for which the calibration peak area is outside the range of 95% to 105% of the average calibration peak area for that day is repeated with a second punch.

Routine QC samples analyzed in the OC/EC Laboratory include (1) daily instrument blanks, (2) weekly three-point calibration standards, (3) daily mid-level calibration check standards, and (4) duplicate analyses on 10% of quartz filter samples analyzed. Each of these is described separately below.

Table 15. OC/EC Laboratory Quality Control Checks, Acceptance Criteria, and Corrective Actions.

QC Element	Frequency	Acceptance Criteria	Corrective Action
Method Detection Limit	after oven replacement or annually, whichever comes first	MDL $\leq$ 0.5 μg C/cm^2	Investigate the source of the problem and initiate corrective action, if necessary, to correct the problem before analyzing samples.
Calibration Peak Area	every analysis	Within 95% to 105% of average calibration peak area for that day	Discard the results of that analysis and, if necessary, repeat the analysis with a second punch from the same filter.
Instrument Blank	daily and after about 30 samples	(1) Blank $\leq$0.3 μg/cm^2, and (2) calibration peak area 90% to 110% of average for the weekly three-point calibration.	Determine if the problem is with the filter or the instrument, and, if necessary, initiate corrective action to identify and solve any instrument problem, and run an acceptable instrument blank before analyzing samples.
Three-Point Calibration	weekly	(1) Correlation Coefficient (R^2) $\geq$0.998 [with force-fit through 0,0], and (2) 93% to 107% recovery for all three standards	Determine the cause of the nonlinearity, and initiate actions that will identify and solve any problem that may have arisen. Then repeat the three-point calibration, which must yield satisfactory results before samples are analyzed.
Calibration Check	daily	(1) 93% to 107% recovery, and (2) calibration peak area 90% to 110% of average for the weekly three-point calibration.	Initiate corrective action, if necessary, to solve the problem before analyzing samples.
Duplicate Analyses	10% of samples	(1) TC Values greater than 10 μg C/cm^2-- Less than 10% RPD, (2) TC Values 5 - 10 μg C/cm^2-- Less than 15% RPD, (3) TC Values less than 5 μg C/cm^2-- Within $\pm$0.75 μg C/cm^2.	Flag analysis results for that filter with non-uniform filter deposit (LFU) flag.

Table 16. Method Detection Limits for TC

Retrofit MDLs (date, μg C/cm^2)	**Second MDLs** (date, μg C/cm^2)	**Third MDLs** (date, μg C/cm^2)	**Fourth MDL** (date, μg C/cm^2)
10/7/03, 0.11 1/12/04, 0.08 5/11/04, 0.07 5/25/04, 0.18	7/22/03, 0.13 1/13/04, 0.10 5/12/04, 0.19	7/22/03, 0.04 1/13/04, 0.05 3/11/04, 0.13	5/3/04, 0.197

Figure 6 shows measured TC for daily instrument blanks and instrument blanks run after about 30 samples on the Retrofit, Second, Third, and Fourth OC/EC analyzers during the reporting period (January 1, 2004, through June 30, 2004). The instrument blank must be ≤0.3 μg C/cm^2 (bold line at the top of Figure OC/EC01). Mean and standard deviation of blank responses by instrument over the reporting period are summarized in **Table 17** below.

Table 17. OC/EC Instrument Blank Statistics

Blank Statistic	**OC/EC Analyzer**			
	Retrofit	**Second**	**Third**	**Fourth**
Number of Instrument Blanks	218	249	247	63
Mean Response (μg C/cm^2)	0.025	0.025	0.022	0.035
Standard Deviation	0.021	0.028	0.023	0.057

No accepted daily instrument blanks or instrument blanks run after 30 samples on any of the four analyzers exceeded the acceptance criterion of ≤0.3 μg C/cm^2.

Figure 7 shows linearity (as correlation coefficient, R^2, of least-squares fit of FID response vs. mass of carbon in calibration standard spiked onto filter punch with the trend line forced-fit through the origin) for all three-point calibrations run on all four instruments during the reporting period. All four instruments met the $R^2 \geq 0.998$ (heavy line in Figure 7) requirement for every three-point calibration.

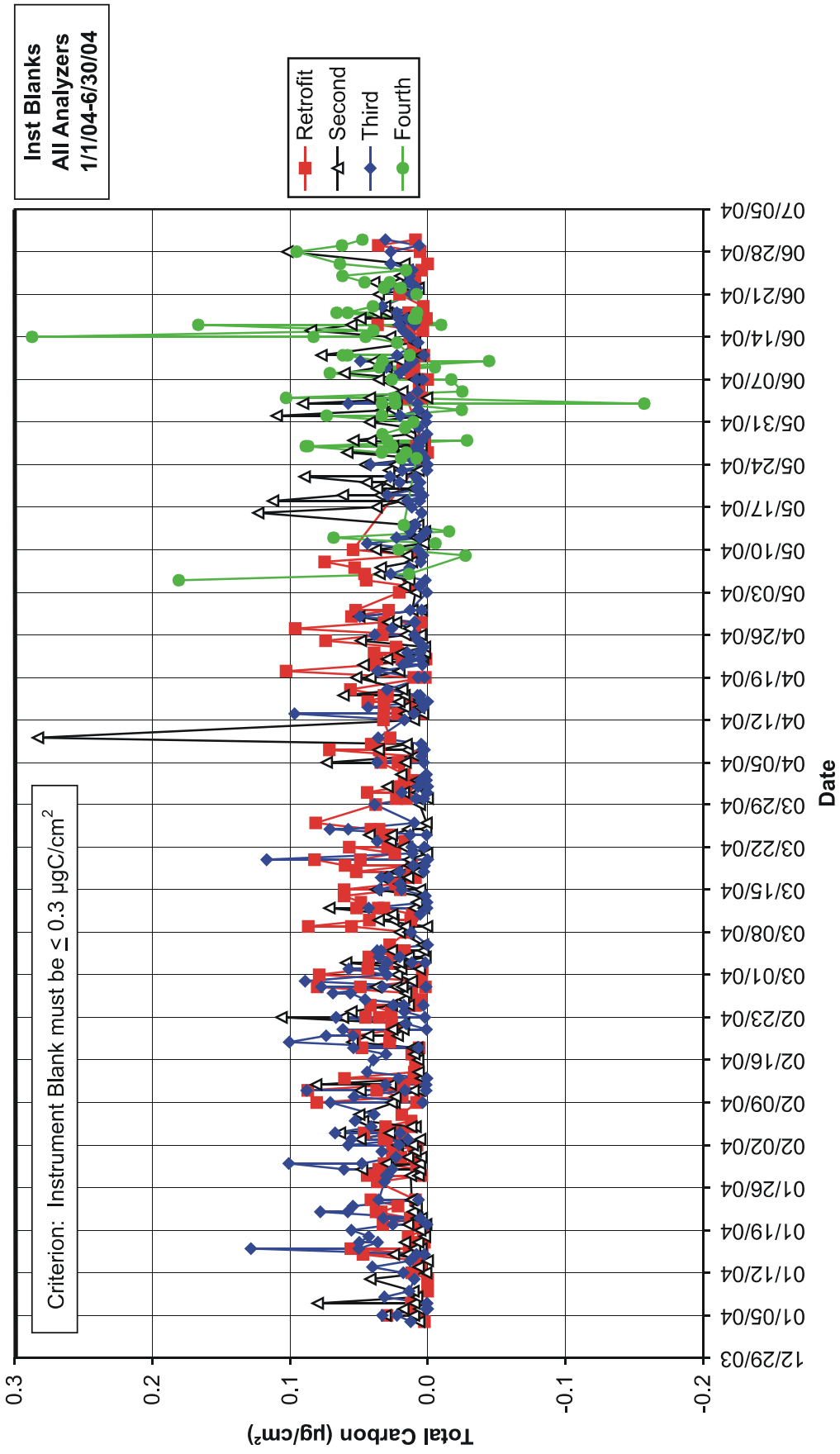


Figure 6. OC/EC Instrument Blanks: All STN OC/EC Analyzers

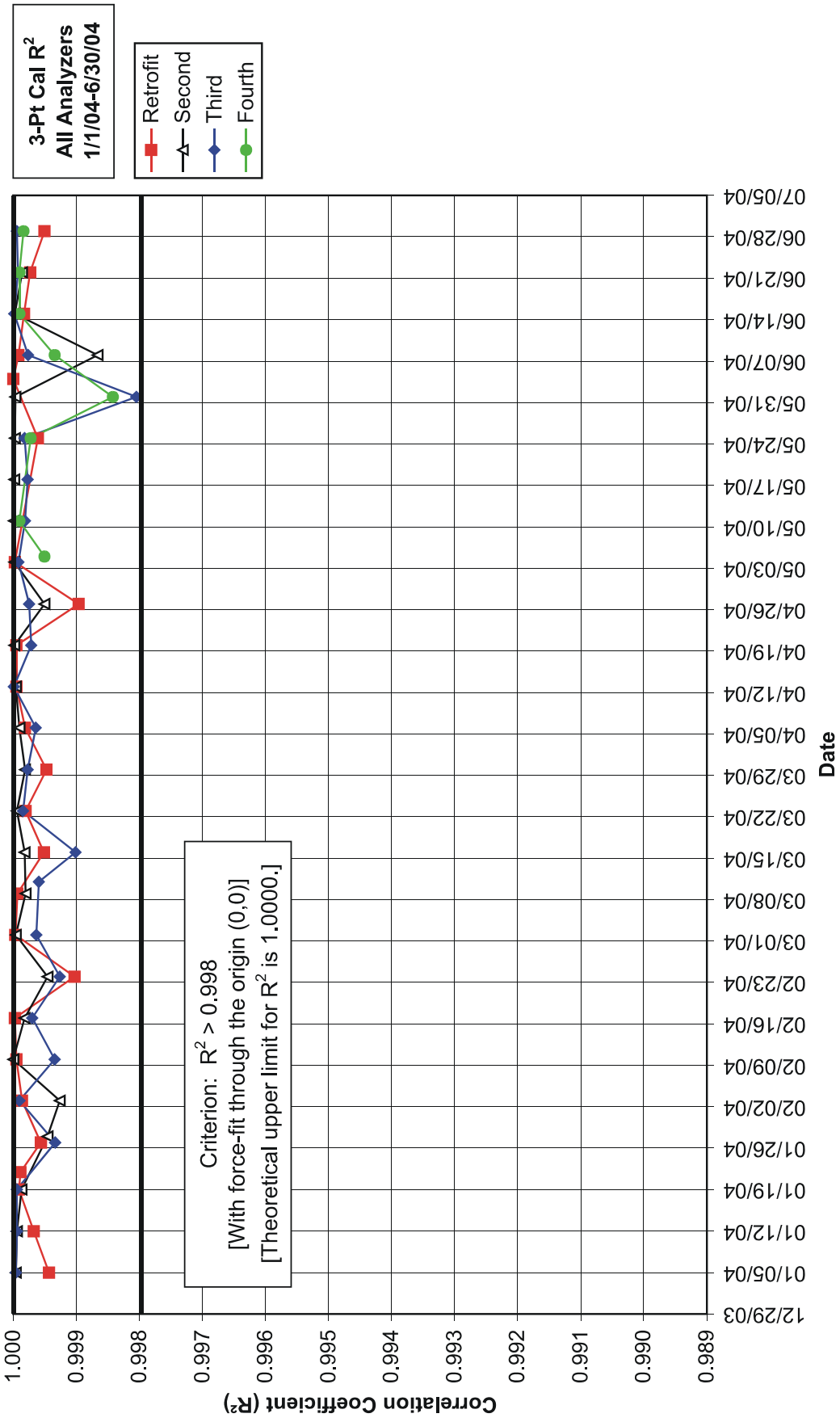


Figure 7. Linearity of Three-Point Calibration Plots: All STN OC/EC Analyzers

Percent recovery of standards is used to make sure the instruments are functioning properly and are still calibrated correctly. **Figures 8, 9, 10, and 11** show percent recovery on the Retrofit, Second, Third, and Fourth analyzers, respectively, for each of the three (low, middle, and high) calibration standards, as well as the average percent recovery for the three, used for each three-point calibration. All four instruments met the 93-107% criterion (heavy lines in figures) for recovery for all three standards in every three-point calibration during the reporting period.

Response factors for the flame ionization detector (FID) are used to monitor FID performance. **Figures 12, 13, 14, and 15** show FID response factors for each of the three calibrations standards and the average FID response factor for each three-point calibration on the Retrofit, Second, Third, and Fourth instruments, respectively, during the reporting period. FID response is affected by slight changes in flow rate for hydrogen and other gases, but use of the internal methane standard at the end of every analysis compensates for such changes. All three-point calibrations on all three analyzers met the acceptance criteria in Section 2.3.1. The ratio of FID area counts for the internal standard to the known mass of carbon in the internal standard injection loop is calculated separately for each analysis and used to calculate the mass of carbon volatilized from the filter punch during that analysis as shown in the following equation.

$$\text{mass } C_{punch} = \frac{\text{FID area counts}_{punch}}{\left[\frac{\text{FID area counts}_{internal\ standard}}{\text{mass } C_{internal\ standard\ loop}}\right]}$$

Figure 16 shows the slopes of three-point calibration plots with force-fit through the origin for all four OC/EC analyzers during the reporting period.

Figure 17 shows percent recovery for all daily calibration checks run on all four OC/EC analyzers during the reporting period. All daily calibration checks met the acceptance criterion of 93% to 107% recovery.

Duplicate measurements are used to monitor the uniformity of filter loading and to indicate instrument stability. The acceptance criteria for duplicate measurements (in the Table in Section 2.3.1 above) are based on a significant absolute uncertainty at low (< 5 μg C/cm^2) TC loadings and the relative uncertainty at higher TC loadings. Figure 18 shows relative percent difference of duplicate measurements versus filter concentration (μg C/cm^2) for the Retrofit, Second, Third, and Fourth OC/EC analyzers during the reporting period, and **Table 18** gives the numbers of duplicates run on each analyzer and the number that failed the applicable duplicate criterion. Filter results that failed to meet the appropriate duplicate acceptance criterion were flagged as having a nonuniform filter deposit (LFU).

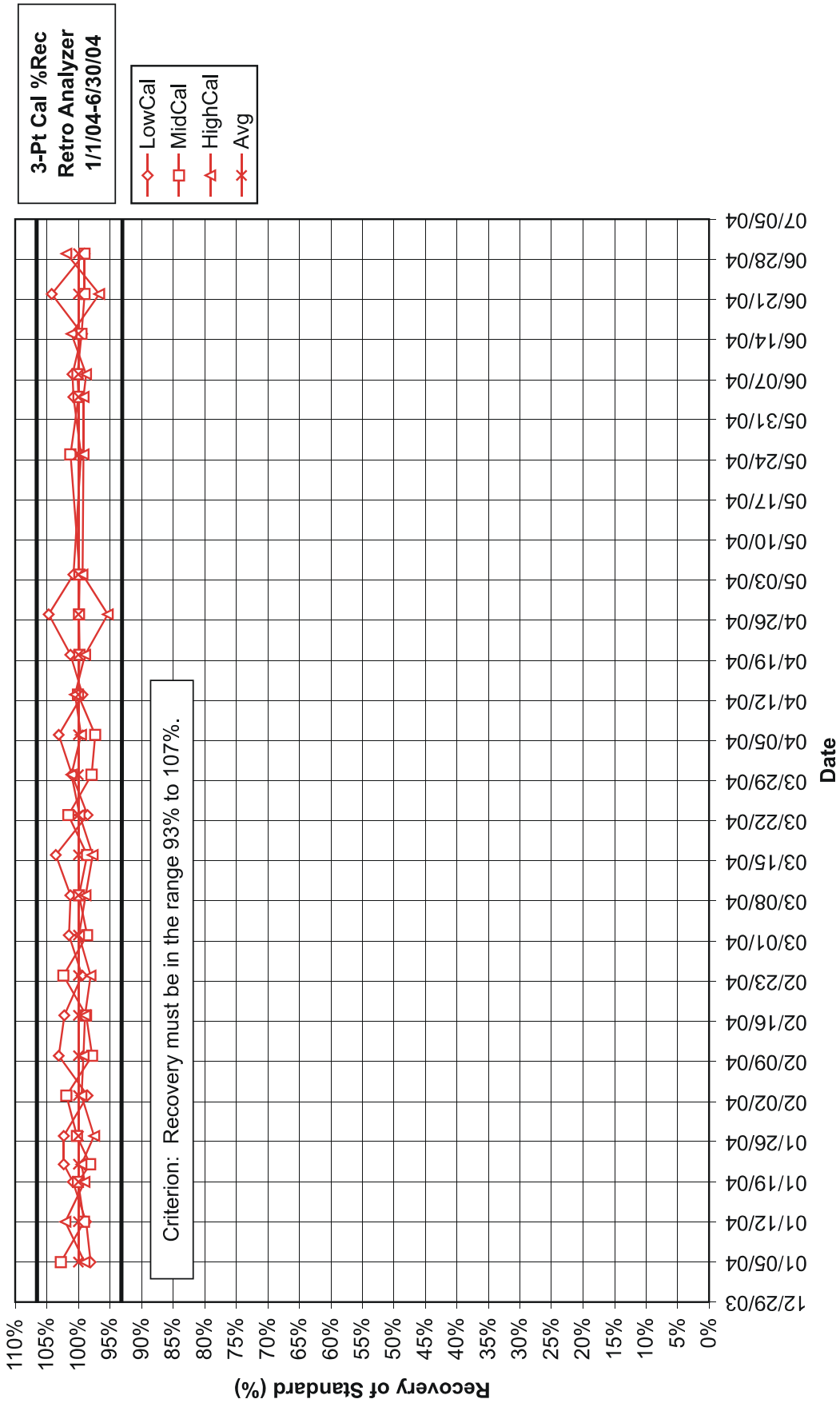


Figure 8. Percent Recoveries for Three-Point Calibration Standards: Retrofit OC/EC Analyzer

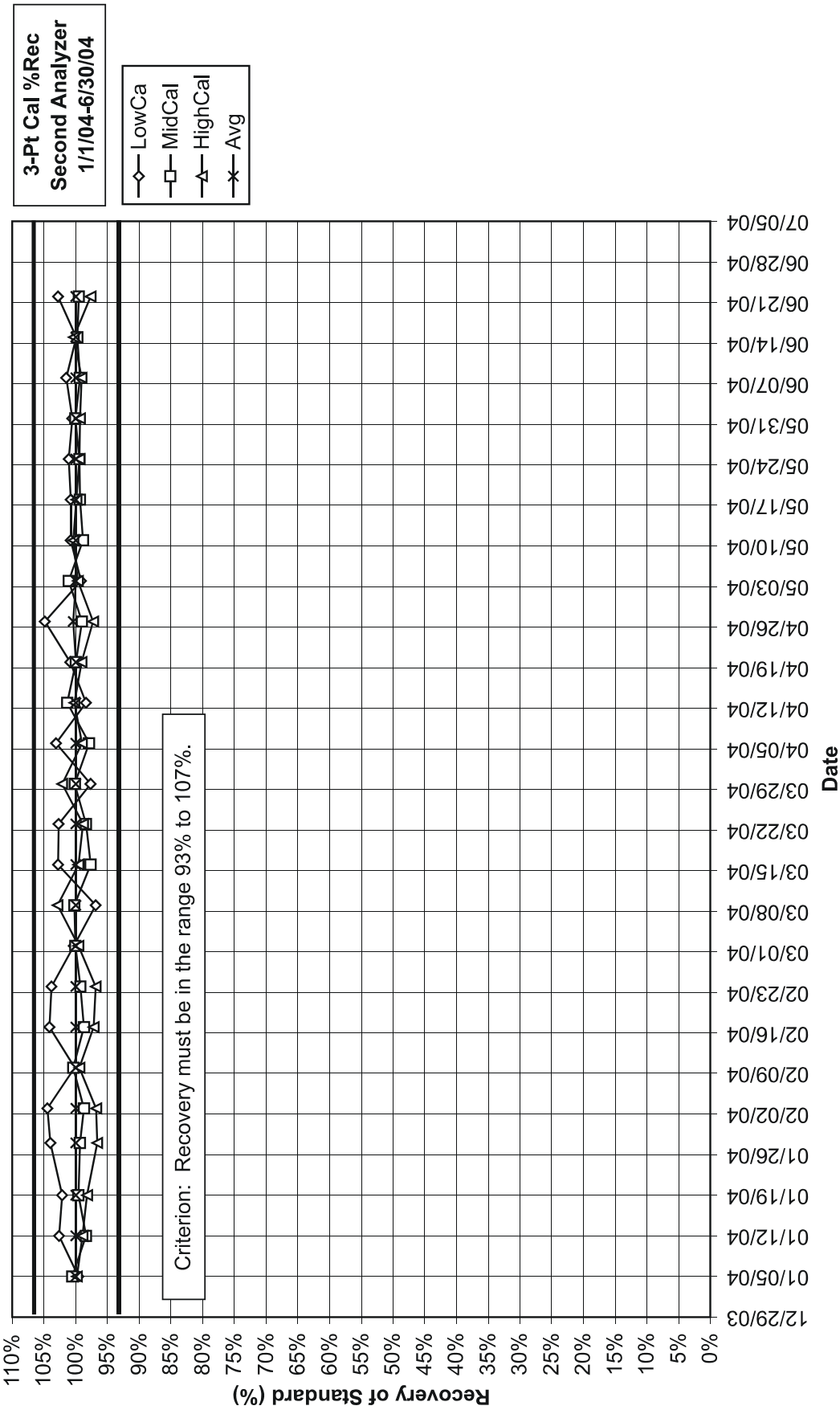


Figure 9. Percent Recoveries for Three-Point Calibration Standards: Second OC/EC Analyzer

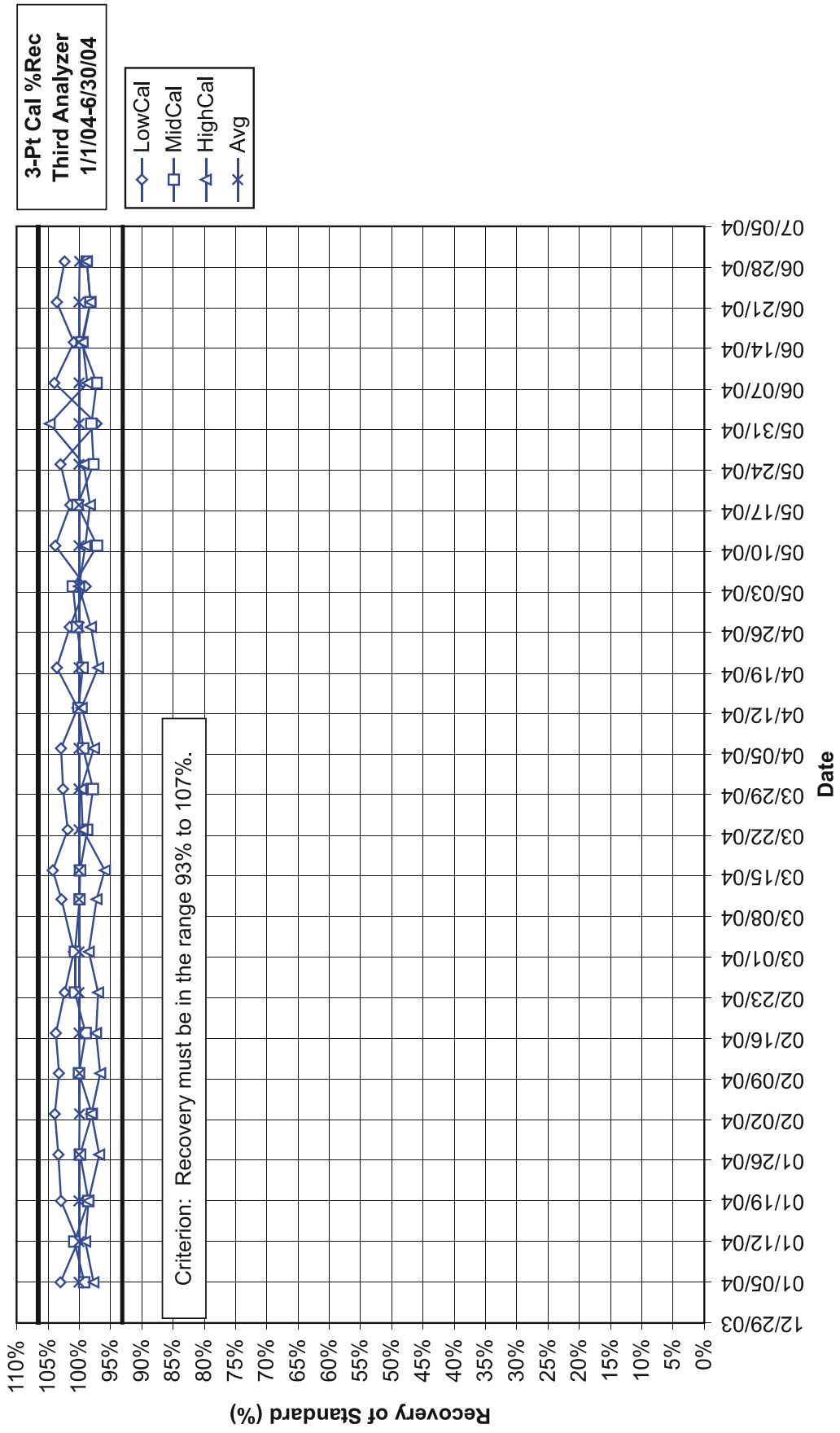


Figure 10. Percent Recoveries for Three-Point Calibration Standards: Third OC/EC Analyzer

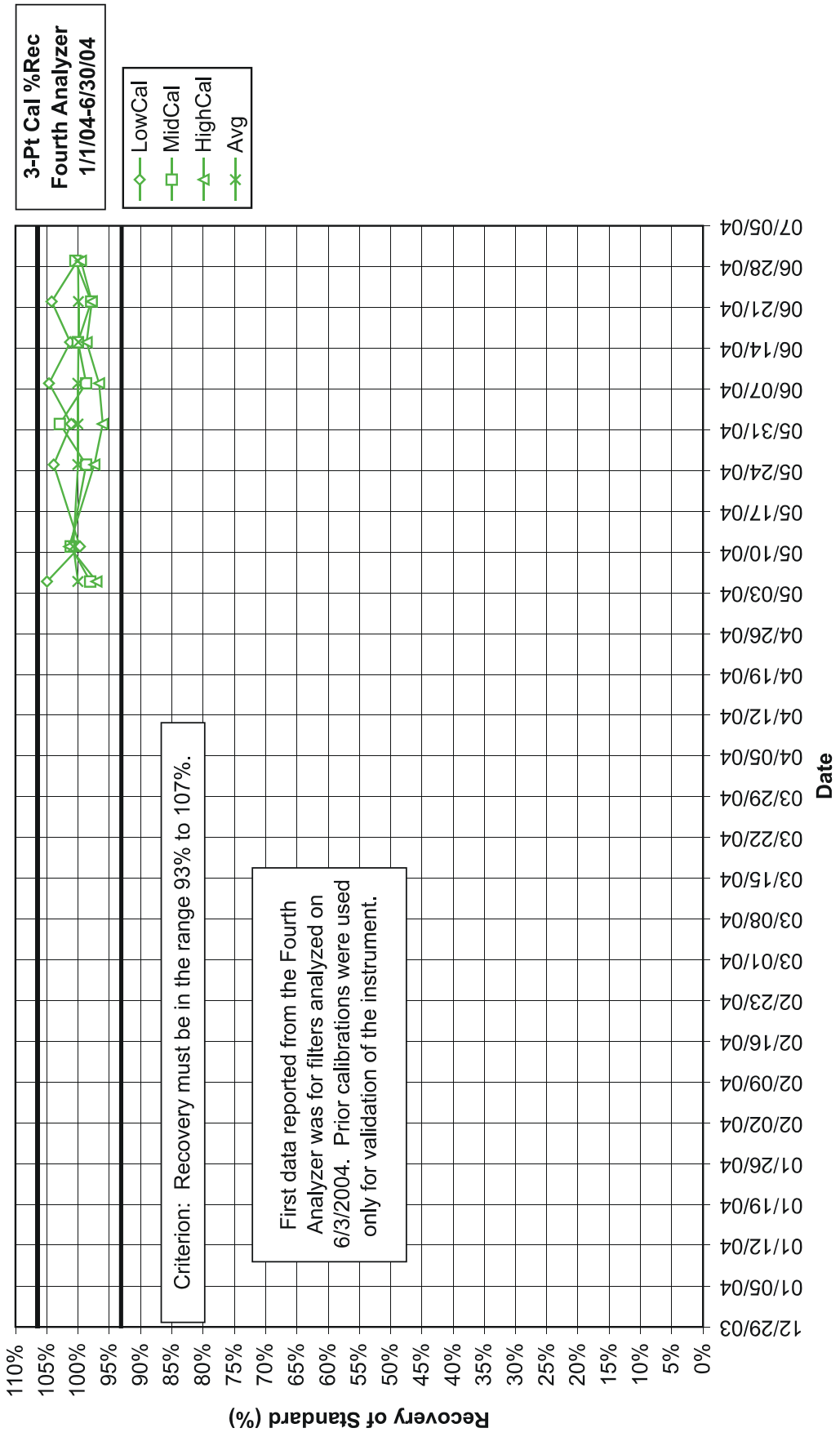


Figure 11. Percent Recoveries for Three-Point Calibration Standards: Fourth OC/EC Analyzer

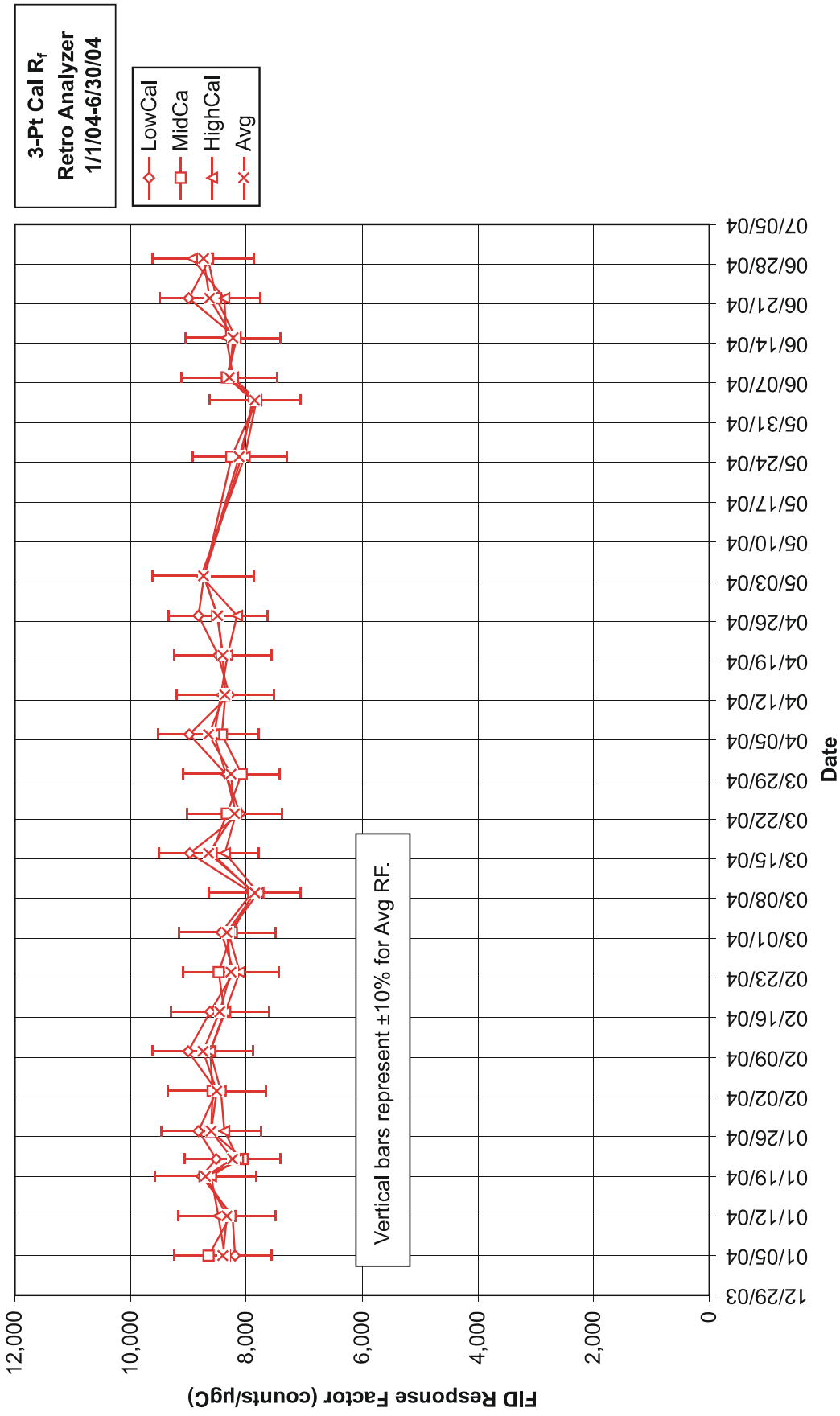


Figure 12. FID Response Factors for Three-Point Calibration Standards: Retrofit OC/EC Analyzer

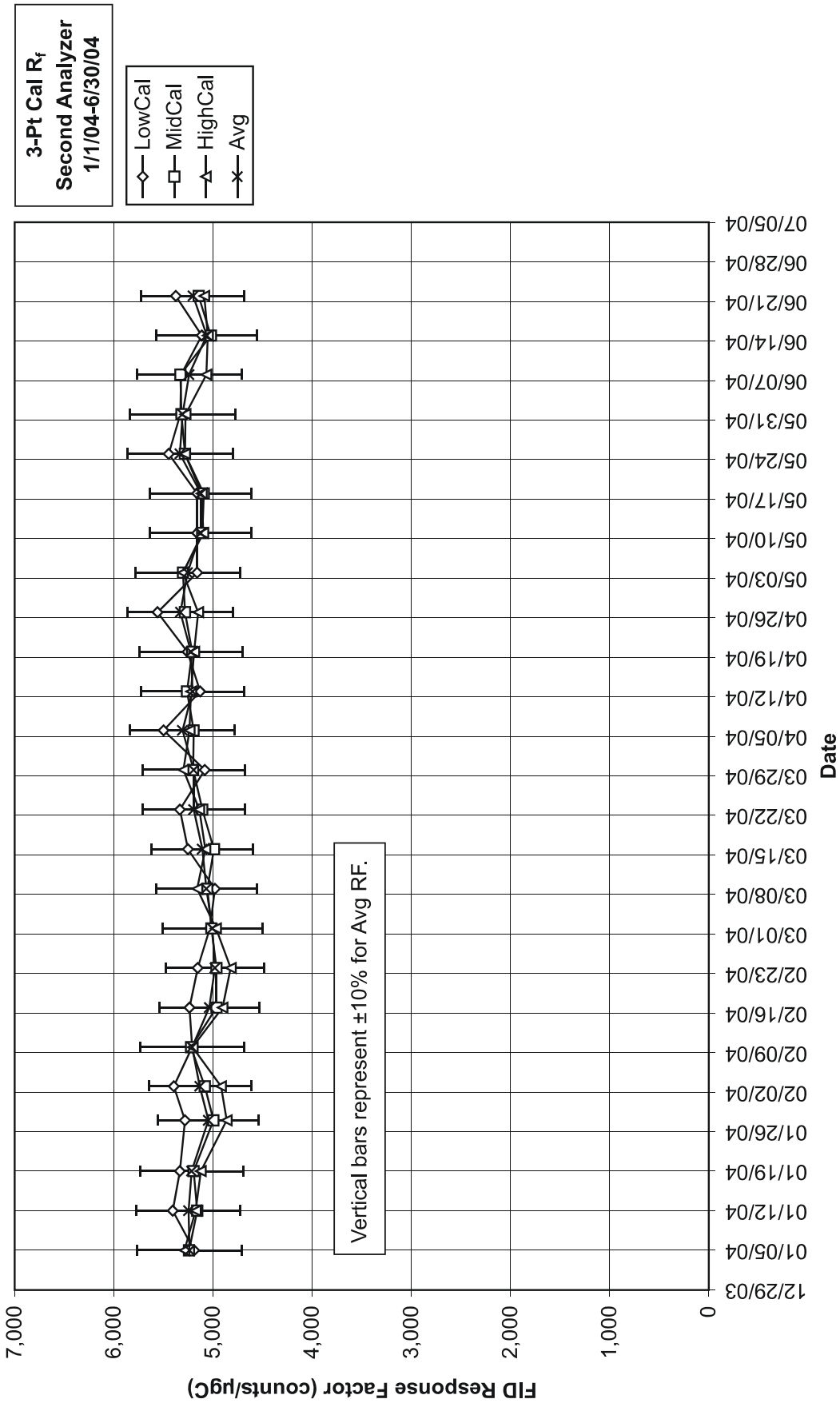


Figure 13. FID Response Factors for Three-Point Calibration Standards: Second OC/EC Analyzer

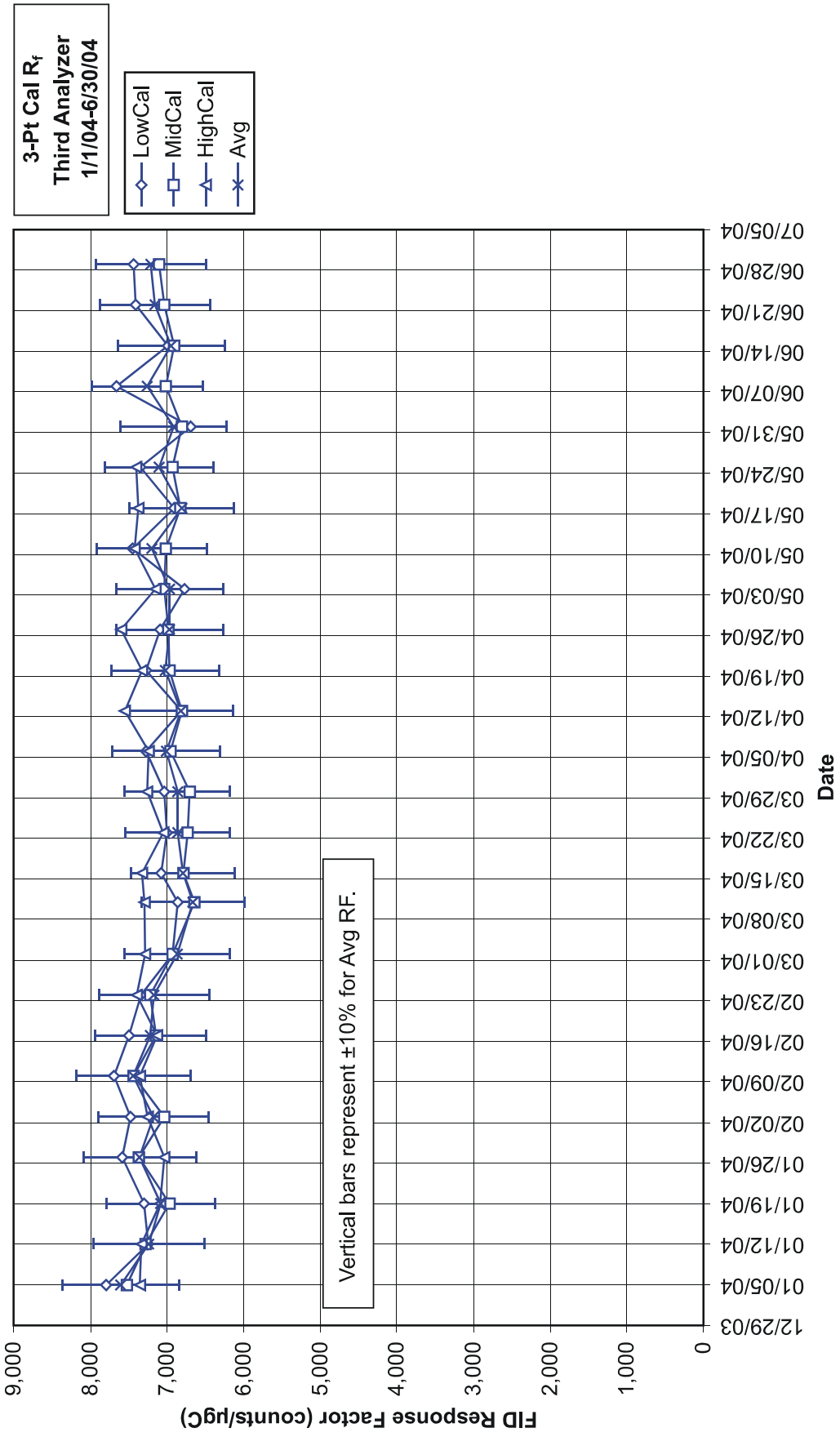


Figure 14. FID Response Factors for Three-Point Calibration Standards: Third OC/EC Analyzer

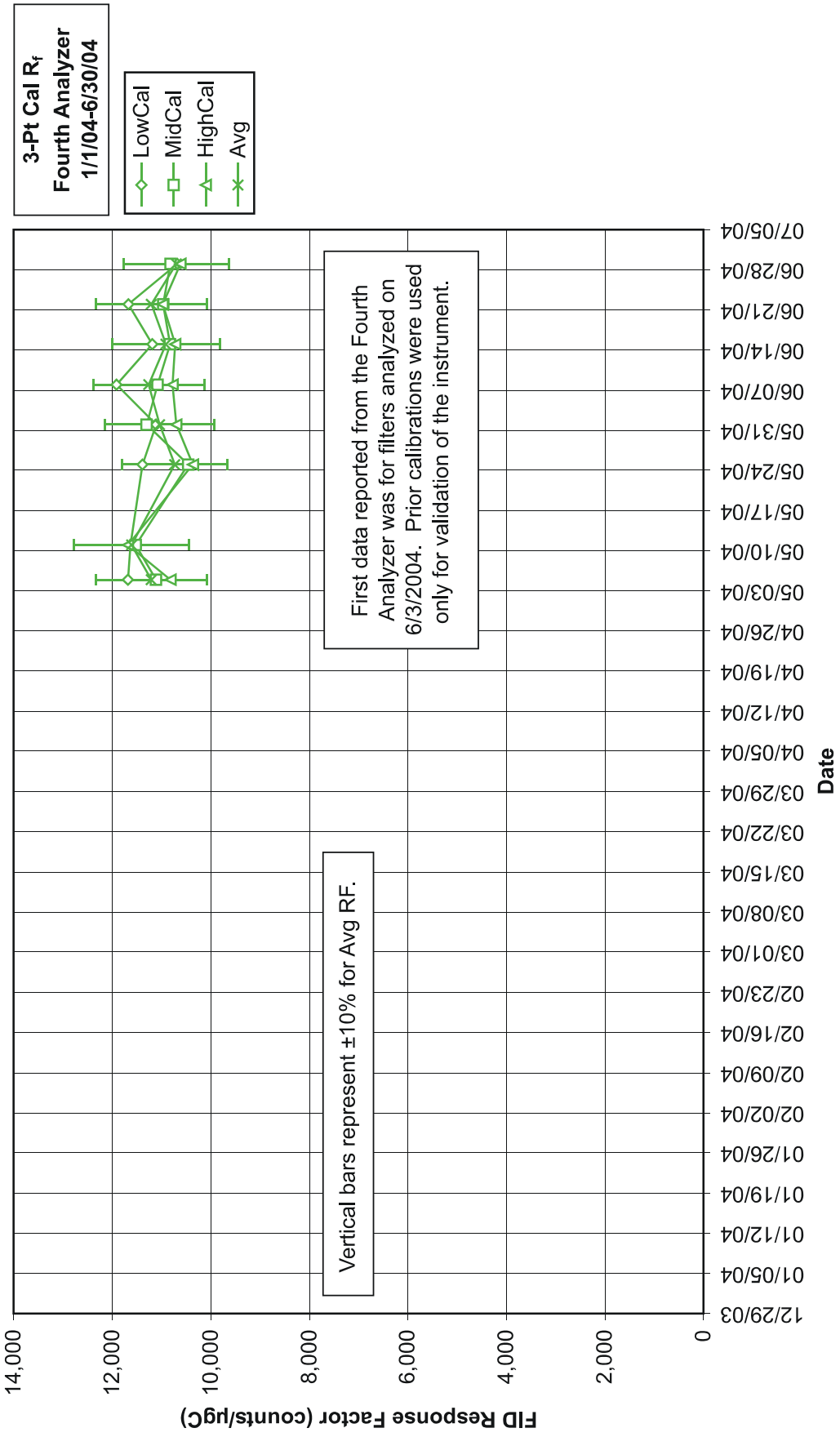


Figure 15. FID Response Factors for Three-Point Calibration Standards: Fourth OC/EC Analyzer

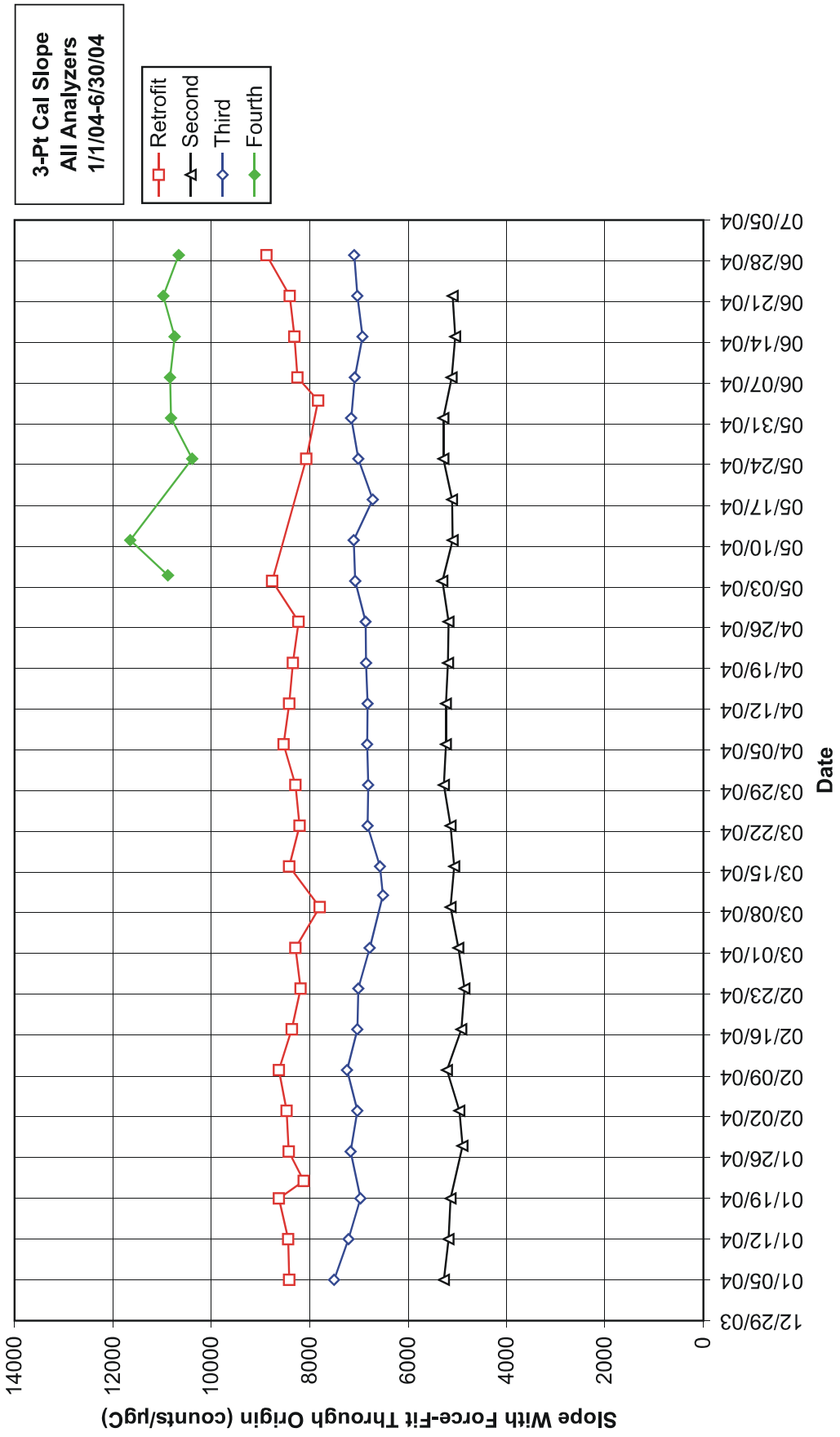


Figure 16. Slopes of Three-Point Calibration Plots With Force-Fit Through Origin (0,0): All STN OC/EC Analyzers

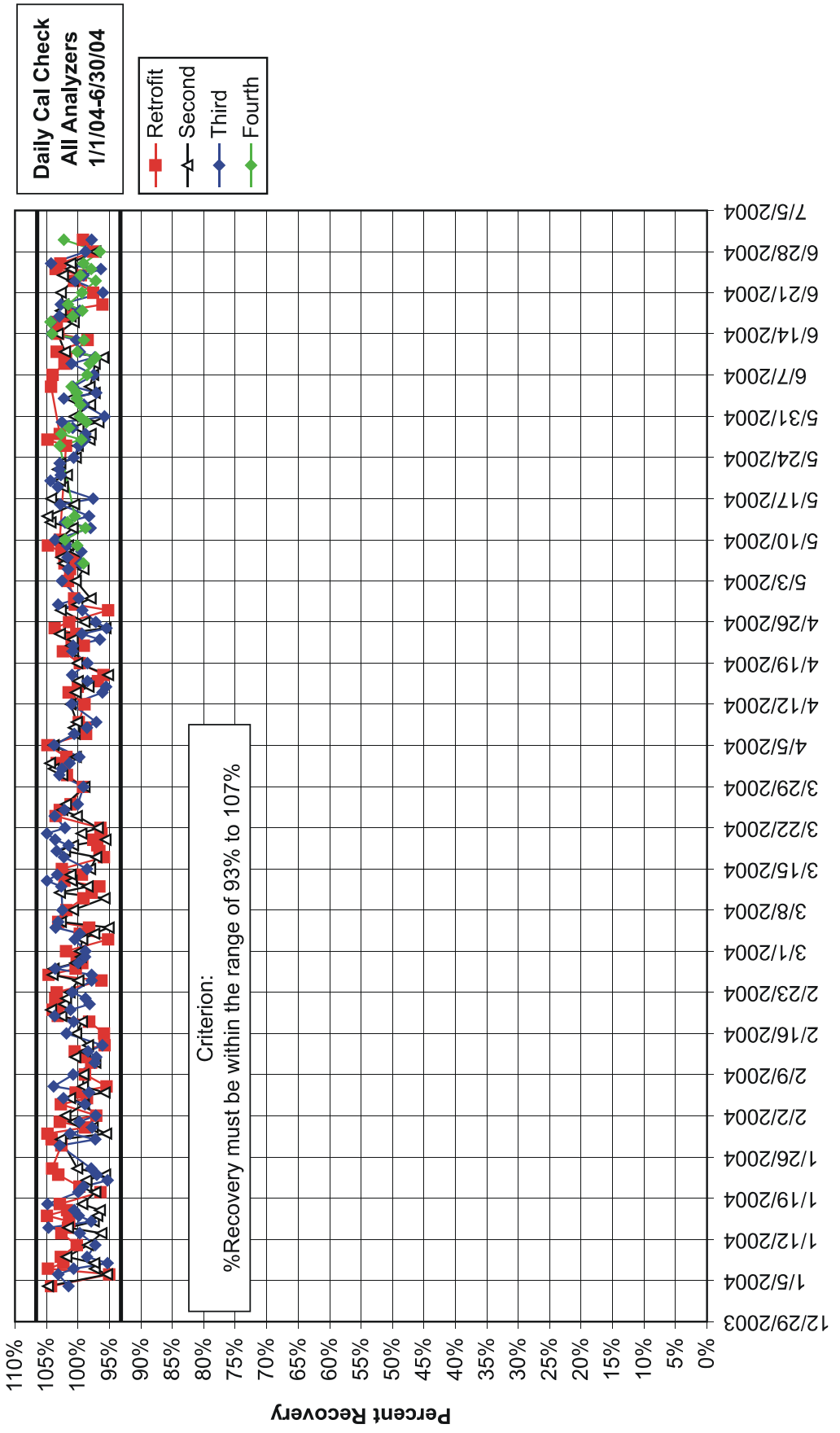


Figure 17. Daily Calibration Checks: All STN OC/EC Analyzers

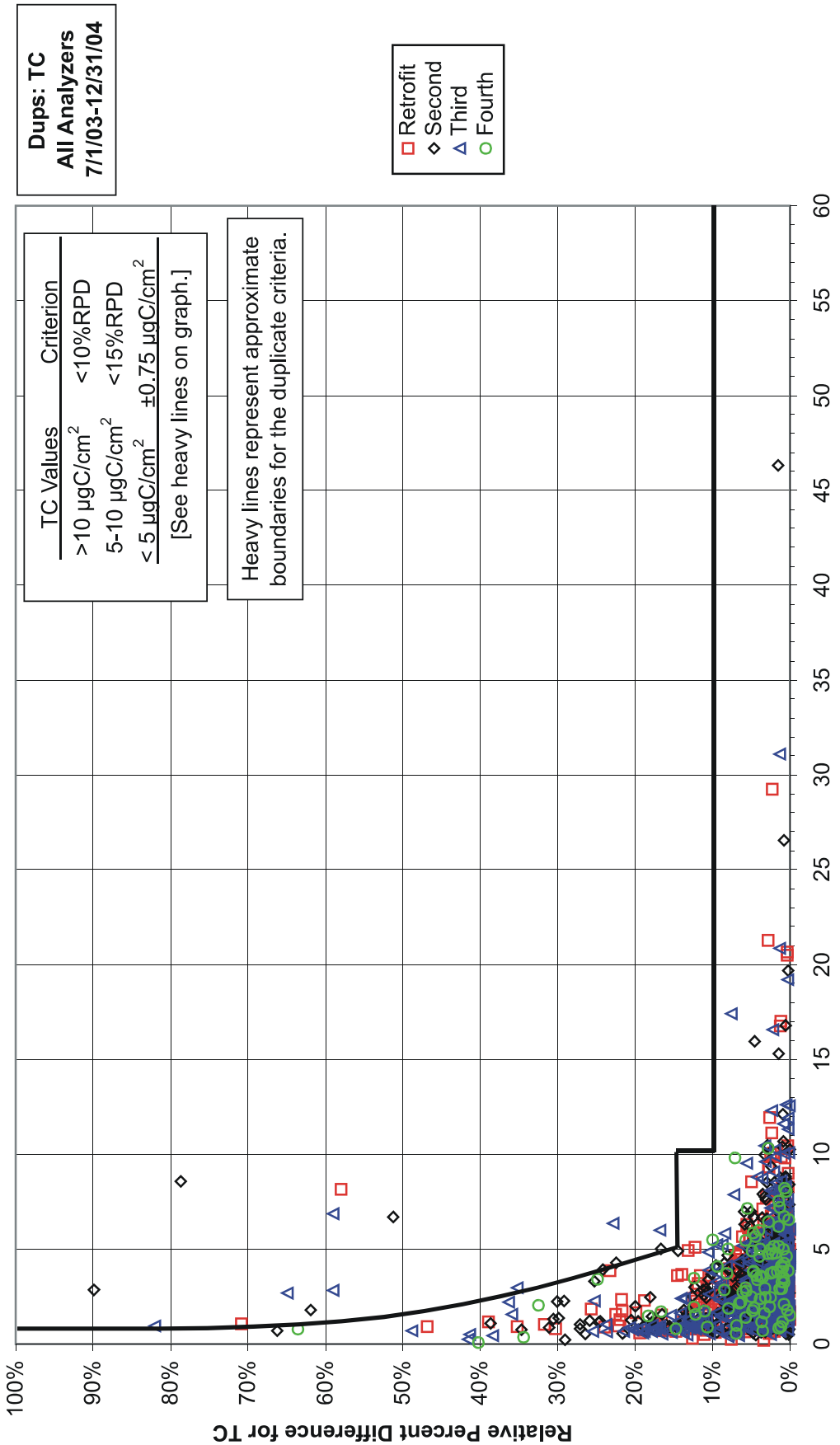


Figure 18: Relative Percent Difference of Duplicates vs. Average Value for TC: All OC/EC Analyzers

Table 18. OC/EC Duplicate Analyses

Duplicate Statistic	OC/EC Analyzer			
	Retrofit	**Second**	**Third**	**Fourth**
Number of Duplicates	366	428	419	73
Number of Duplicates that Failed Acceptance Criterion	3	9	8	2
Percentage of Duplicates that Failed Acceptance Criterion	0.82%	2.10%	1.91%	2.74%

In addition to OC, EC, and TC, the new speciation laboratory contract requires the reporting of fractions of OC (usually referred to as OC Peaks). The five new values reported include carbon evolved during each of the four temperature ramps (Pk1C, Pk2C, Pk3C, and Pk4C) under non-oxidizing conditions plus pyrolyzed carbon (PyrolC), which is used to correct OC for organic carbon that forms char (or light-absorbing carbon) under non-oxidizing conditions. Reporting of these additional fractions without the option of changing the heating profile presents additional challenges. The remainder of the figures in this section provide at least some insight into within-analyzer variability for OC, EC, and TC and for Pk1C, Pk2C, Pk3C, Pk4C, and PyrolC. The data points in each plot are color-coded, and the trend line equation (linear least-squares fit) is given along with the correlation coefficient (R^2) for each variable plotted. The data in the figures are all from samples analyzed at RTI between January 1, 2004, and June 30, 2004. In order to obtain reasonable data for within-instrument variability, results for duplicates that failed the appropriate duplicate criterion were not included in these plots; all of the data points shown are from duplicates that passed the appropriate duplicate criterion.

Figures 19, 20, 21, and 22 show plots of sample vs. duplicate measurements for OC, EC, and TC on the Retrofit, Second, Third, and Fourth analyzers, respectively. Correlation coefficients for all three fractions from all three analyzers were 0.96 or better.

Figures 23, 24, 25, and 26 show plots of sample vs. duplicate measurements for Pk1C, Pk2C, Pk3C, Pk4C, and PyrolC on the Retrofit, Second, Third, and Fourth analyzers, respectively. PyrolC on the Fourth analyzer plots (Figure 26) had a correlation coefficient of 0.17, primarily due to the very small values (maximum value 0.28, only three values larger than 0.1) measured for PyrolC. Correlation coefficients for all remaining fractions from all four analyzers were 0.95 or better.

Figures 27, 28, 29, 30, and 31 show plots of sample vs. duplicate measurements on the Retrofit, Second, and Third analyzers for Pk1C, Pk2C, Pk3C, Pk4C, and PyrolC, respectively. Correlation coefficients for the Pk1C plots were 0.98 or better; correlation coefficients for the Pk2C plots were 0.95 or better; correlation coefficients for the Pk3C plots were 0.97 or better; correlation coefficients for the Pk4C plots were 0.95 or better; and correlation coefficients for the PyrolC plots were 0.99 or better for all analyzers except the Fourth analyzer, which had a PyrolC correlation coefficient of only 0.17 for the reasons cited above.

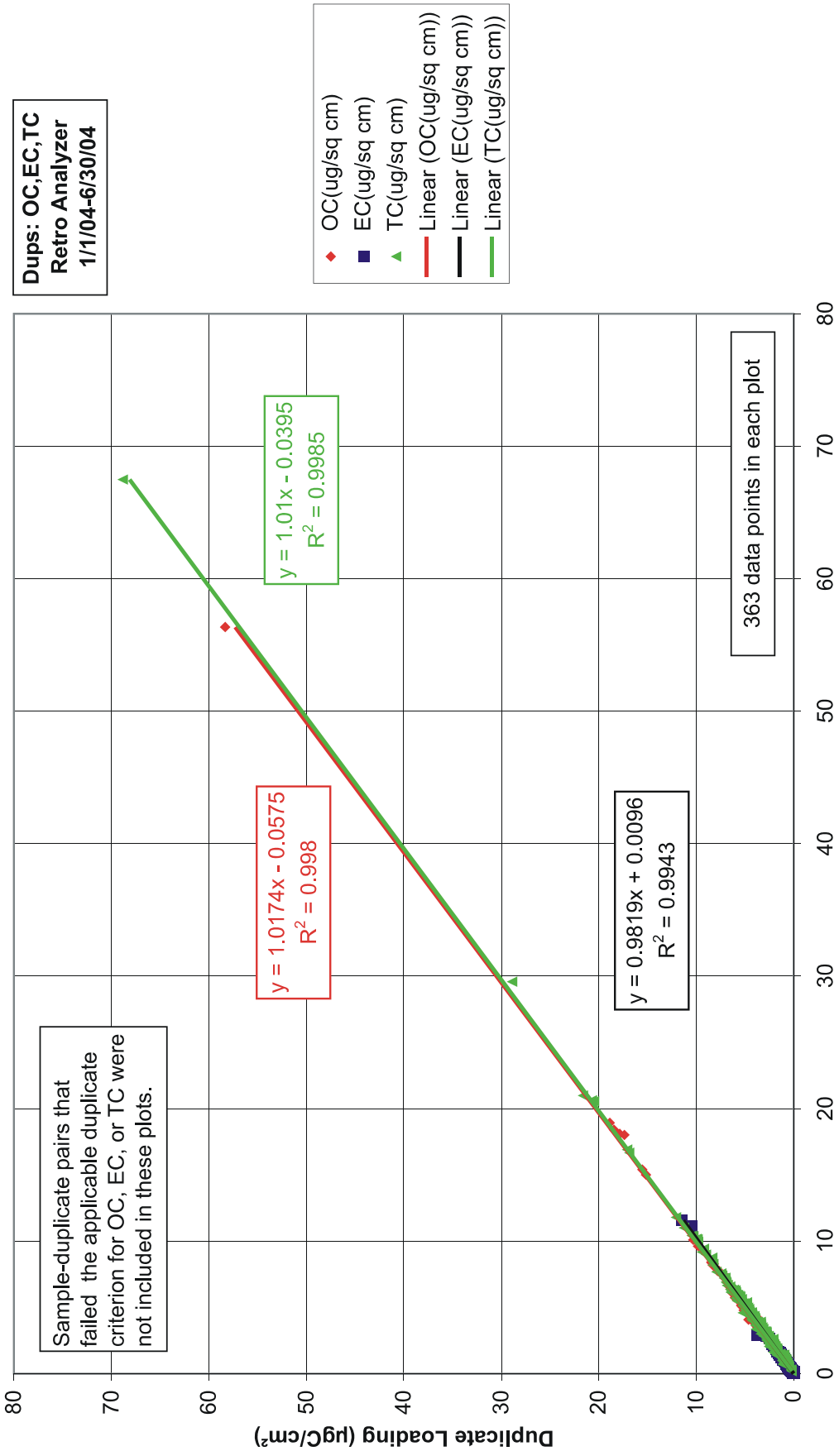


Figure 19. Duplicate vs. Sample: OC, EC, and TC: Retrofit Analyzer

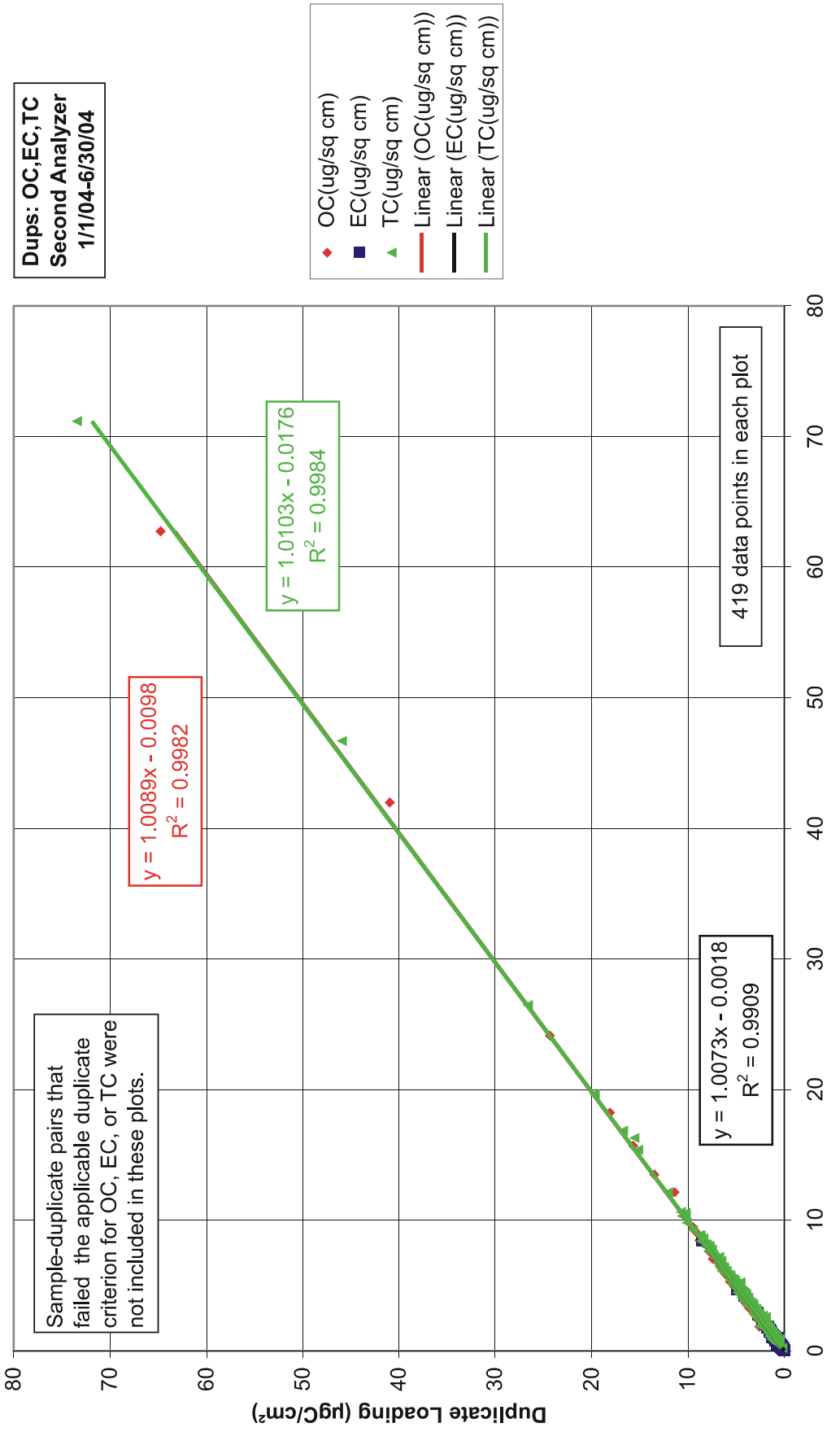


Figure 20. Duplicate vs. Sample: OC, EC, and TC: Second Analyzer

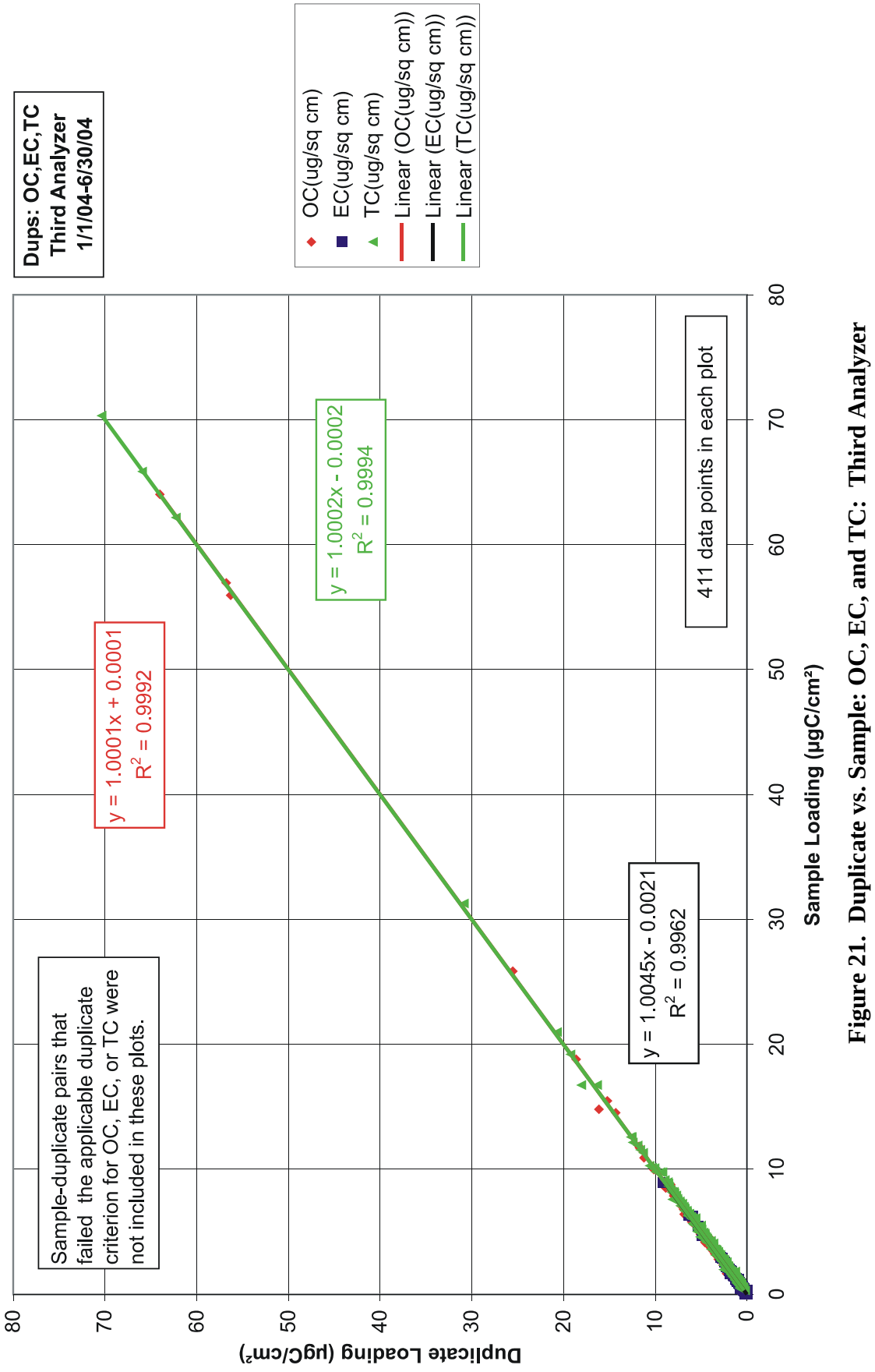


Figure 21. Duplicate vs. Sample: OC, EC, and TC: Third Analyzer

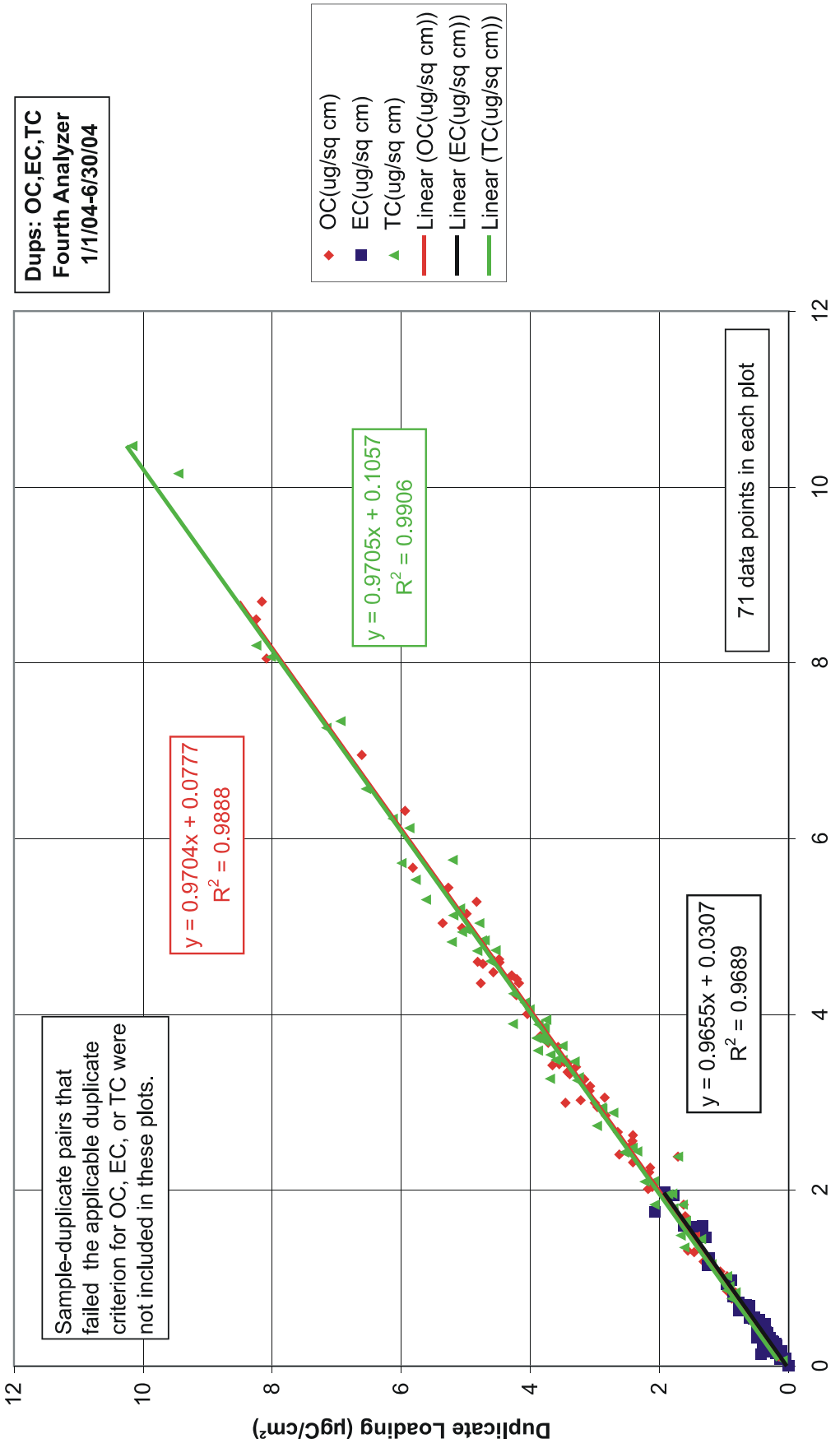


Figure 22. Duplicate vs. Sample: OC, EC, and TC: Fourth Analyzer

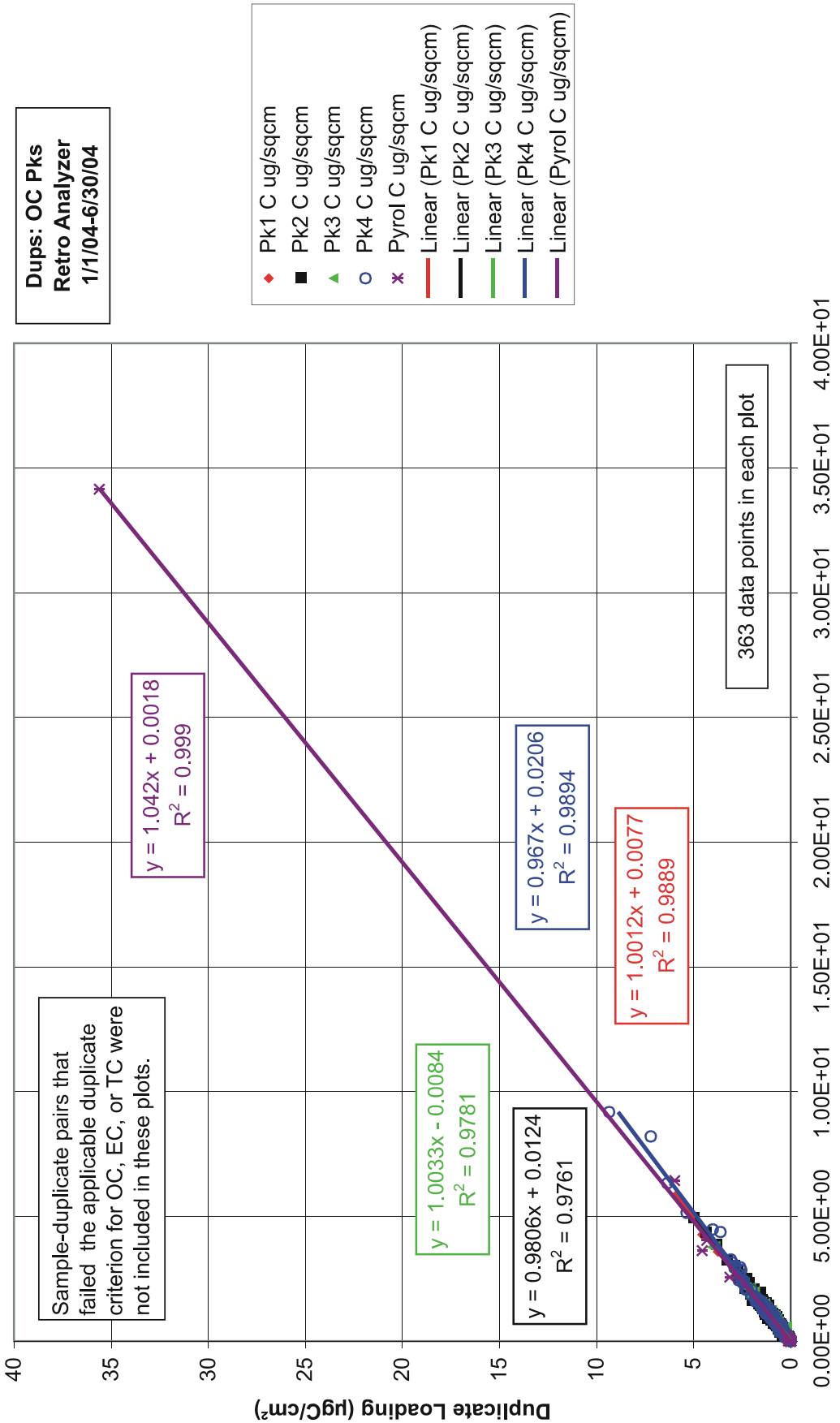


Figure 23. Duplicate vs. Sample: OC Peaks: Retrofit Analyzer

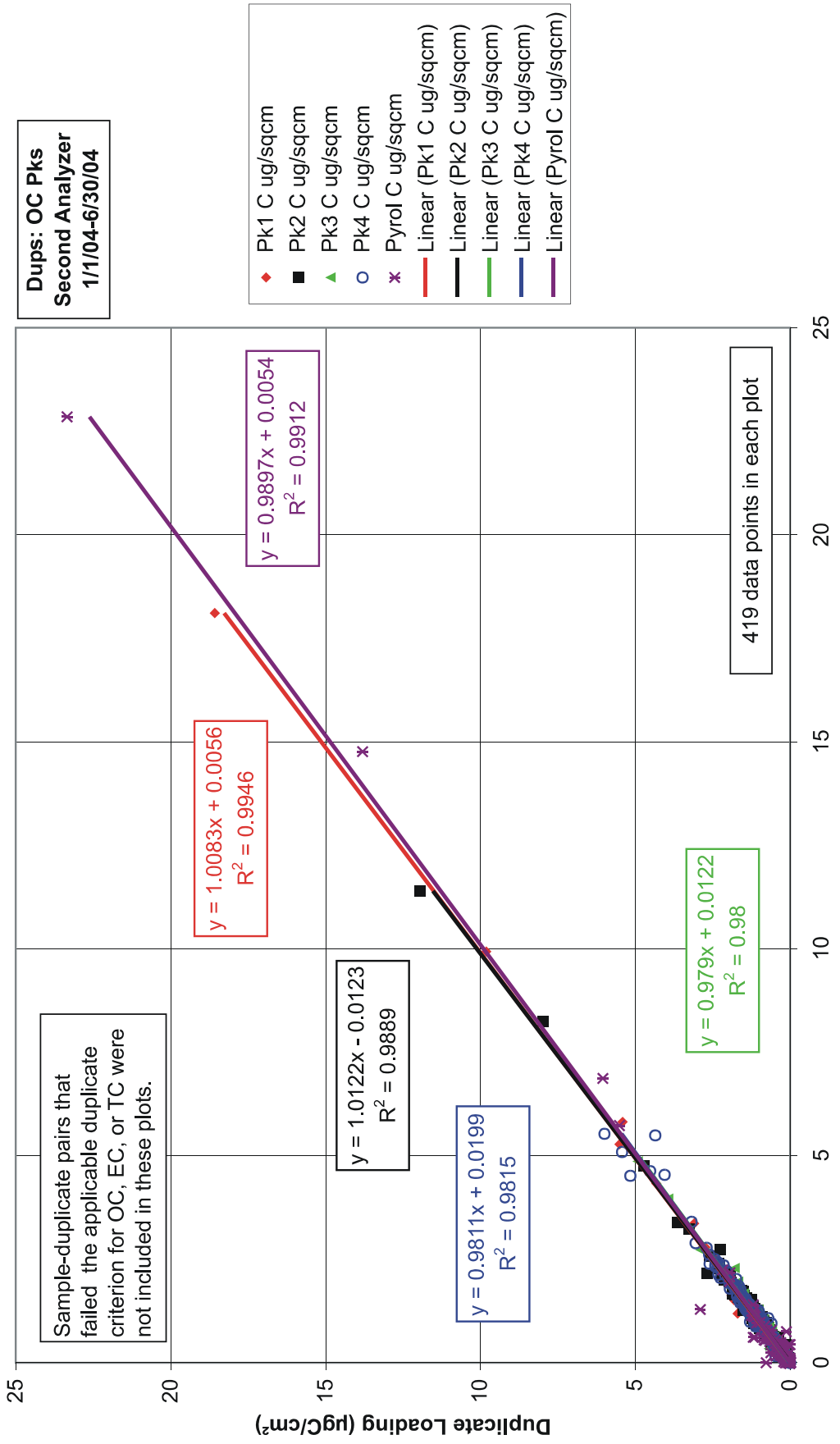


Figure 24. Duplicate vs. Sample: OC Peaks: Second Analyzer

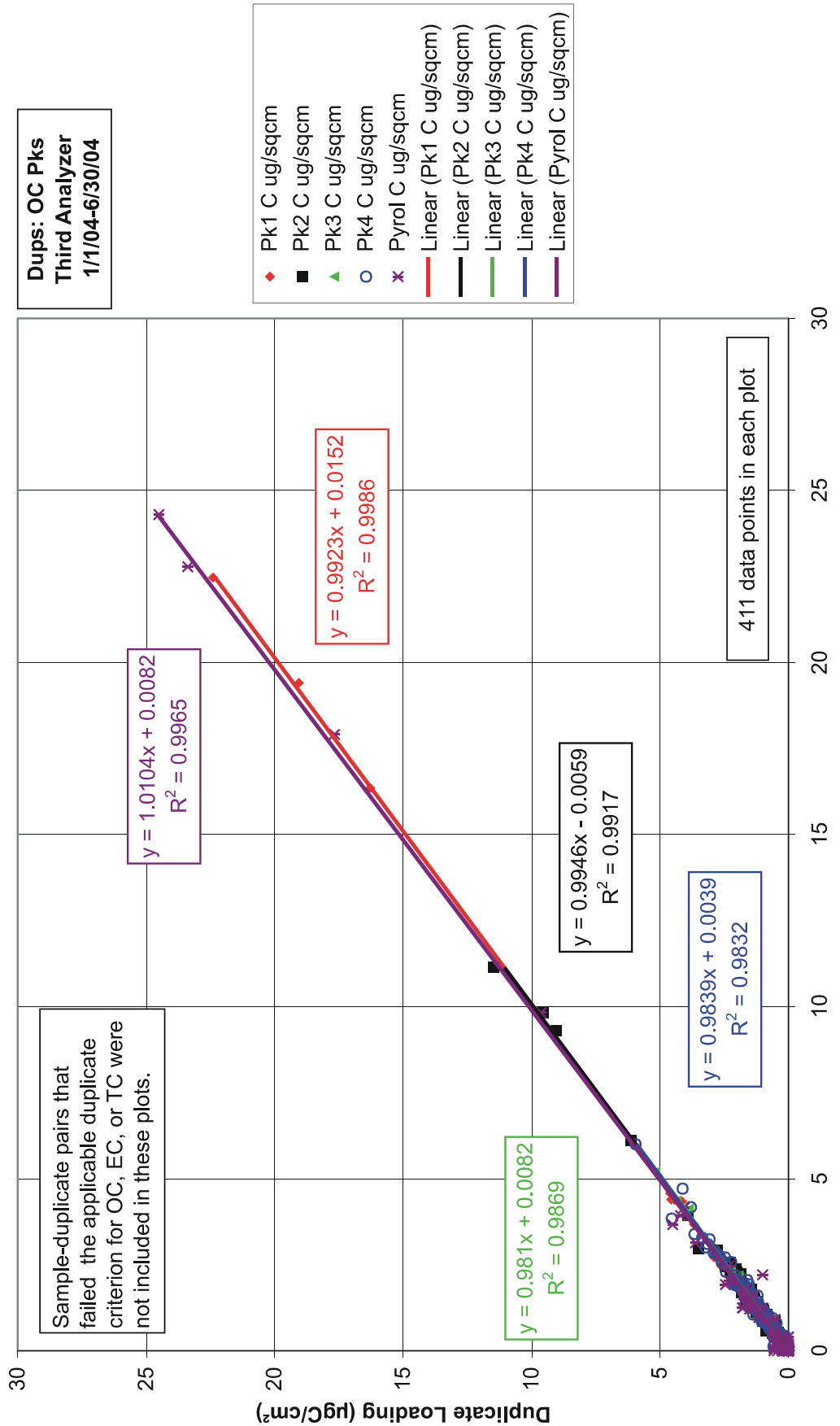


Figure 25. Duplicate vs. Sample: OC Peaks: Third Analyzer

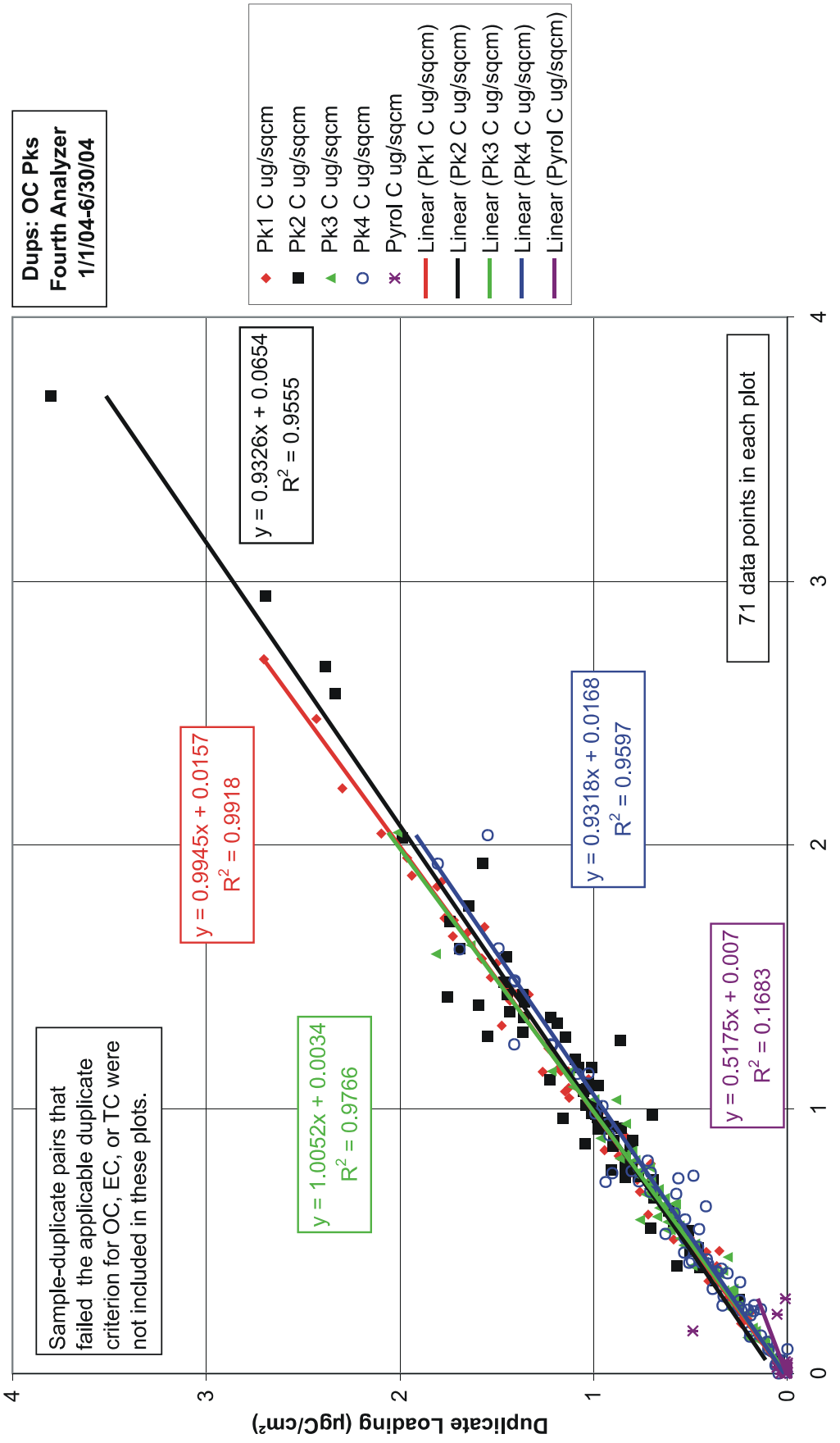


Figure 26. Duplicate vs. Sample: OC Peaks: Fourth Analyzer

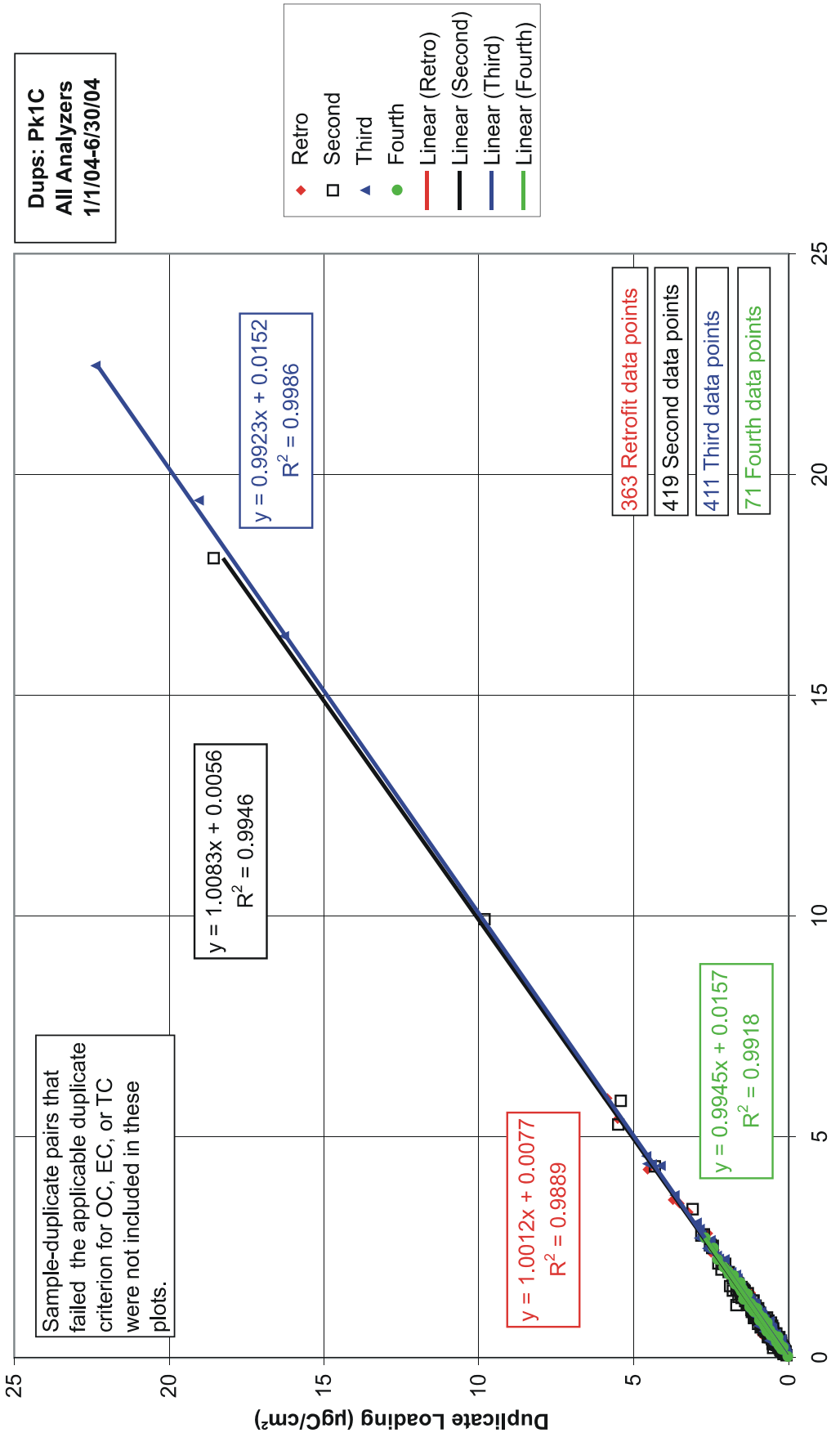


Figure 27. Duplicate vs. Sample: Pk1C Plots, All STN OC/EC Analyzers

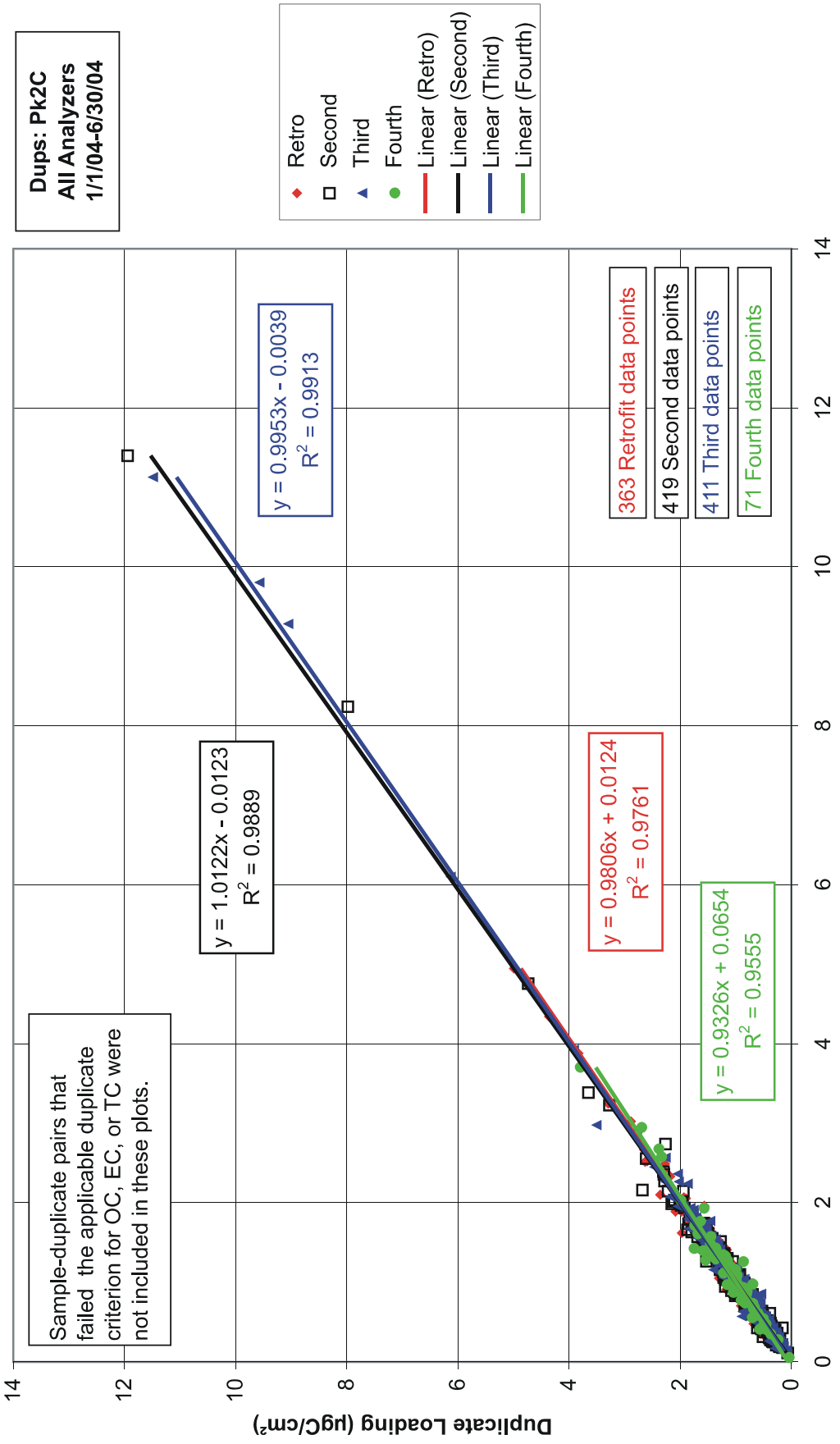


Figure 28. Duplicate vs. Sample: Pk2C Plots, All STN OC/EC Analyzers

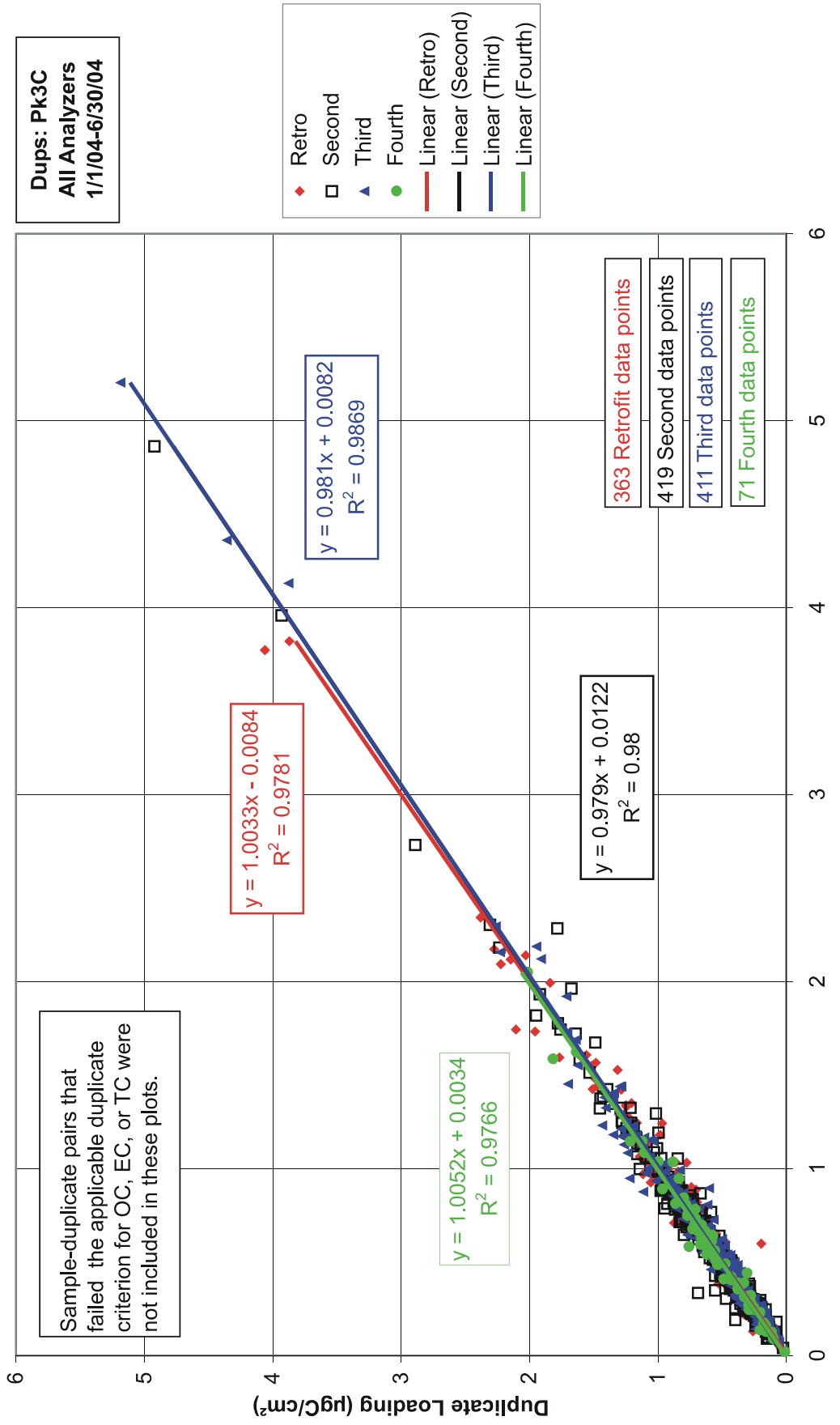


Figure 29. Duplicate vs. Sample: Pk3C Plots, All STN OC/EC Analyzers

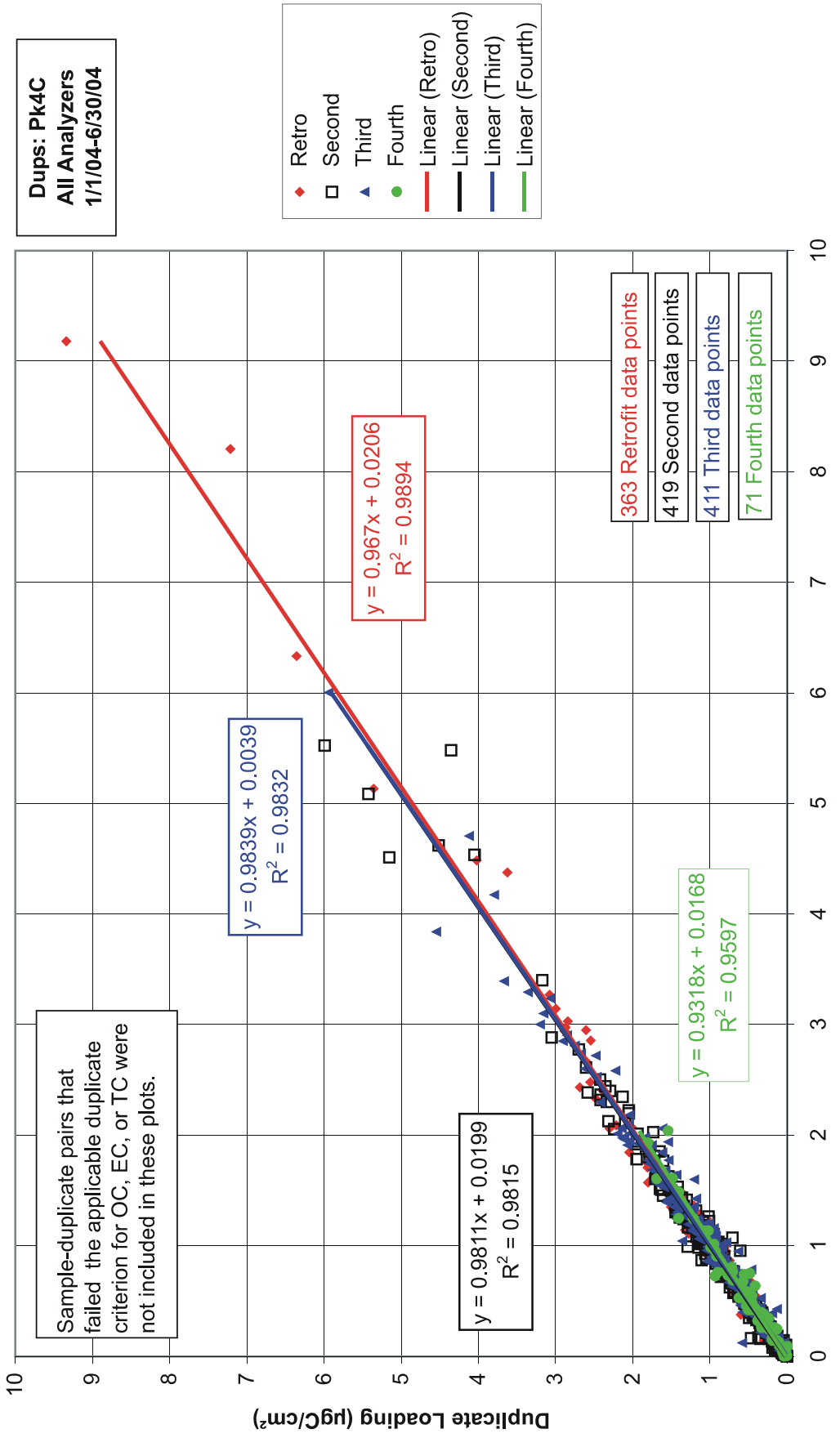


Figure 30. Duplicate vs. Sample: Pk4C Plots, All STN OC/EC Analyzers

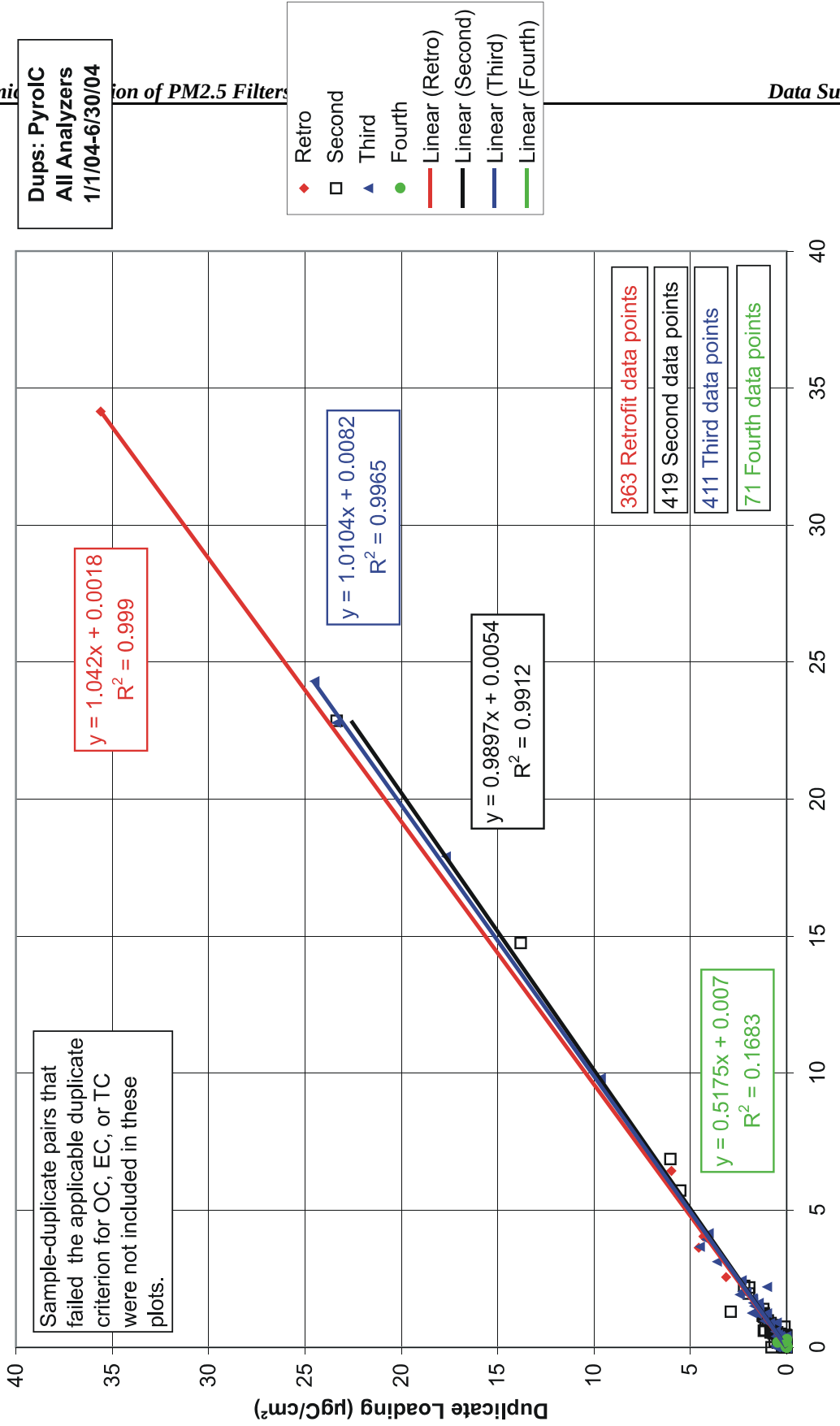


Figure 31. Duplicate vs. Sample: PyrolC Plots, All STN OC/EC Analyzers

2.3.3 Data Validity Discussion

Invalid Data Due to OC/EC Laboratory Errors. The ability to take a second or third punch from a quartz filter for analysis allows the OC/EC analyst to avoid invalidating data due to OC/EC Laboratory error except in extreme cases when an entire filter (or half-filter aliquot) is involved in an error. So far, this has occurred only when a filter or half-filter aliquot arrived at the OC/EC Laboratory in pieces so small that a full punch could not be taken as a single piece. Quartz filters are almost always torn around the edges during removal from the cassette filter holder in the SHAL but are only flagged as torn (1) by SHAL personnel if they arrive at RTI damaged or (2) by the OC/EC analyst if there is no portion of the filter large enough for the removal of a full punch for analysis as a single piece. The second occurrence is extremely rare.

On even rarer occasions, an OC/EC Laboratory analyst has dropped a filter. Any filter dropped prior to removing a punch for analysis is not analyzed, and a Laboratory Error flag is assigned to that filter ID.

Invalid Data Due to Other Causes. The OC/EC Laboratory simply analyzes filters that are delivered from the SHAL without any knowledge of the sampling or other field and transport data associated with those filters. OC/EC Laboratory personnel do not know if data for a filter will be invalidated for causes other than those associated with the OC/EC analysis.

2.3.4 Summary of Audit Findings and Recommendations

There were no findings during the annual audit of the RTI OC/EC Laboratory.

2.3.5 Corrective Actions Taken

No corrective actions were required during the reporting period.

2.4 X-ray Fluorescence Laboratories

During the reporting period, four XRF instruments were in use. Included were two at RTI, and two at Chester LabNet. Each has been tested and accepted by the EPA for use in the PM2.5 Speciation Program.

Section 2.4.1 describes the checks common to all laboratories (and instruments within each laboratory). Sections 2.4.2, 2.4.3, and 2.4.4, respectively, describe the specific QC results for Chester and RTI.

2.4.1 Description of QC Checks Applied

QC activities for the analysis of elements by EDXRF, their frequency of application and control limits, and corrective actions are shown in **Table 19**.

Table 19. QC Procedures Performed in Support of EDXRF Elemental Analysis

QC Activities	Frequency	Control Limits	Corrective Action
Calibration	as needed	--	--
Calibration verification	weekly	within NIST uncertainties	recalibrate
Instrument precision	once per batch of $\leq$ 15	90–110% recovery	batch reanalysis
Excitation condition check	every sample	within analysis uncertainty	sample reanalysis
Sample replicate precision	5%	± 50 RPD	batch reanalysis

The two-sigma (95 percent confidence level) detection limits in units of µg/cm^2 were calculated from the analysis of a blank Teflon filter as follows:

$$\text{detection limit for element i} = 2\delta_i = \frac{2(2B_i)^{1/2}}{s_i t}$$

where,

B_i is the background counts for element i,
s_i is the sensitivity factor for element i,
and t is the counting lifetime.

Theoretically, detection limits may be decreased by simply increasing the counting lifetime. In practice, a point of diminishing returns is reached for real-world samples in which the background increases along with the analyte signal. At this point, further improvement in detection limits by increasing the counting time is not possible.

Note that all detection limits are now being reported as 3-sigma limits to AQS. The detection limit in the equation above is multiplied by a factor of 1.5 for reporting to AQS.

2.4.2 Chester LabNet

Chester LabNet was the original XRF subcontractor laboratory used for the STN program. During this period, Chester operated two Kevex XRF instruments which have been designated 770 and 771.

2.4.2.1 Statistical Summary of QC Results –

Precision

Precision is monitored by the reproducibility of the XRF signal in counts per second using standard samples. The counts for select elements are measured for each of the targets used. The comparison of the counts during calibration and during the run gives the measure of reproducibility or precision. The data used to monitor precision are presented in **Figures 32 through 44**. **Tables 20a and 20b** provide summaries of the precision data. The last three columns, R and Slope/Year: Current and Previous indicate the uncorrected systematic drift that took place during the reporting period. Comparison of the annualized slopes of the current vs. period in the previous semiannual STN QC report shows whether or not there was a continuing trend across reporting periods.

Table 20a. Summary of Chester QC Precision Recovery Data, Kevex 770, 7/1/03 through 12/31/03.

Percent Recoveries

Element	Avg.	Std Dev	% RSD	Max	Min	R	Slope/Year	
							Current	Previous
Si(0)	99.1	4.57	4.61	106.8	88.0	0.62484	0.05656	-4.05
Si(1)	98.4	3.06	3.11	105.6	90.1	-0.18423	-0.01119	-6.94
Ti(2)	99.8	2.73	2.74	108.5	91.5	-0.00677	-0.00037	-9.28
Fe(3)	98.4	2.66	2.71	107.9	90.3	0.26914	0.01424	-2.91
Se(4)	100.1	2.86	2.86	106.6	90.3	0.31333	0.01780	-3.61
Pb(4)	101.3	3.05	3.01	108.5	92.9	0.49070	0.02976	-3.35
Cd(5)	98.5	3.61	3.66	106.3	91.0	0.69772	0.05003	-7.96

N=185 for all elements.

Table 20b. Summary of Chester QC Precision Recovery Data, Kevex 771, 7/1/03 through 12/31/03.

Percent Recoveries

Element	Avg.	Std Dev	% RSD	Max	Min	R	Slope
							Current
Si(1)	95.1	2.06	2.17	101.4	88.0	-0.21261	-0.0087
Ti(2)	100.0	2.85	2.85	106.0	90.7	-0.41183	-0.0232
Fe(3)	99.7	2.07	2.08	103.6	92.9	-0.56874	-0.0233
Se(4)	99.4	2.34	2.36	105.8	93.1	-0.21360	-0.0099
Pb(4)	98.6	2.44	2.48	104.4	91.4	0.11937	0.0058
Cd(5)	99.0	2.69	2.72	104.9	89.9	-0.16785	-0.0089

N=185 for all elements.

Figure 32. Recovery Precision for Chester Kevex 770 XRF
Si(0) - Rh L/7.5kV/0.1mA

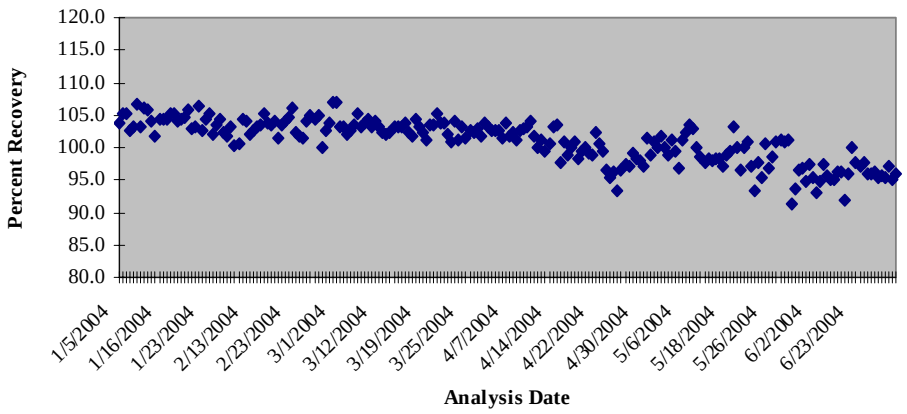


Figure 33. Recovery Precision for Chester Kevex 770 XRF
Si(1) - Ti target/25kV/1.0mA

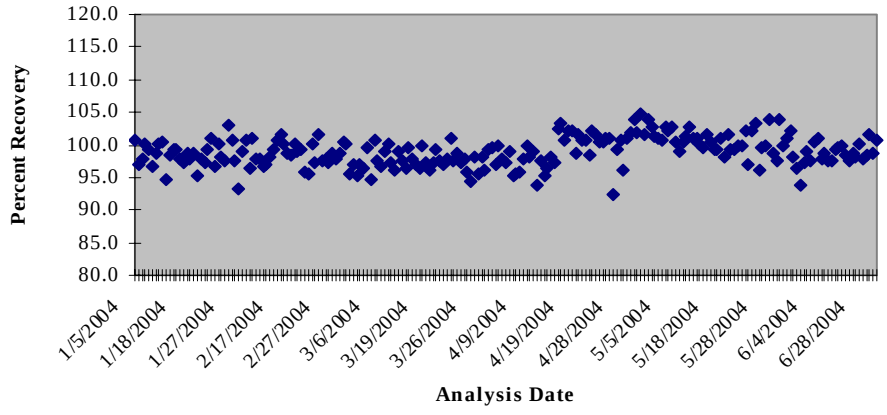


Figure 34. Recovery Precision for Chester Kevex 770 XRF
Ti(2) - Fe target/35kV/0.5mA

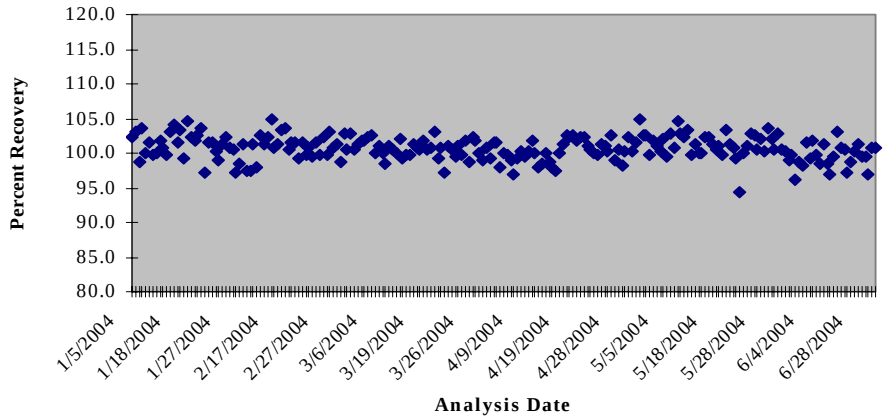


Figure 35. Recovery Precision for Chester Kevex 770 XRF
Fe(3) - Ge target/35kV/0.5mA

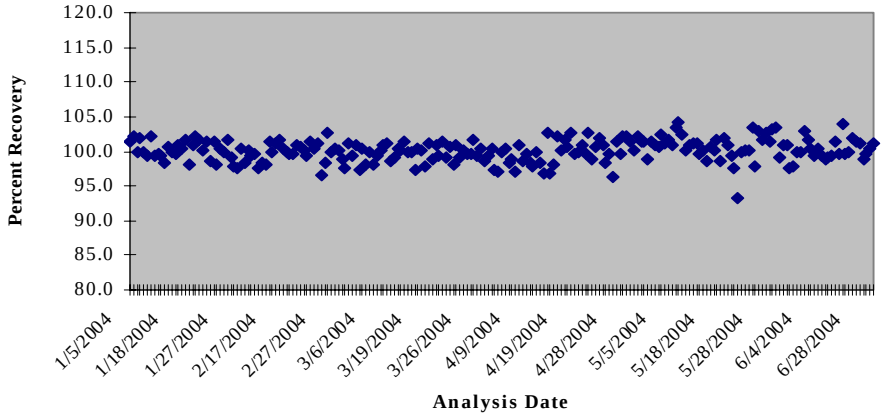


Figure 36. Recovery Precision for Chester Kevex 770 XRF
Se(4) - Rh K/35kV/0.25mA

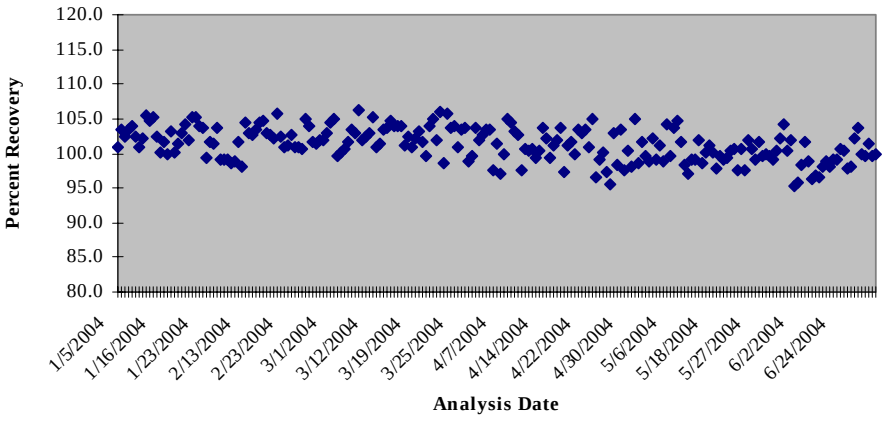


Figure 37. Recovery Precision for Chester Kevex 770 XRF
Pb(4) - Rh K/35kV/0.25mA

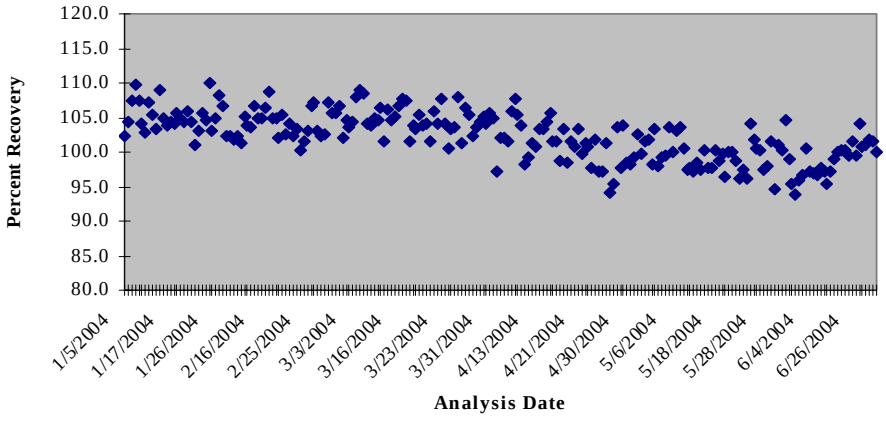


Figure 38. Recovery Precision for Chester Kevex 770 XRF
Cd(5) - Rh K/W filter/55kV/0.25mA

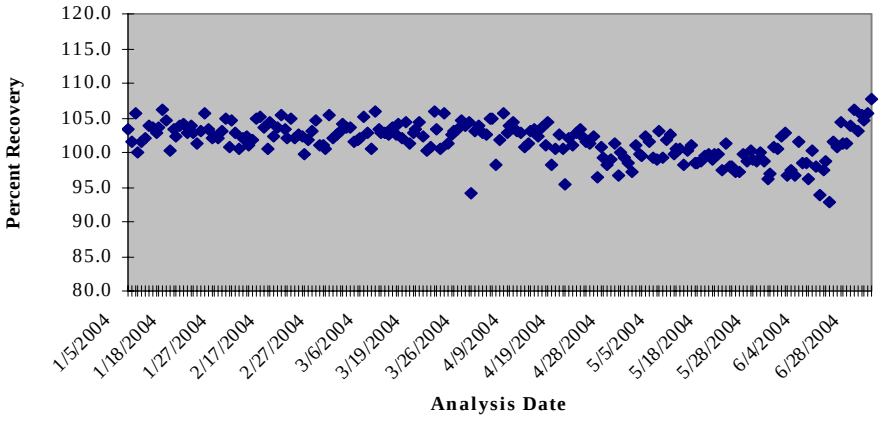


Figure 39. Recovery Precision for Chester Kevex 771 XRF
Si(1) - Rh L-alpha 6.0kV

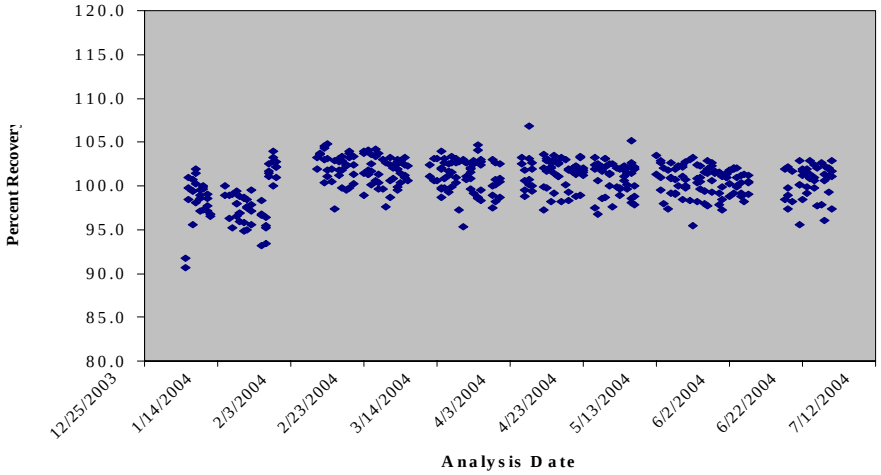


Figure 40. Recovery Precision for Chester Kevex 771 XRF
Ti(2) - Fe target 35kV

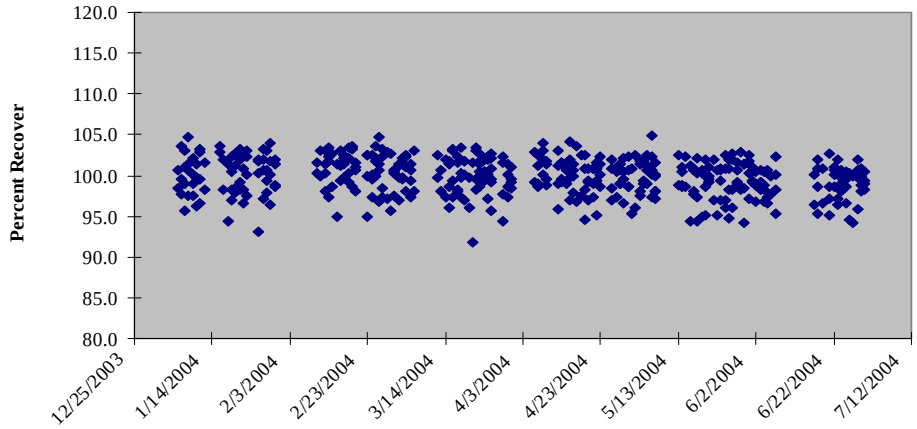


Figure 41. Recovery Precision for Chester Kevex 771 XRF
Fe(3) - Ge target 45kV

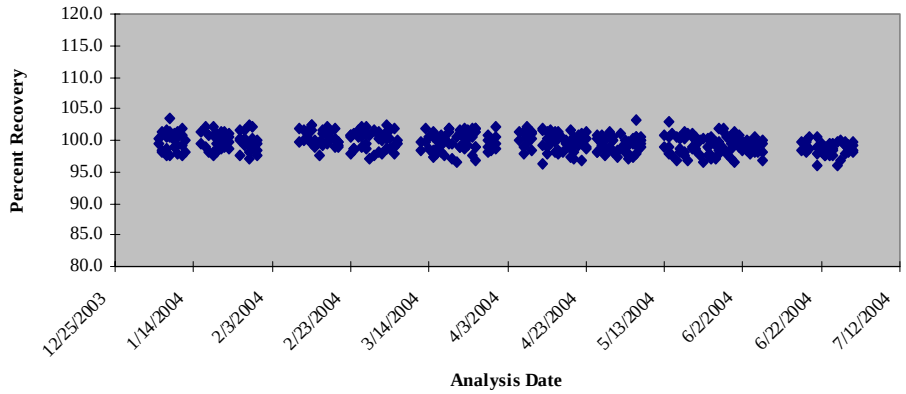


Figure 42. Recovery Precision for Chester Kevex 771 XRF
Se(4) - Rh K-alpha 35kV

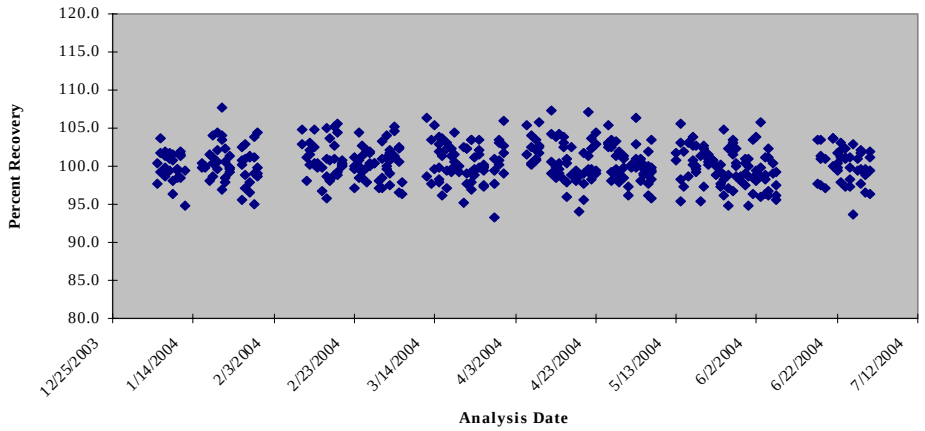
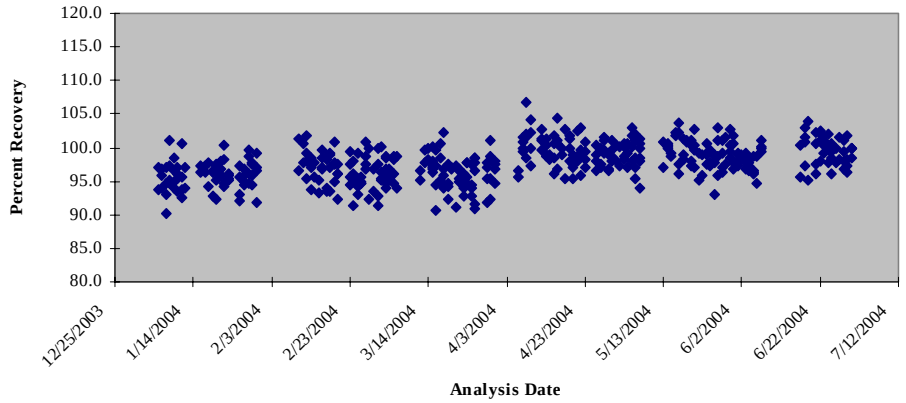
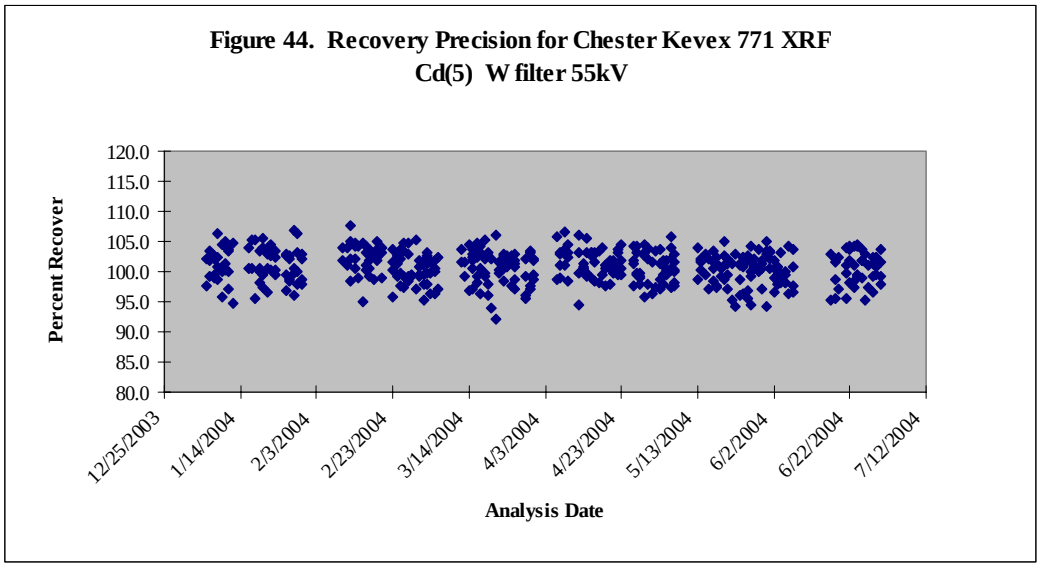


Figure 43. Recovery Precision for Chester Kevex 771 XRF
Pb(4) Rh K-alpha 35kV





Recovery

Recovery (accuracy) is determined based on periodic analysis of NIST standards. These results are tabulated in Table 21 for both the Kevex 770 and 771 instruments.

Recovery or system accuracy is determined by the analysis of a series of NIST Standard Reference Materials filters. Recovery is calculated by comparison of measured and expected values. **Figures 45 through 70** show recovery for 12 select elements spanning the range of the 48 elements normally measured. The recovery values for all elements ranged between 91 and 107 percent for the 770 and between 91 and 113 percent for the 771, as shown in **Table 21**. For the 771 instrument, the high value of 113% was for sulfur, which had several points above the 110% limit. All other elements were in control (> 90%, < 110%) at all times.

Table 21. Recovery Determined from Analysis of NIST Standard Reference Material Filters, Kevex 770 and 771, 7/1/03 through 12/31/03.

Element	Kevex 770	Kevex 771
	Range % Recovery	Range % Recovery
Al	93 - 105	94 - 101
Si*	95 - 107	94 - 101
Si**	91 - 102	91 - 97
S	93 105	95 113
K	94 - 103	98 - 105
Ca	94 - 103	100 - 107
Ti	96 - 101	92 - 98
V	95 - 103	96 - 105
Mn	95 - 103	94 - 103
Fe	94 - 103	96 - 102
Cu	95 - 103	96 - 102
Zn	92 - 101	96 - 104
Pb	98 - 106	97 - 105

*SRM 1832. **SRM 1833.

Figure 45. Recovery of Aluminum (Al) in NIST SRM 1832 with Chester Kevex 770

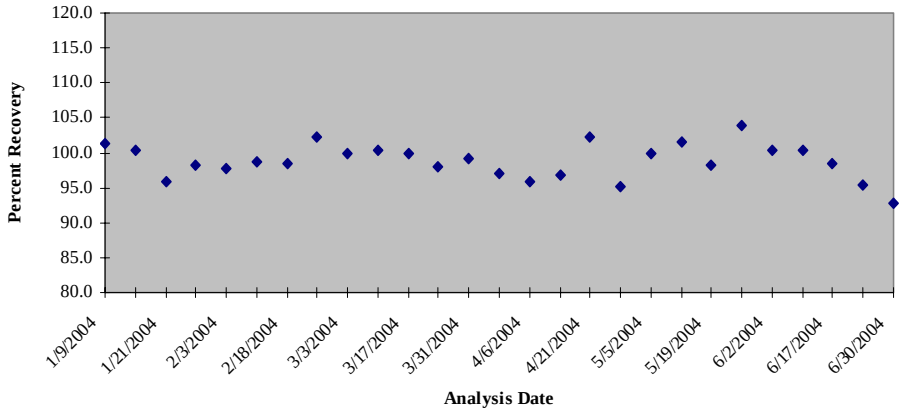


Figure 46. Recovery of Silicon (Si) in NIST SRM 1832 with Chester Kevex 770

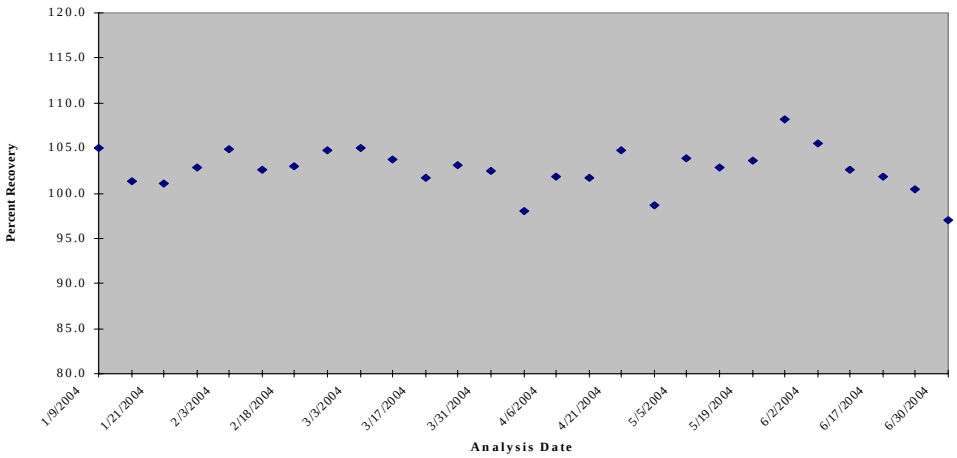


Figure 47. Recovery of Silicon (Si) in NIST SRM 1833 with Chester Kevex 770

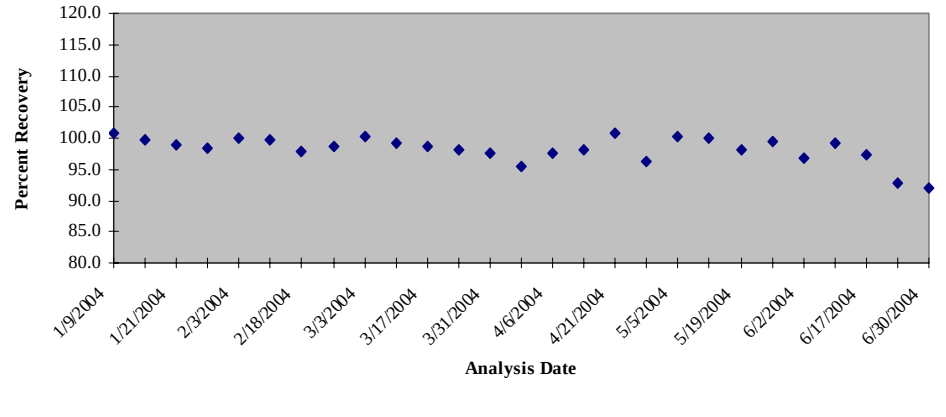


Figure 48. Recovery of Sulfur (S) in NIST SRM 2708 with Chester Kevex 770

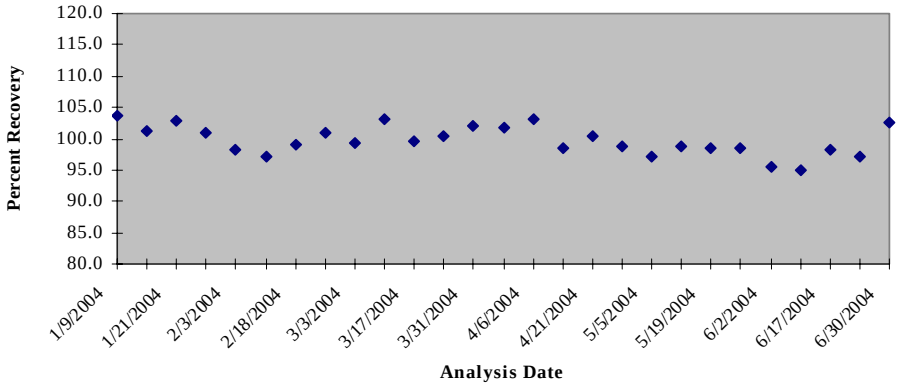


Figure 49. Recovery of Potassium (K) in NIST SRM 1833 with Chester Kevex 770

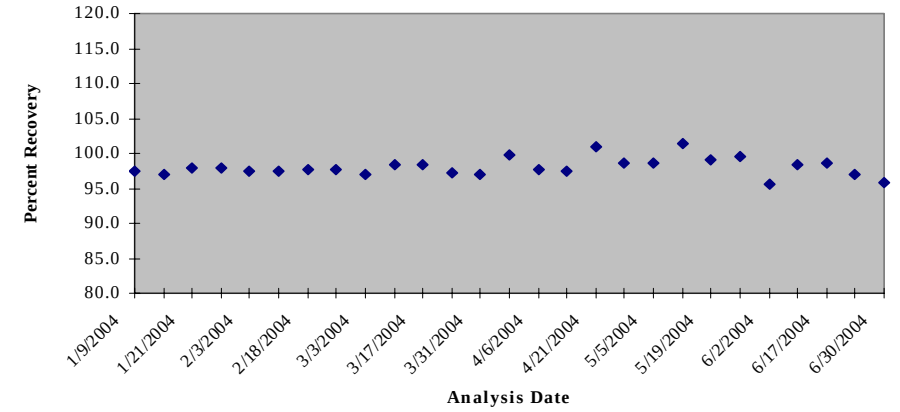


Figure 50. Recovery of Calcium (Ca) in NIST SRM 1832 with Chester Kevex 770

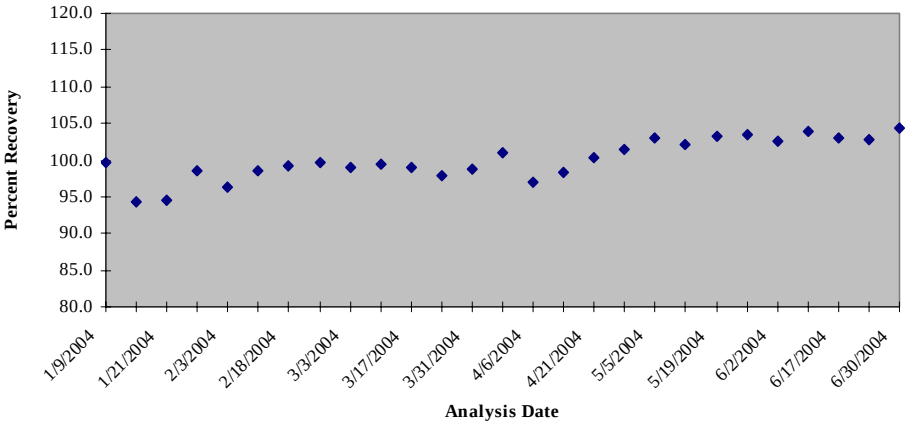


Figure 51. Recovery of Titanium (Ti) in NIST SRM 1833 with Chester Kevex 770

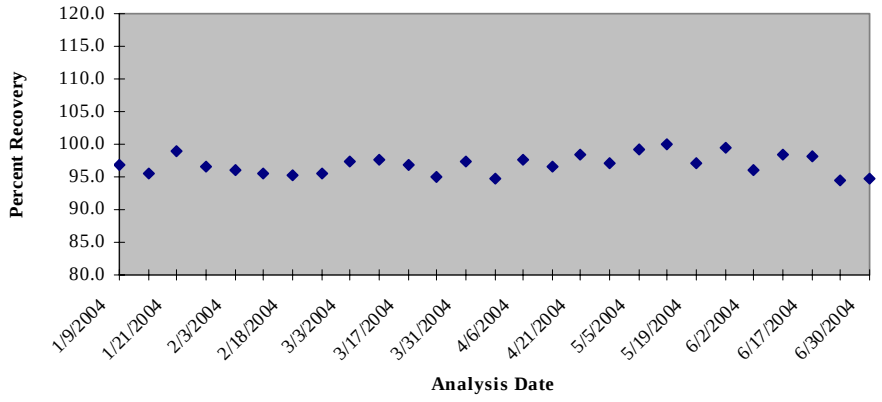


Figure 52. Recovery of Vanadium (V) in NIST SRM 1832 with Chester Kevex 770

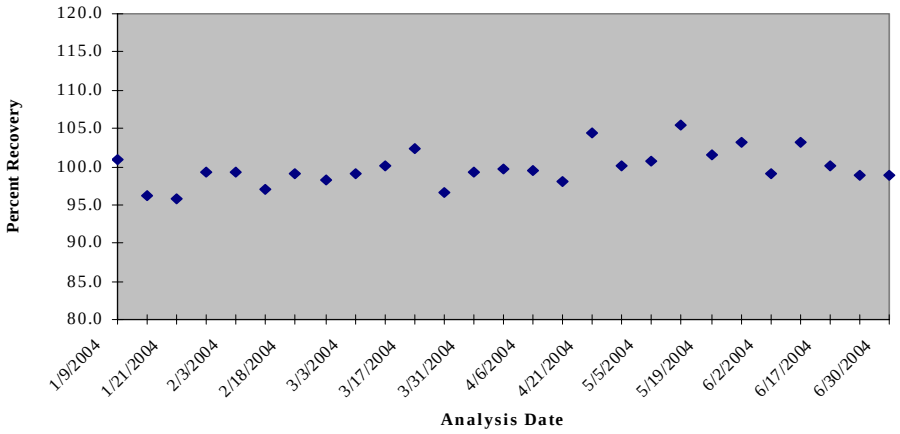


Figure 53. Recovery of Manganese (MN) in NIST SRM 1832 with Chester Kevex 770

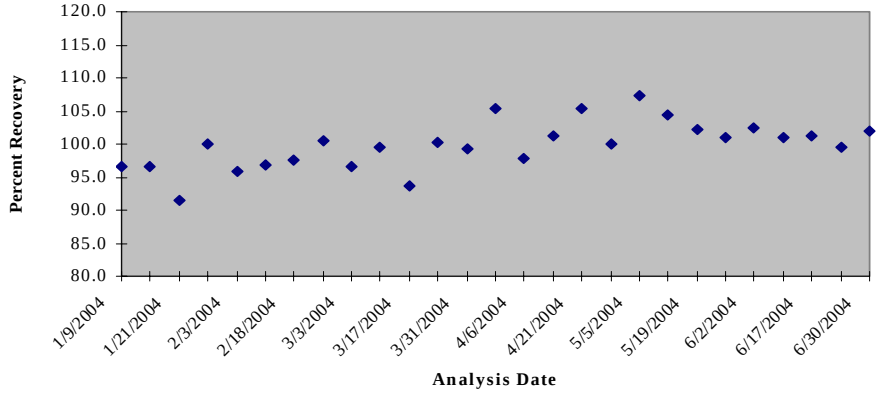


Figure 54. Recovery of Iron (Fe) in NIST SRM 1833 with Chester Kevex 770

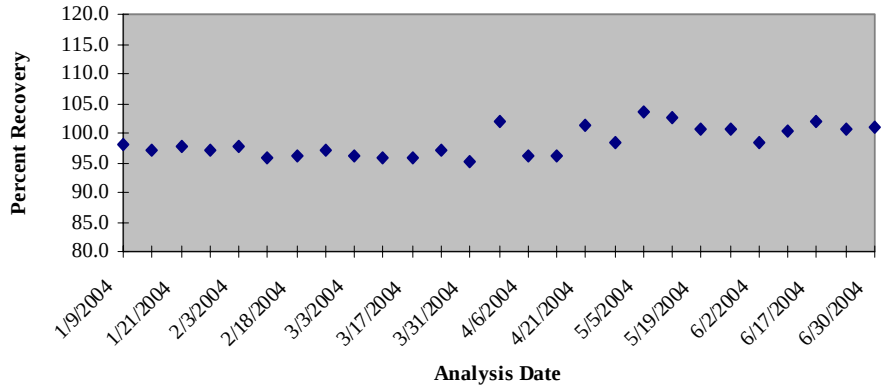


Figure 55. Recovery of Copper (Cu) in NIST SRM 1832 with Chester Kevex 770

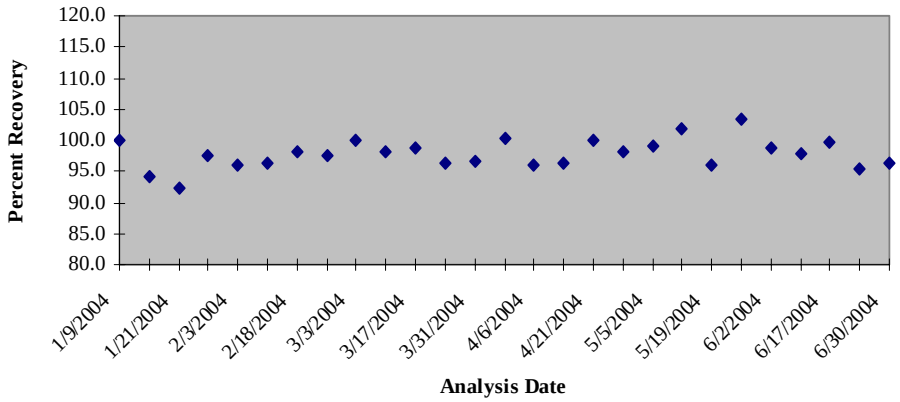


Figure 56. Recovery of Zinc (Zn) in NIST SRM 1833 with Chester Kevex 770

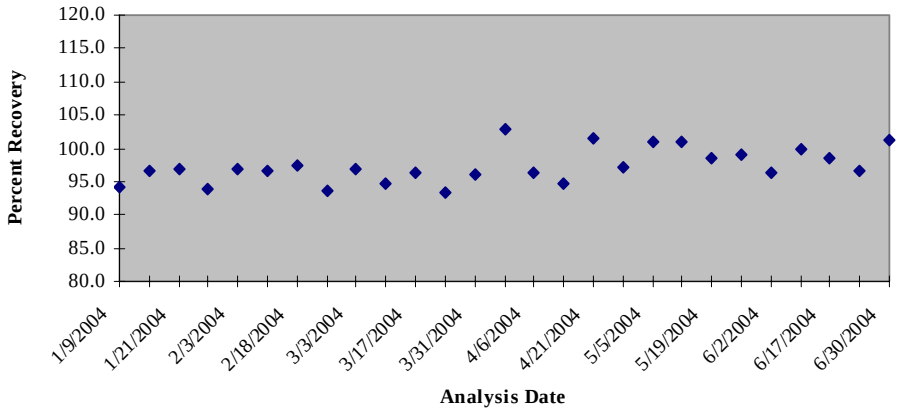


Figure 57. Recovery of Lead (Pb) in NIST SRM 1833 with Chester Kevex 770

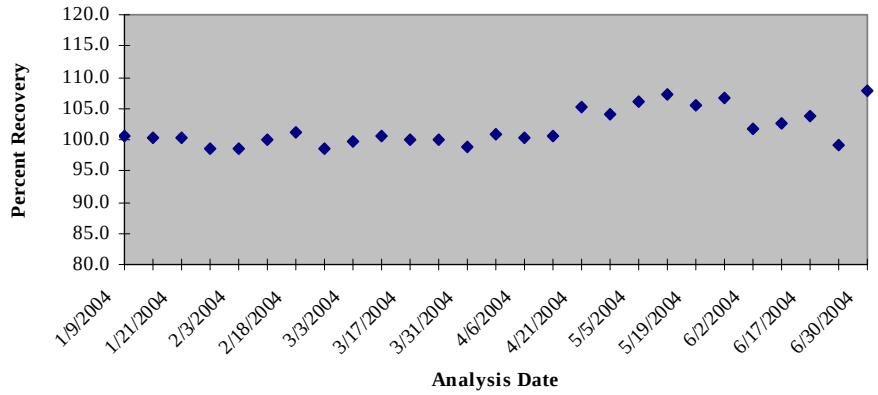


Figure 58. Recovery of Aluminum (Al) in NIST SRM 1832 with Chester Kevex 771

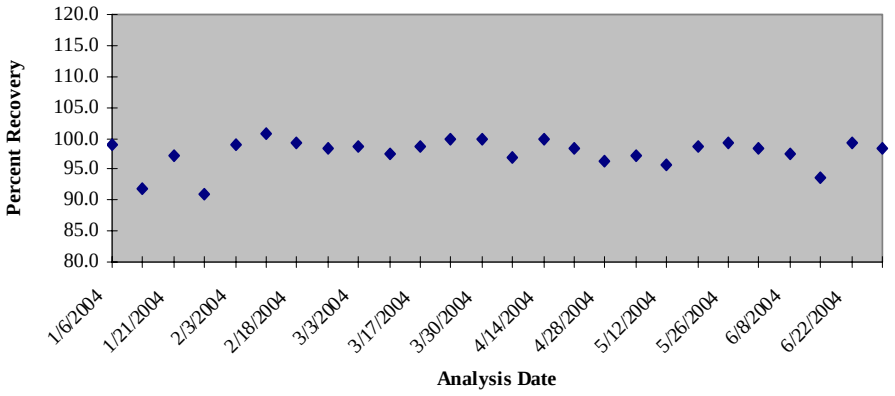


Figure 59. Recovery of Silicon (Si) in NIST SRM 1832 with Chester Kevex 771

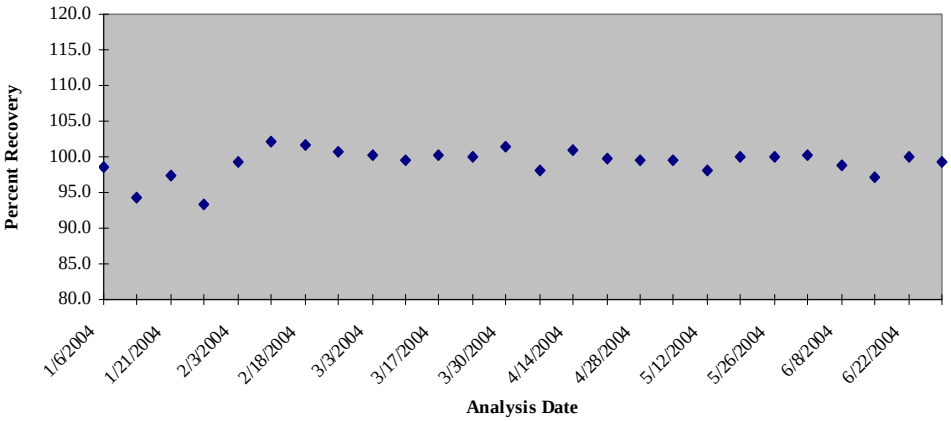


Figure 60. Recovery of Silicon (Si) in NIST SRM 1833 with Chester Kevex 771

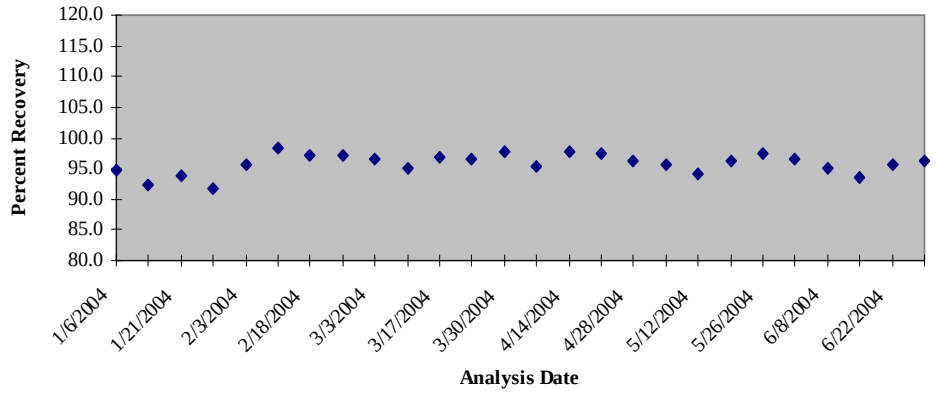


Figure 61. Recovery of Sulfur (Su) in NIST SRM 2708 with Chester Kevex 771

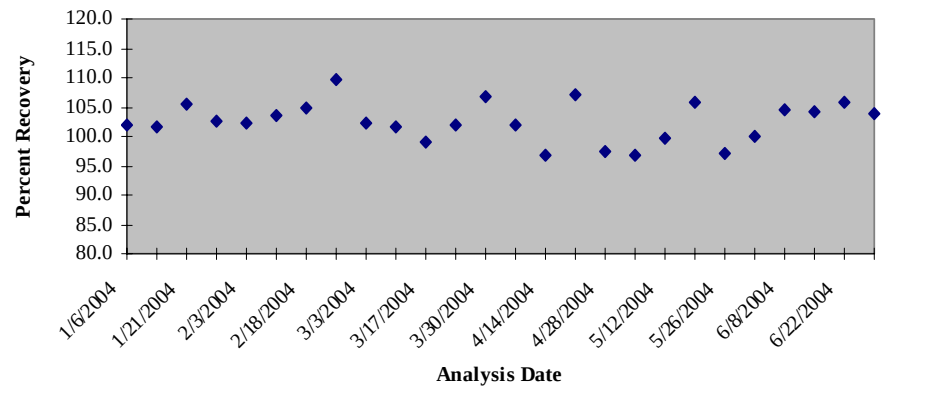


Figure 62. Recovery of Potassium (K) in NIST SRM 1833 with Chester Kevex 771

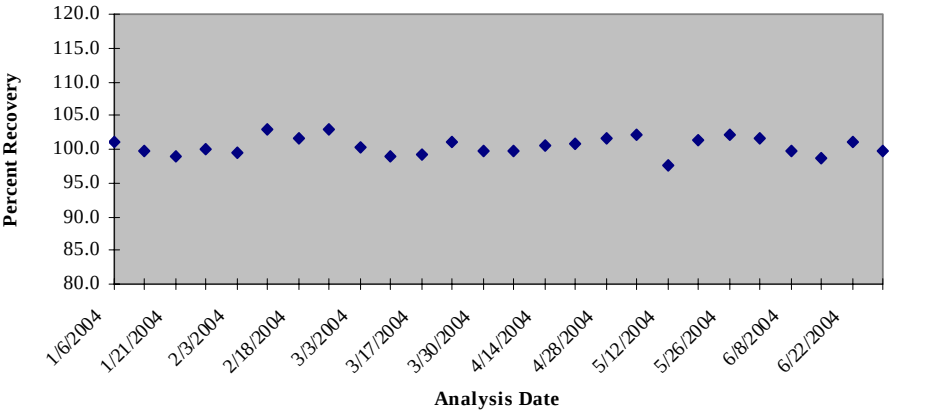


Figure 63. Recovery of Titanium (Ti) in NIST SRM 1833 with Chester Kevex 771

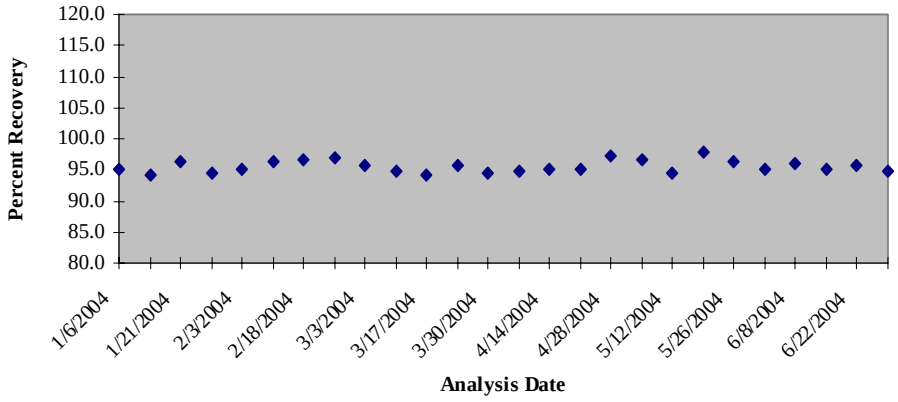


Figure 64. Recovery of Calcium (Ca) in NIST SRM 1832 with Chester Kevex 771

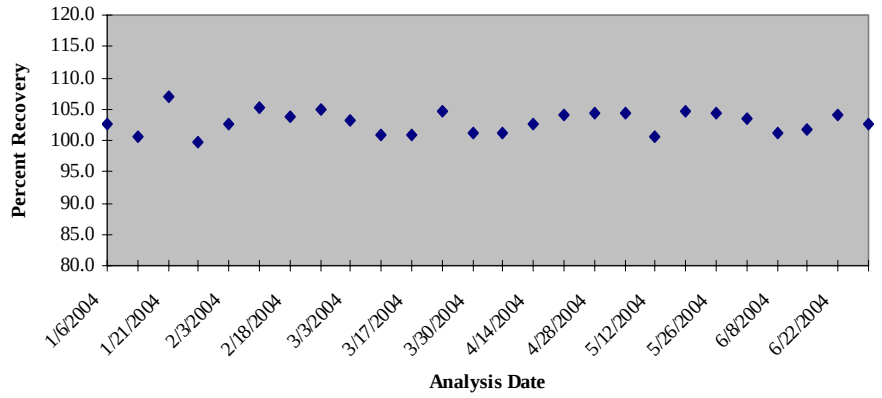


Figure 65. Recovery of Vanadium (V) in NIST SRM 1832 with Chester Kevex 771

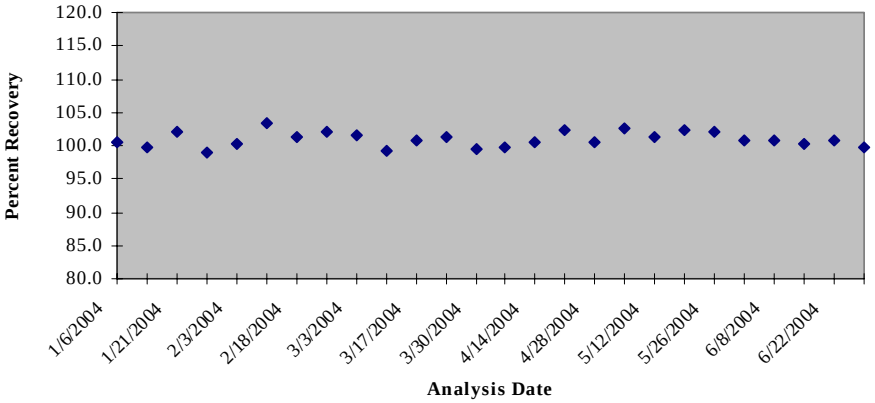


Figure 66. Recovery of Manganese (Mn) in NIST SRM 1833 with Chester Kevex 771

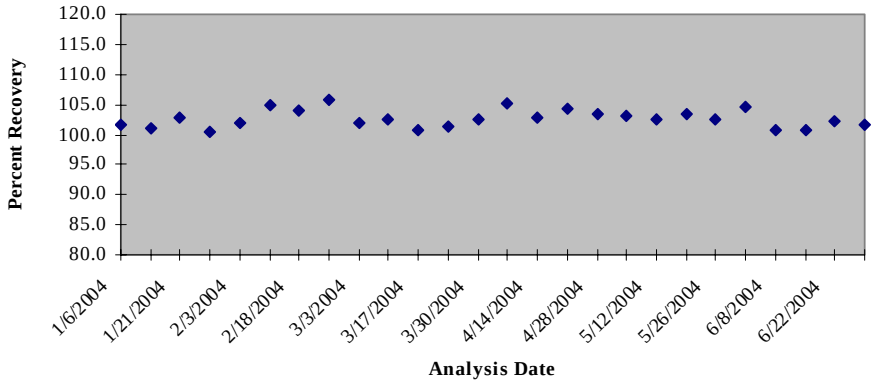


Figure 67. Recovery of Iron (Fe) in NIST SRM 1833 with Chester Kevex 771

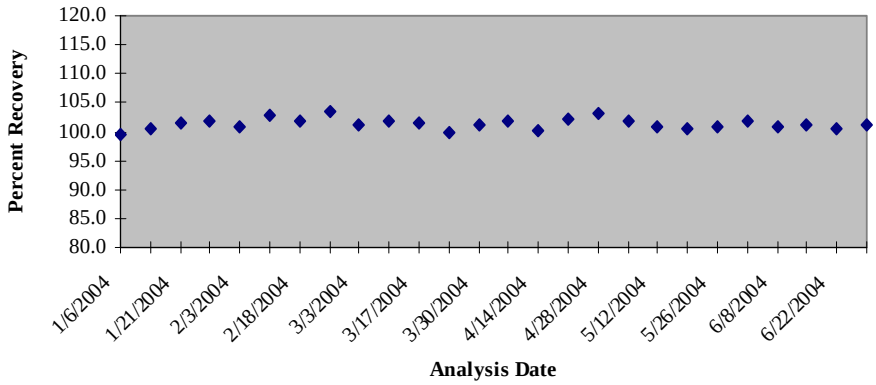


Figure 68. Recovery of Copper (Cu) in NIST SRM 1833 with Chester Kevex 771

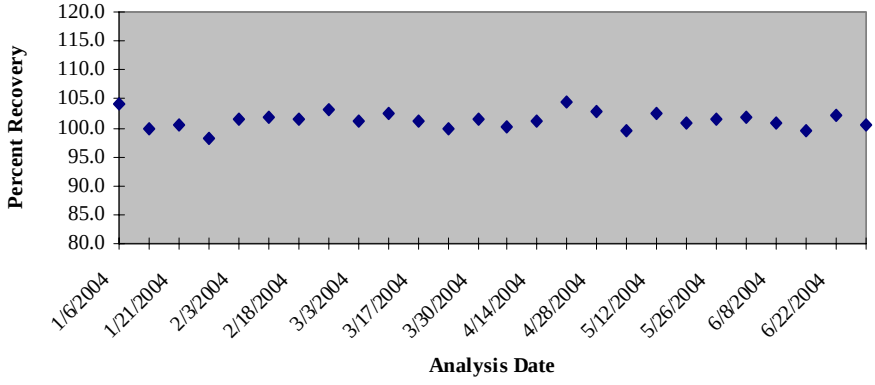


Figure 69. Recovery of Zinc (Zn) in NIST SRM 1833 with Chester Kevex 771

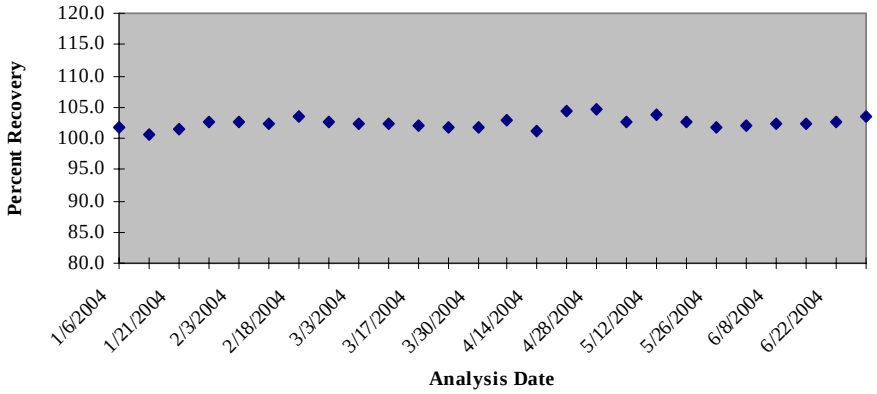
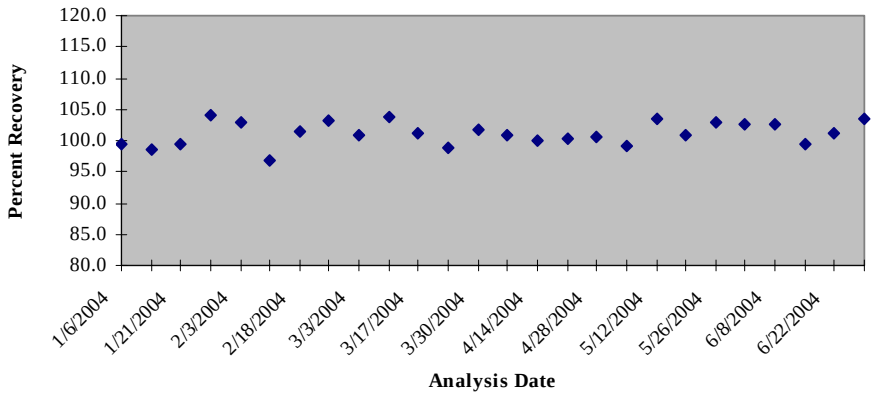


Figure 70. Recovery of Lead (Pb) in NIST SRM 1833 with Chester Kevex 771



Replicates

Five percent of the filters are re-analyzed and the results for select elements are compared. **Figures 71 through 82** compare replicate values for elements through regression analysis.

2.4.2.2 Data Validity Discussion – The data presented in Section 2.4.2 indicate no problems with the XRF data.

2.4.2.2 Corrective Actions – No changes were made in the analytical procedures used by the Chester LabNet XRF laboratory.

2.4.3 RTI XRF Laboratory

2.4.3.1 Statistical Summary of QC Results –

Precision

The precision was monitored by the reproducibility of the multi-element Micromatter QC. The Micromatter QC has six selected elements and is analyzed with each tray of samples. The comparision of the elements percent recoveries gives the measure of reproducibility or precision. (**Tables 22, 23, and 24**). The data used to monitor precision are presented in **Figures 83 through 94**. The percent coefficient of variation (%CV) for the six elements ranged between 0.34 and 0.96 percent for XRF 1 and between 0.85 and 2.17 percent for XRF 2, but after the repair the %CV for XRF 2 ranged from 0.45 to 0.98 percent. Note that during February 2004 to May 2004, XRF 2 experienced a hardware and software failure. During that time, the instrument was not used to analyze any PM2.5 Teflon filters.

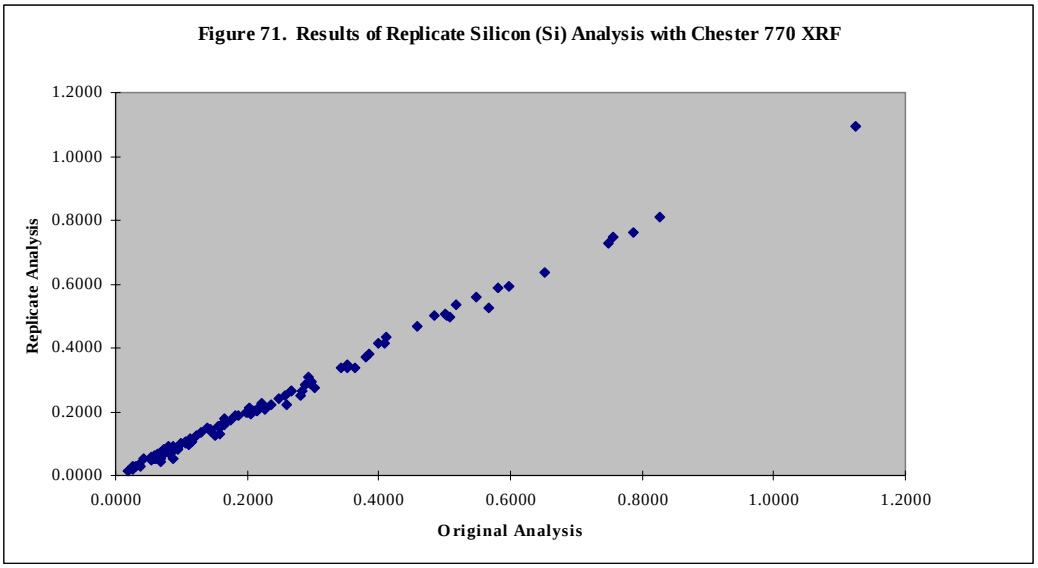


Table 22. Summary of RTI XRF 1 Laboratory QC Precision Recovery Data, ug/cm^2 1/1/04 through 6/30/04

Element	n	Min	Max	Average	Std Dev	%CV
Si	612	10.2	10.6	10.5	0.07	0.66
Ti	612	8.96	9.20	9.04	0.03	0.34
Fe	612	10.2	10.5	10.4	0.04	0.63
Cd	612	5.62	5.86	5.75	0.04	0.62
Se	612	3.96	4.17	4.09	0.04	0.96
Pb	612	10.3	10.7	10.5	0.07	0.64

Table 23. Summary of RTI XRF 2 Laboratory QC Precision Recovery Data, ug/cm^2 1/1/04 through 2/10/04

Element	n	Min	Max	Average	Std Dev	%CV
Si	100	5.04	5.29	5.20	0.06	1.11
Ti	100	6.03	6.31	6.15	0.13	2.17
Fe	100	6.20	6.42	6.33	0.08	1.32
Cd	100	5.91	6.19	6.09	0.05	0.85
Se	100	3.62	3.86	3.74	0.08	2.07
Pb	100	8.02	8.28	8.13	0.11	1.37

Table 24. Summary of RTI XRF 2 Laboratory QC Precision Recovery Data, ug/cm^2 5/10/04 through 6/30/04

Element	n	Min	Max	Average	Std Dev	%CV
Si	135	5.35	5.49	5.43	0.02	0.45
Ti	135	7.21	7.46	7.32	0.04	0.58
Fe	135	6.87	7.10	7.03	0.04	0.53
Cd	135	5.82	6.21	6.05	0.06	0.98
Se	135	4.24	4.39	4.32	0.03	0.75
Pb	135	9.00	9.20	9.08	0.04	0.48

n = number of observations
Min = minimum value observed
Max = maximum value observed
Std Dev = standard deviation
%CV = percent coefficient of variation (Std Dev/Average*100)

Figure 72. Results of Replicate Sulfur (S) Analysis with Chester 770 XRF

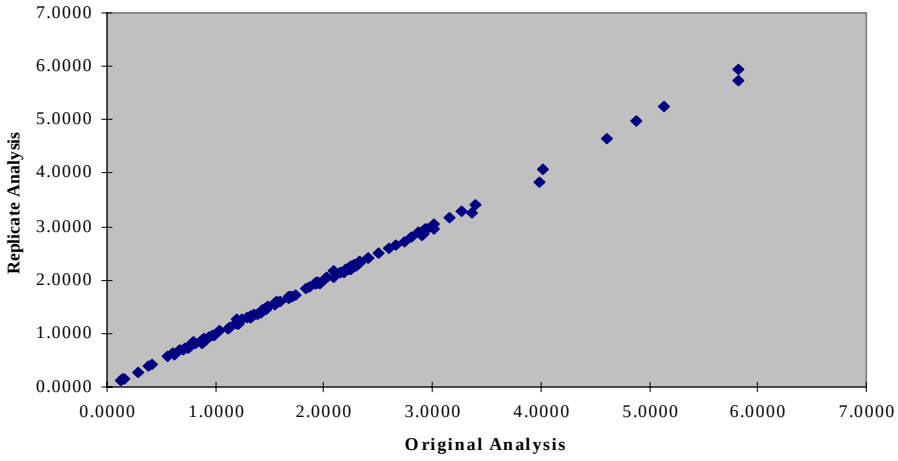


Figure 73. Results of Replicate Potassium (K) Analysis with Chester 770 XRF

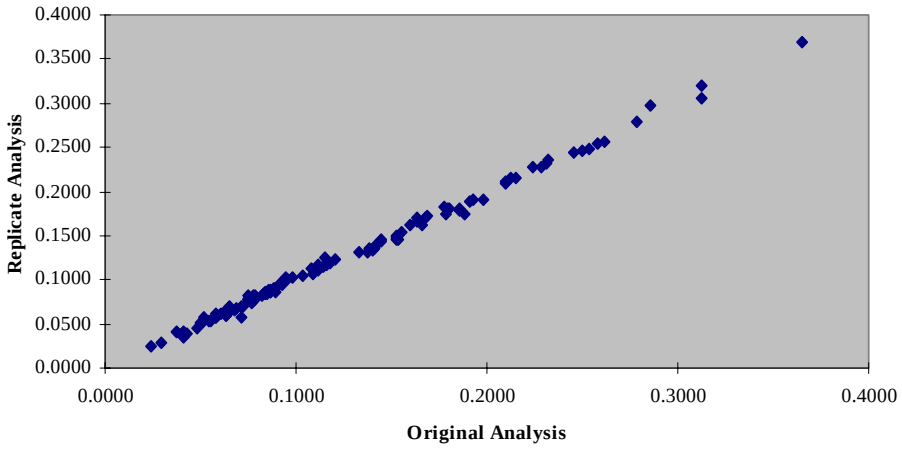


Figure 74. Results of Replicate Calcium (Ca) Analysis with Chester 770 XRF

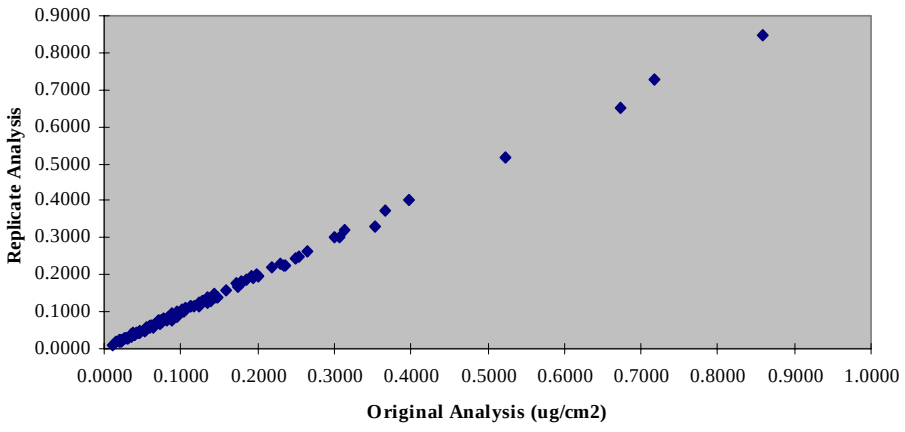


Figure 75. Results of Replicate Iron (Fe) Analysis with Chester 770 XRF

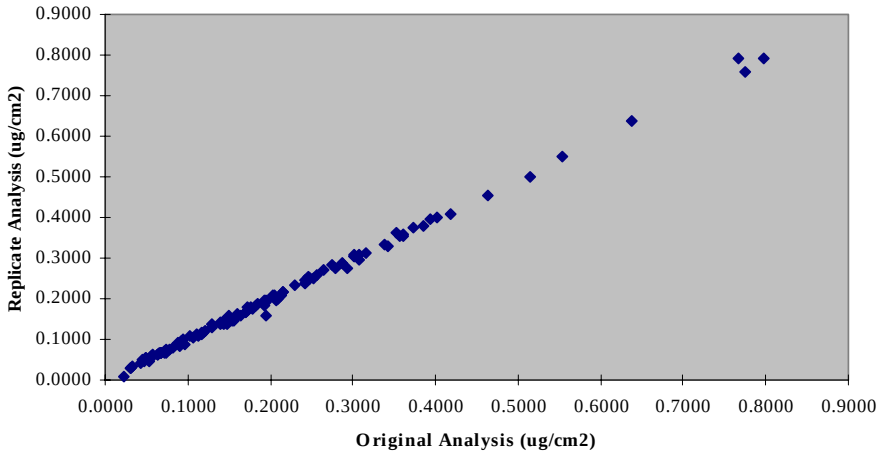


Figure 76. Results of Replicate Zinc (Zn) Analysis with Chester 770 XRF

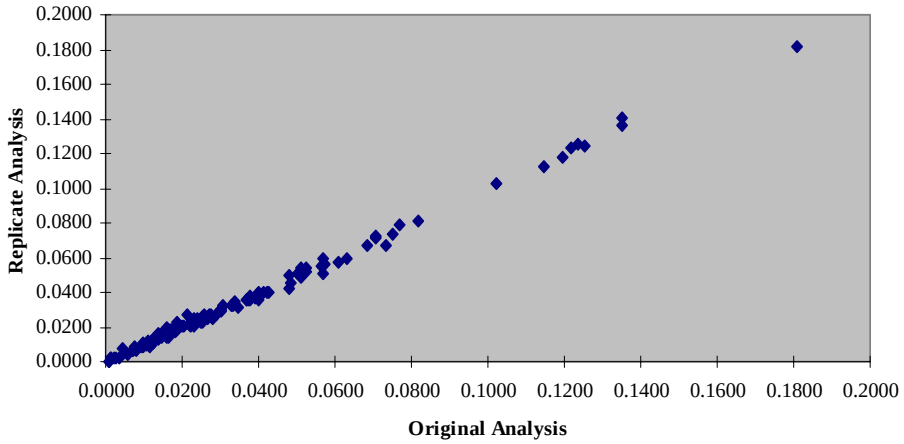


Figure 77. Results of Replicate Silicon (Si) Analysis with Chester 771 XRF

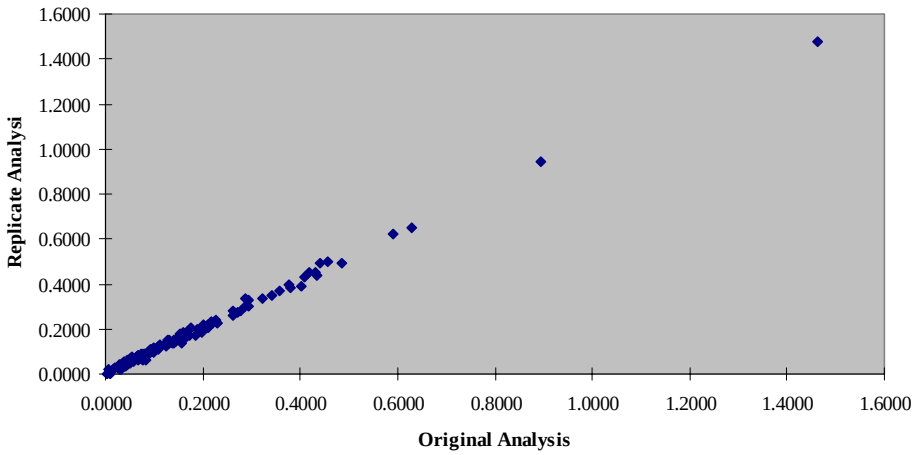


Figure 78. Results of Replicate Sulfur (S) Analysis with Chester 771 XRF

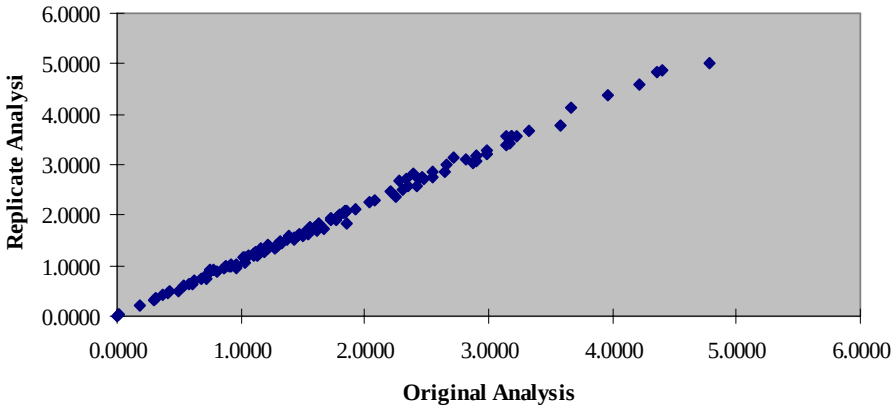


Figure 79. Results of Replicate Potassium (K) Analysis with Chester 771 XRF

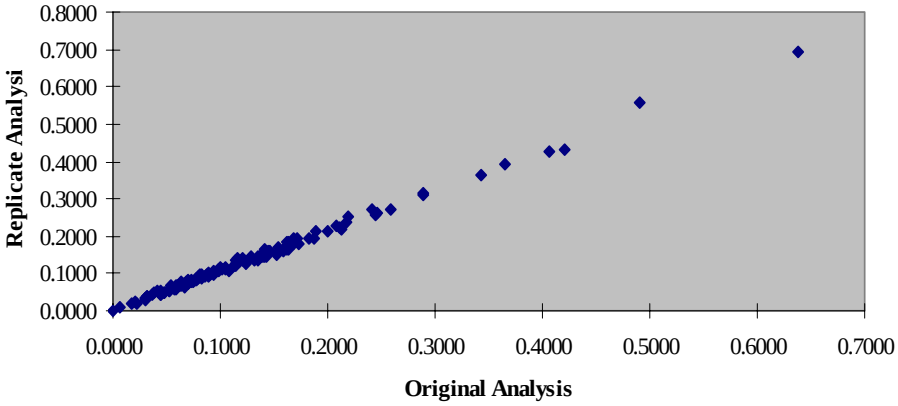


Figure 80. Results of Replicate Calcium (Ca) Analysis with Chester 771 XRF

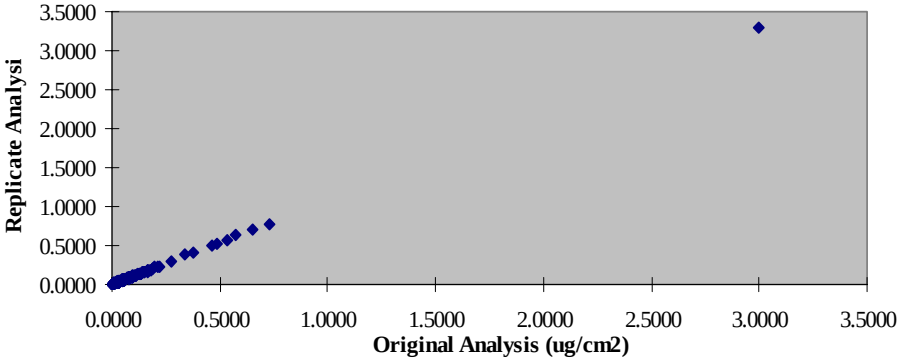


Figure 81. Results of Replicate Iron (Fe) Analysis with Chester 771 XRF

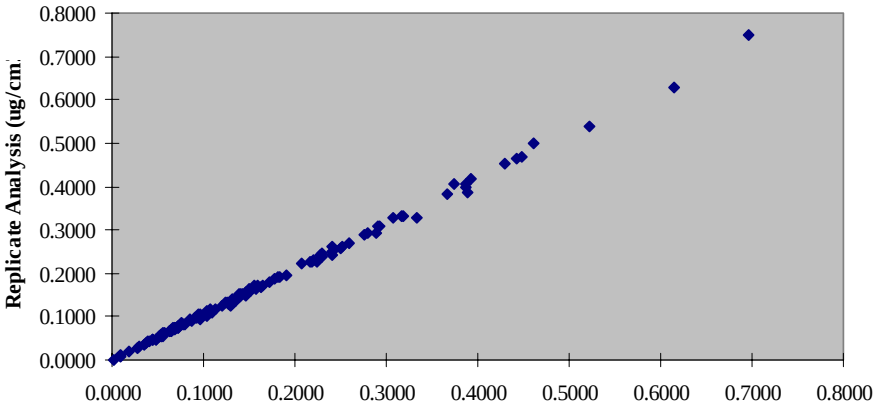


Figure 82. Results of Replicate Zinc (Zn) Analysis with Chester 771 XRF

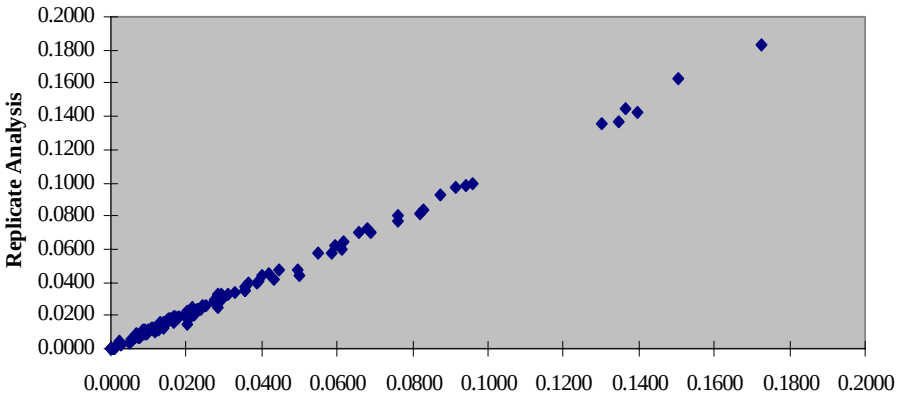


Figure 83. Recovery Precision for RTI XRF 1 with Silicon (Si)

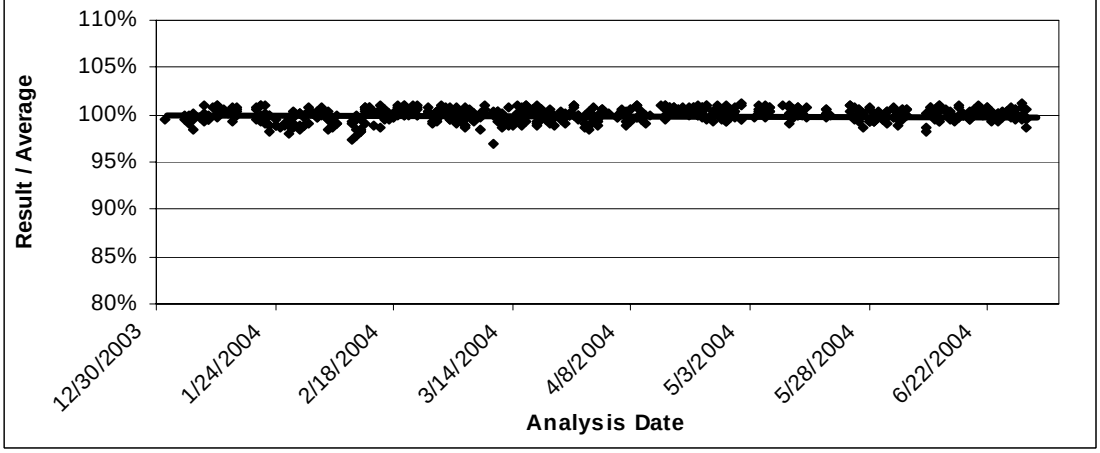


Figure 84. Recovery Precision for RTI XRF 1 with Iron (Fe)

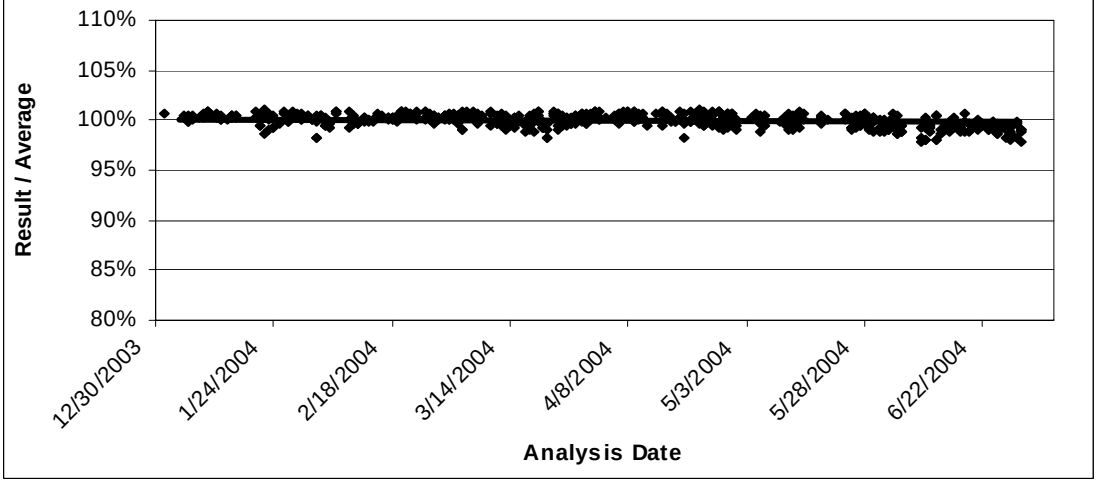
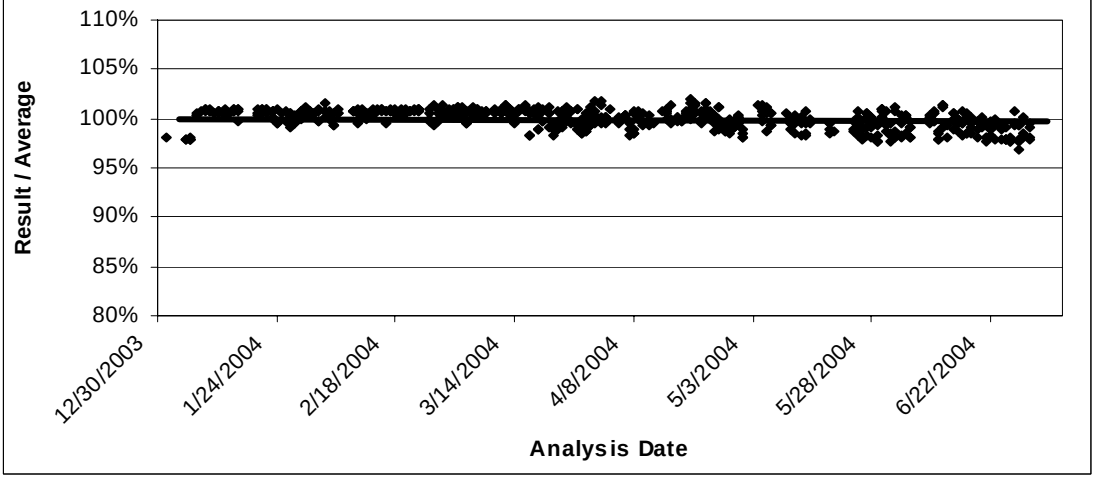


Figure 85. Recovery Precision for RTI XRF 1 with Selenium (Se)



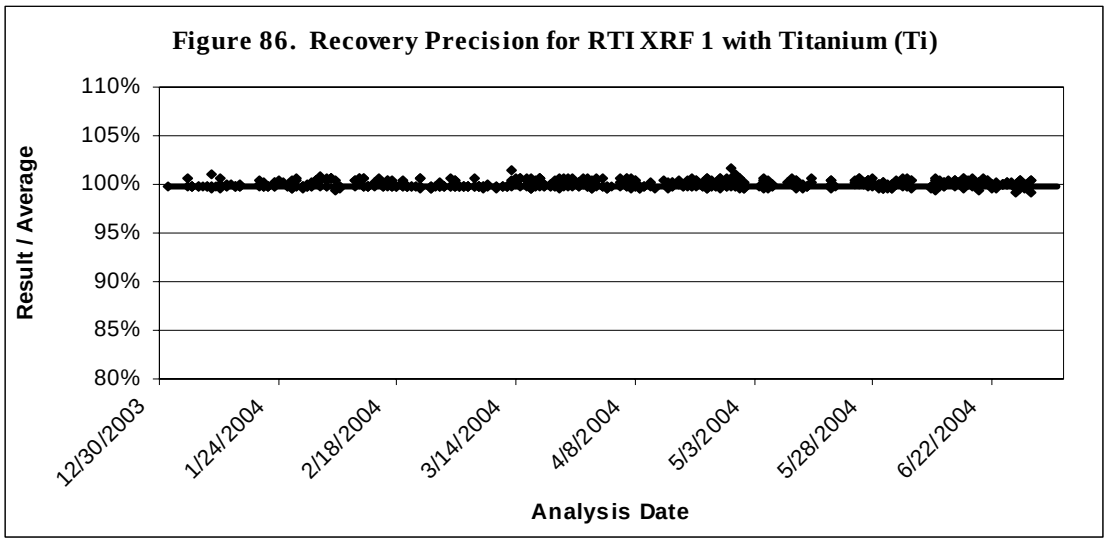


Figure 86. Recovery Precision for RTI XRF 1 with Titanium (Ti)
110%
105%
100%
95%
90%
85%
80%
Result / Average
12/30/2003
1/24/2004
2/18/2004
3/14/2004
4/8/2004
5/3/2004
5/28/2004
6/22/2004
Analysis Date

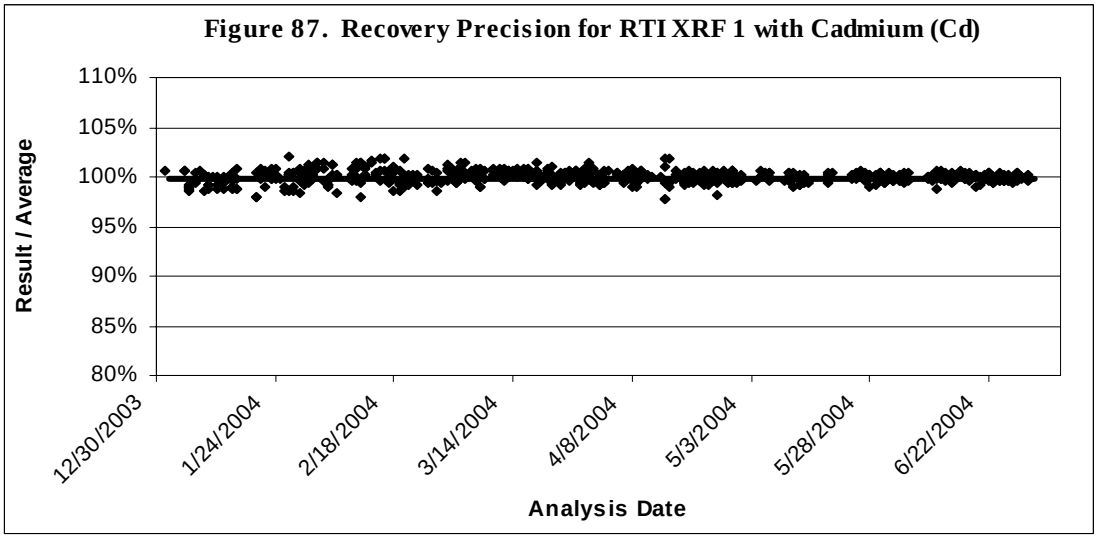


Figure 87. Recovery Precision for RTI XRF 1 with Cadmium (Cd)
110%
105%
100%
95%
90%
85%
80%
Result / Average
12/30/2003
1/24/2004
2/18/2004
3/14/2004
4/8/2004
5/3/2004
5/28/2004
6/22/2004
Analysis Date

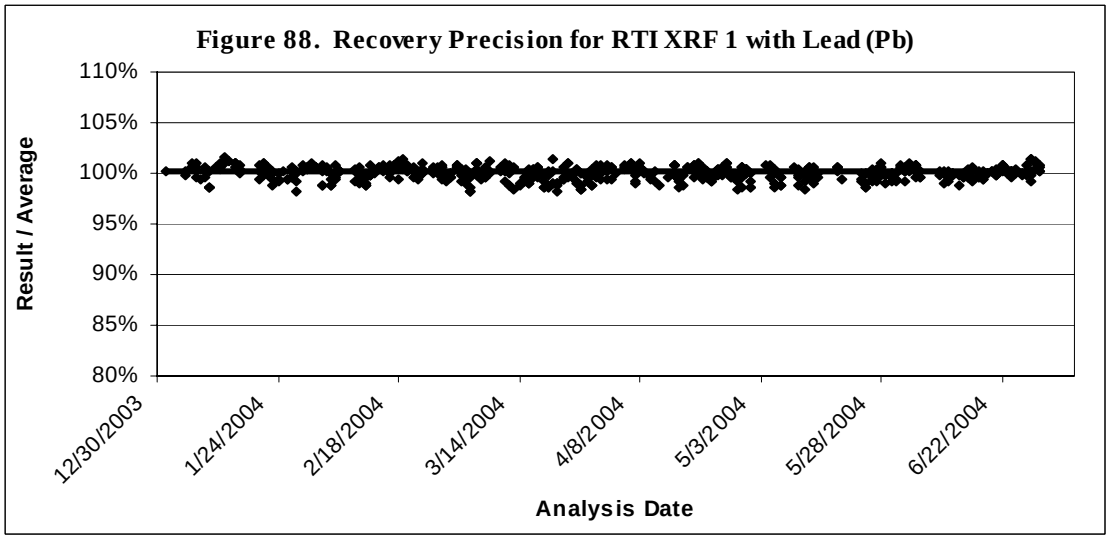


Figure 88. Recovery Precision for RTI XRF 1 with Lead (Pb)
110%
105%
100%
95%
90%
85%
80%
Result / Average
12/30/2003
1/24/2004
2/18/2004
3/14/2004
4/8/2004
5/3/2004
5/28/2004
6/22/2004
Analysis Date

Figure 89. Recovery Precision for RTI XRF 2 with Silicon (Si)

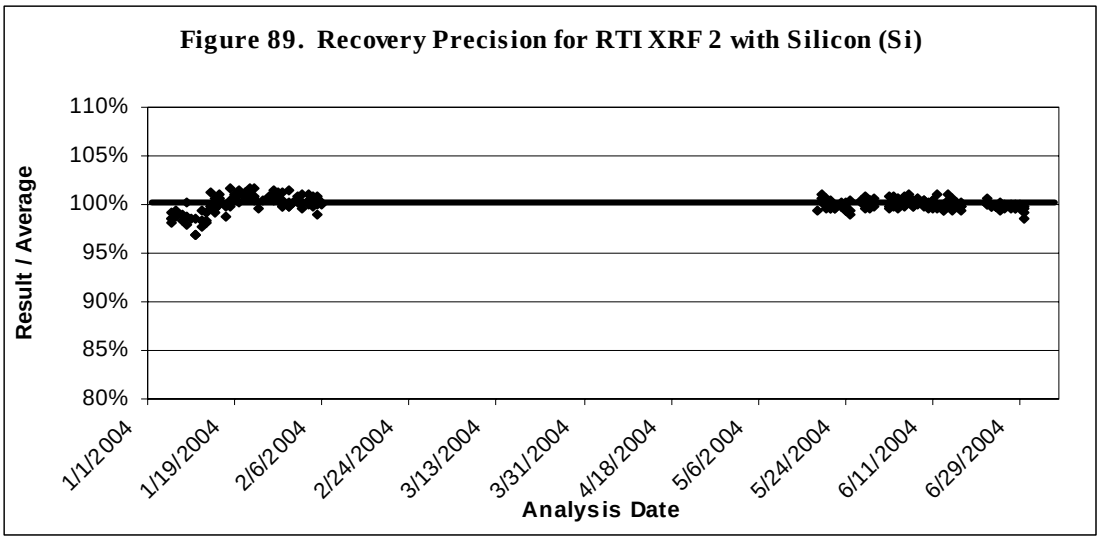


Figure 90. Recovery Precision for RTI XRF 2 with Iron (Fe)

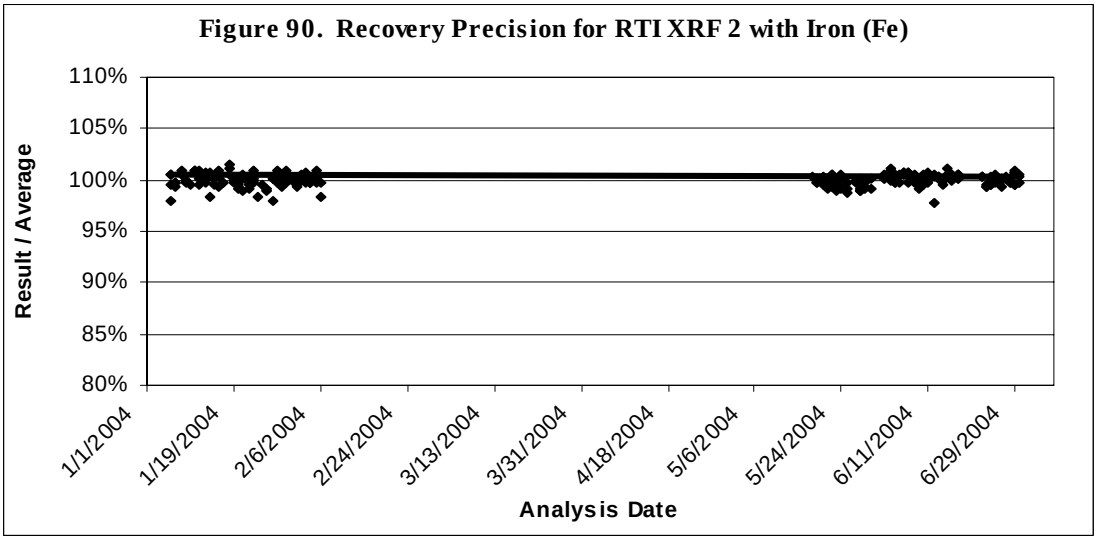
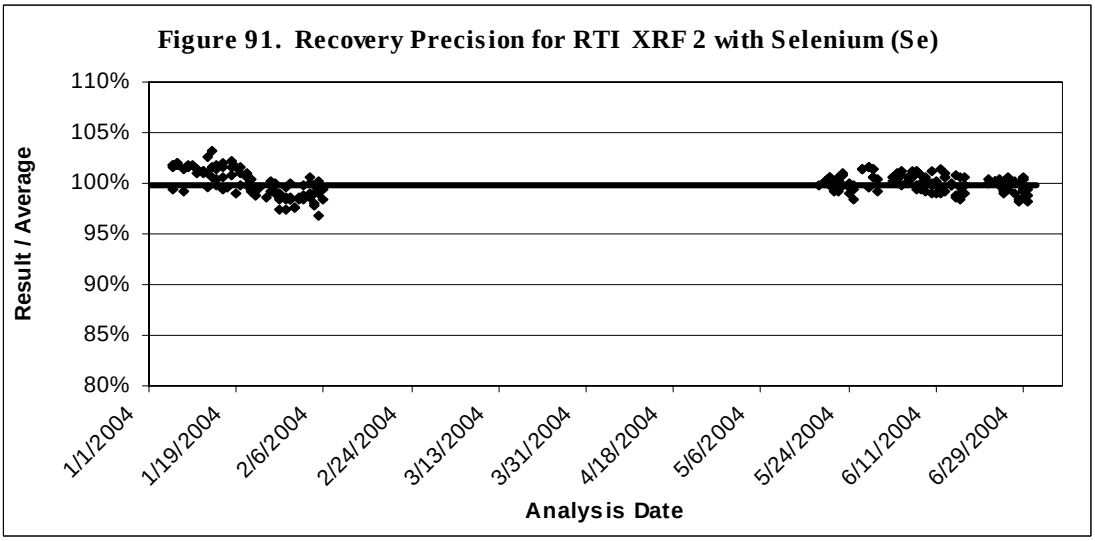


Figure 91. Recovery Precision for RTI XRF 2 with Selenium (Se)



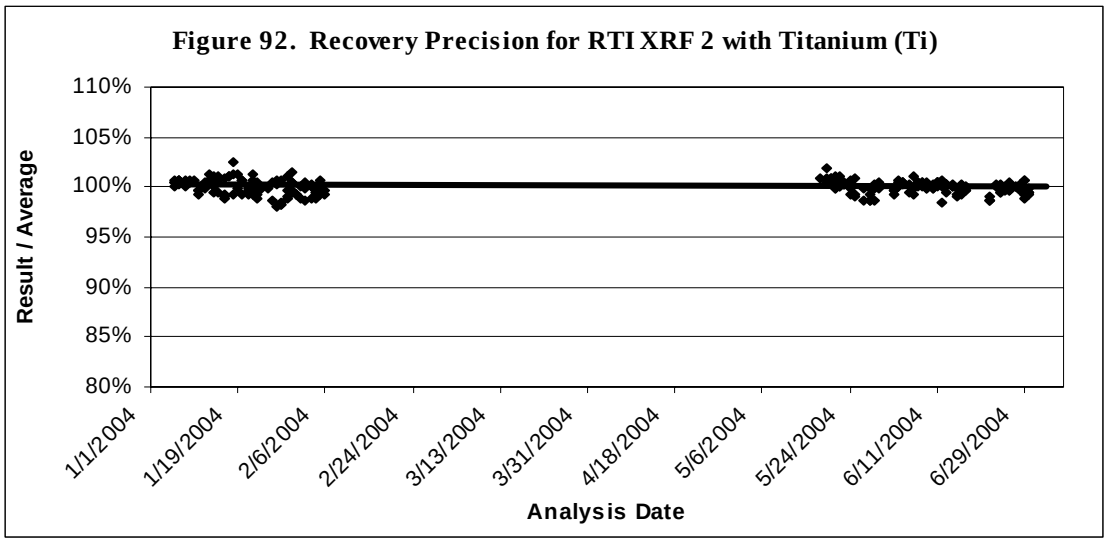


Figure 92. Recovery Precision for RTI XRF 2 with Titanium (Ti)
110%
105%
100%
95%
90%
85%
80%
Result / Average
1/1/2004
1/19/2004
2/6/2004
2/24/2004
3/13/2004
3/31/2004
4/18/2004
5/6/2004
5/24/2004
6/11/2004
6/29/2004
Analysis Date

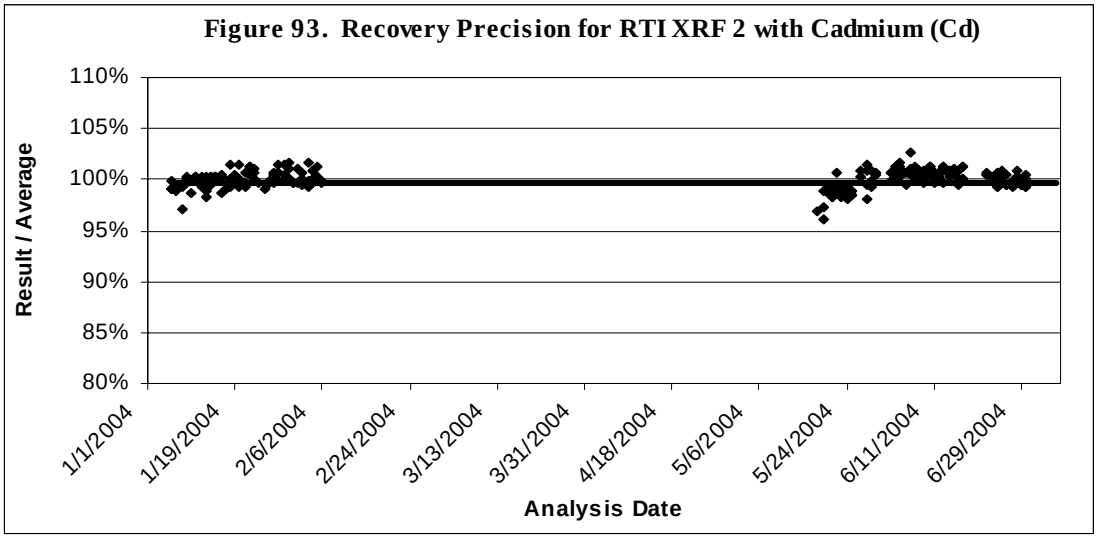


Figure 93. Recovery Precision for RTI XRF 2 with Cadmium (Cd)
110%
105%
100%
95%
90%
85%
80%
Result / Average
1/1/2004
1/19/2004
2/6/2004
2/24/2004
3/13/2004
3/31/2004
4/18/2004
5/6/2004
5/24/2004
6/11/2004
6/29/2004
Analysis Date

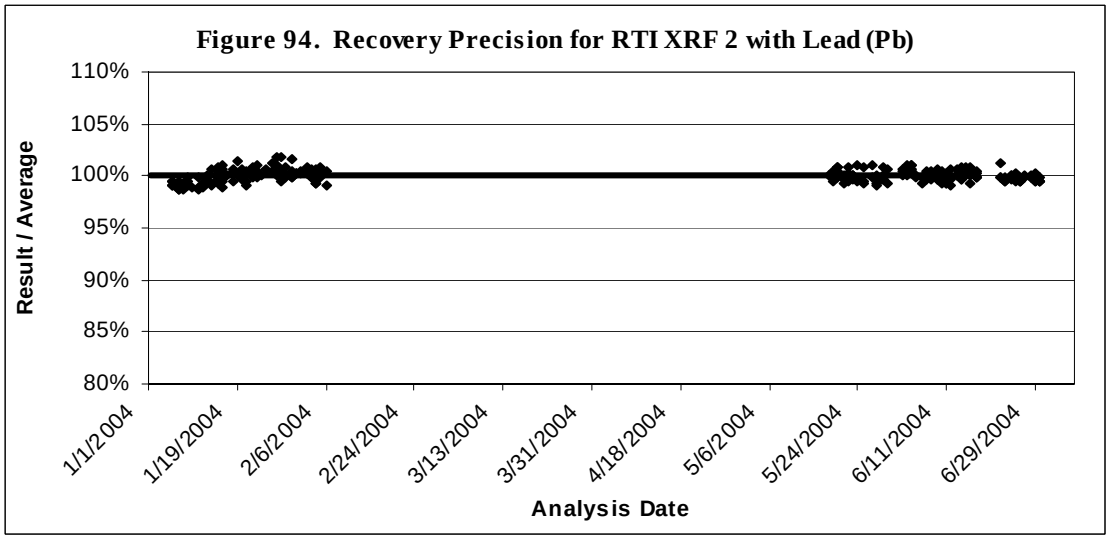


Figure 94. Recovery Precision for RTI XRF 2 with Lead (Pb)
110%
105%
100%
95%
90%
85%
80%
Result / Average
1/1/2004
1/19/2004
2/6/2004
2/24/2004
3/13/2004
3/31/2004
4/18/2004
5/6/2004
5/24/2004
6/11/2004
6/29/2004
Analysis Date

Recovery

Recovery or system accuracy was determined by the analysis of a series of NBS Standard Reference Materials filters. Recovery is calculated by comparison of measured and expected values. **Figures 95 through 120** show recovery for 12 elements spanning the range of the 48 elements normally measured. The recovery values for all elements ranged between 90 and 102 percent for XRF 1 and between 91 and 105 percent for XRF 2, as shown in **Table 25.** Also, note that during February 2004 to May 2004, XRF 2 experienced hardware and software failures and no data was produced during that time period.

Table 25. Recovery Determined from Analysis of NBS SRMs 1832 and 1833 for RTI XRF 1 and XRF 2. 1/1/2004 through 6/30/2004

Element	XRF 1	XRF 2
	Range % Recovery	Range % Recovery
Al	92 - 101	96 - 105
Si*	92 - 95	92 - 95
Si**	94 - 100	93 - 97
K	90 - 95	91 - 97
Ca	95 - 99	96 - 100
Ti	93 - 101	95 - 101
V	96 - 101	97 - 100
Mn	95 - 99	99 - 101
Fe	90 - 95	92 - 96
Co	95 - 101	99 - 101
Cu	93 - 99	95 - 98
Zn	92 - 95	95 - 96
Pb	96 - 102	93 - 98

*SRM 1832
**SRM 1833

Replicates

Five percent of the filters were re-analyzed and the results for select elements compared. **Figures 121 through 132** compare replicate values for six elements through regression analysis. Note that slopes are all greater than 0.9970. The values and correlation coefficients for XRF 1 range from 0.9971 to 0.9999, and the values and correlation coefficients for XRF 2 range from 0.9989 to 1.0000, indicating acceptable replication on both instruments.

2.4.3.2 Data Validity Discussion – The data presented in Section 2.4.3 indicate no problems with the XRF data. The only problems encountered were occasional tears and/or pinholes in the filters.

Figure 83. Recovery Precision for RTI XRF 1 with Silicon (Si)

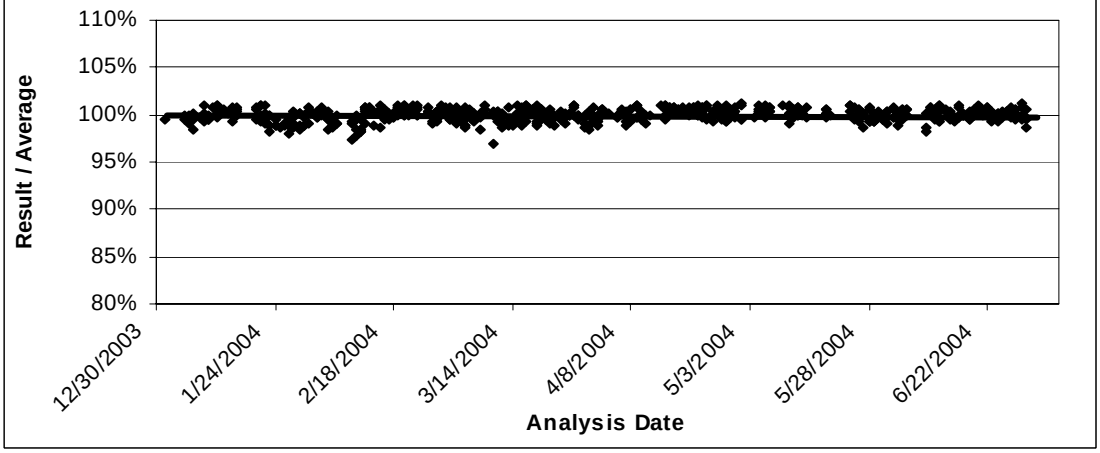


Figure 84. Recovery Precision for RTI XRF 1 with Iron (Fe)

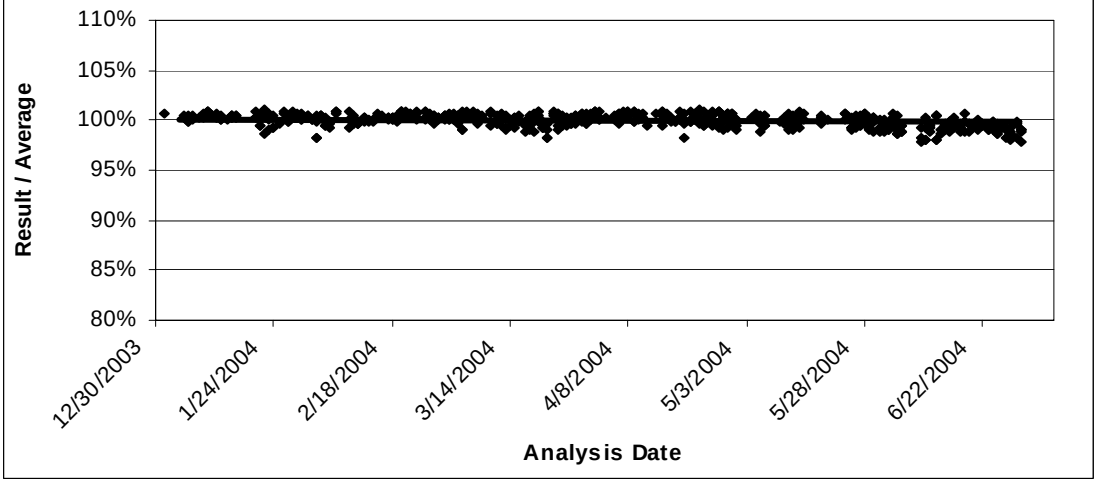
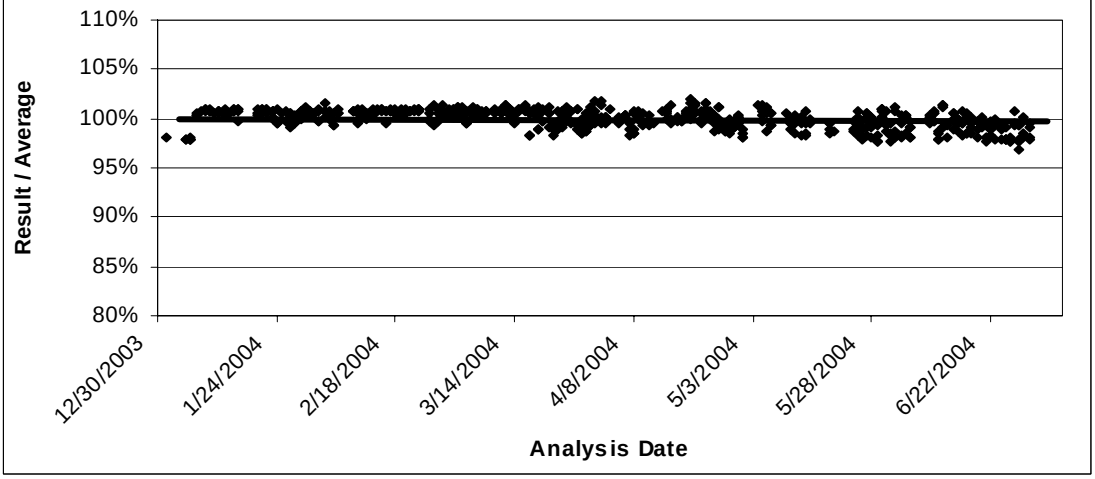


Figure 85. Recovery Precision for RTI XRF 1 with Selenium (Se)



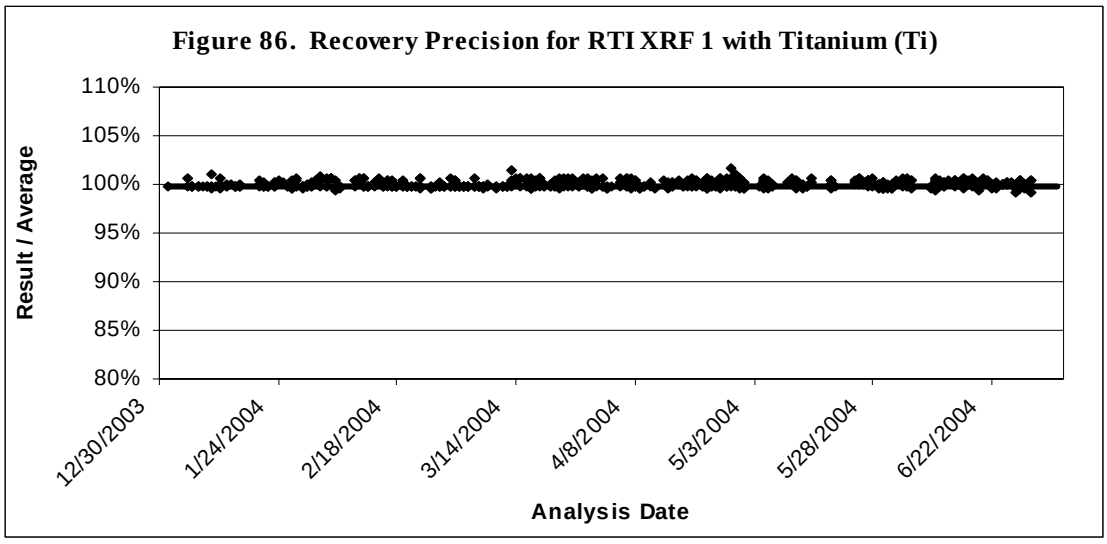


Figure 86. Recovery Precision for RTI XRF 1 with Titanium (Ti)
110%
105%
100%
95%
90%
85%
80%
Result / Average
12/30/2003
1/24/2004
2/18/2004
3/14/2004
4/8/2004
5/3/2004
5/28/2004
6/22/2004
Analysis Date

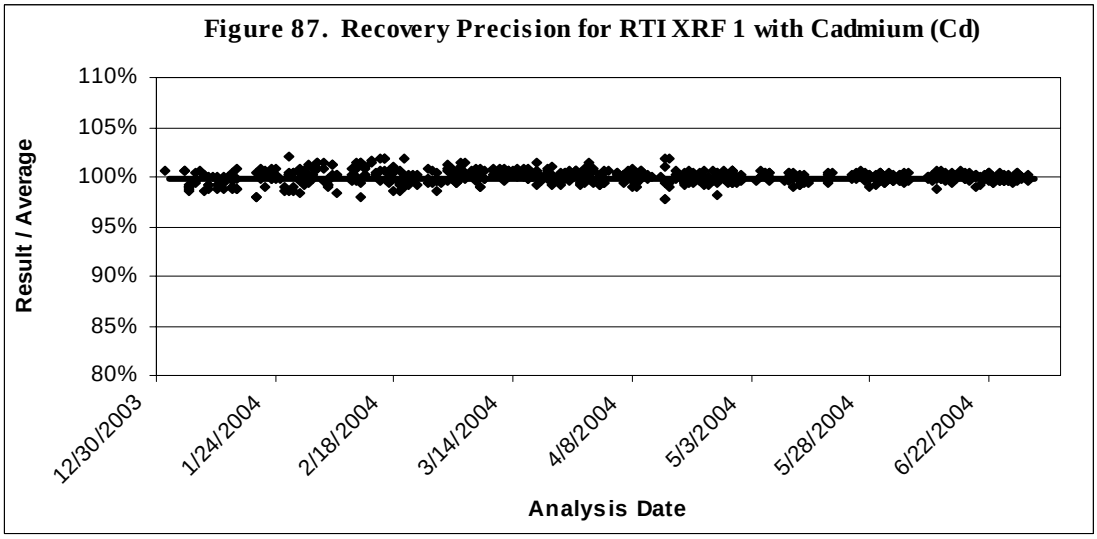


Figure 87. Recovery Precision for RTI XRF 1 with Cadmium (Cd)
110%
105%
100%
95%
90%
85%
80%
Result / Average
12/30/2003
1/24/2004
2/18/2004
3/14/2004
4/8/2004
5/3/2004
5/28/2004
6/22/2004
Analysis Date

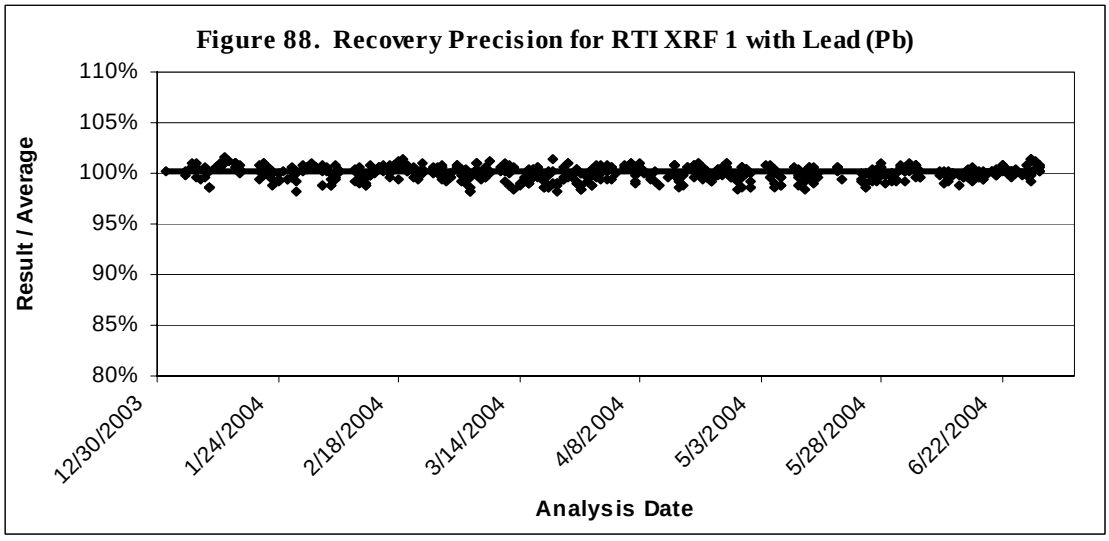


Figure 88. Recovery Precision for RTI XRF 1 with Lead (Pb)
110%
105%
100%
95%
90%
85%
80%
Result / Average
12/30/2003
1/24/2004
2/18/2004
3/14/2004
4/8/2004
5/3/2004
5/28/2004
6/22/2004
Analysis Date

Figure 89. Recovery Precision for RTI XRF 2 with Silicon (Si)

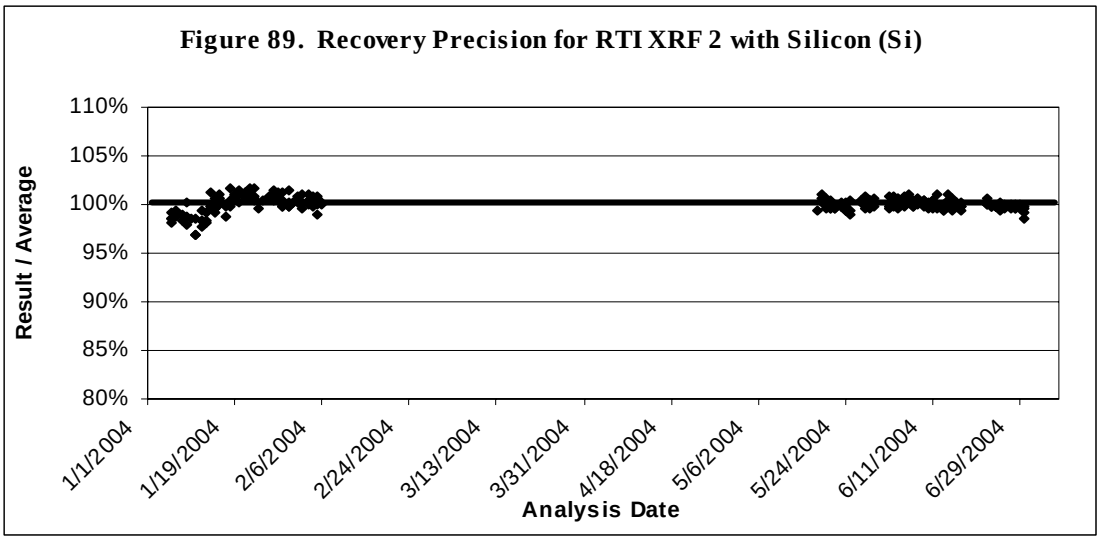


Figure 90. Recovery Precision for RTI XRF 2 with Iron (Fe)

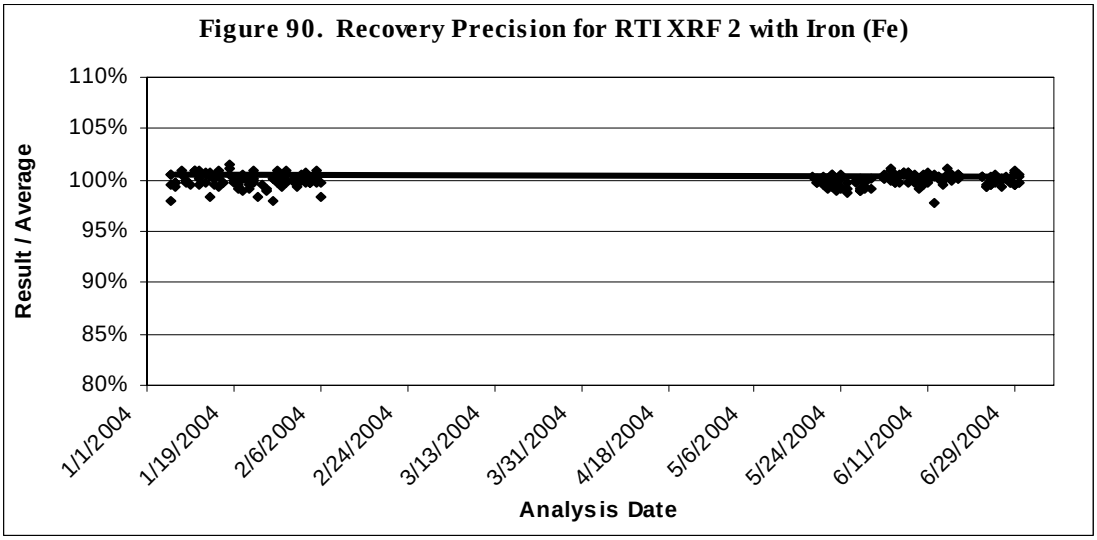
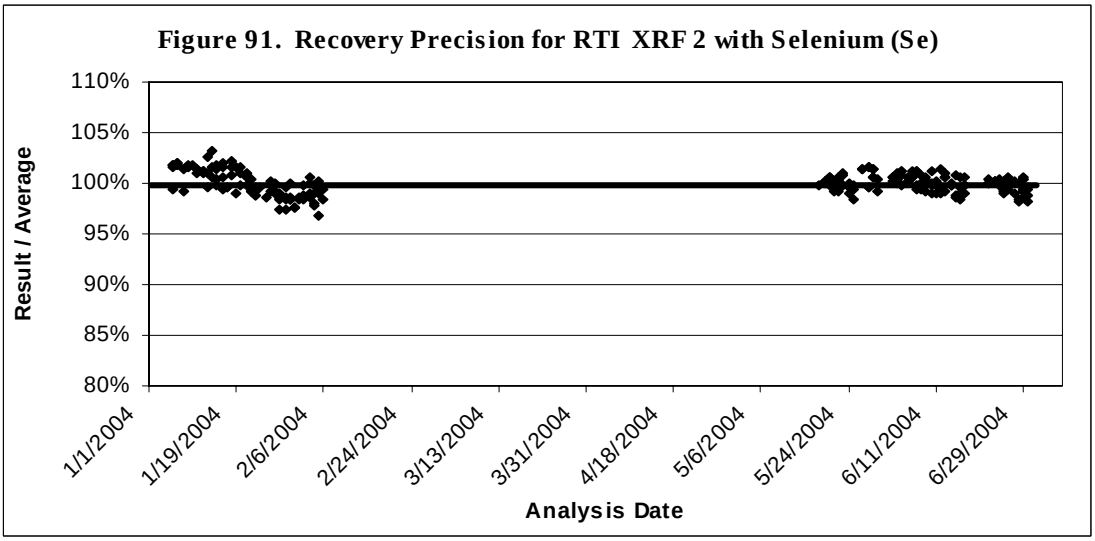


Figure 91. Recovery Precision for RTI XRF 2 with Selenium (Se)



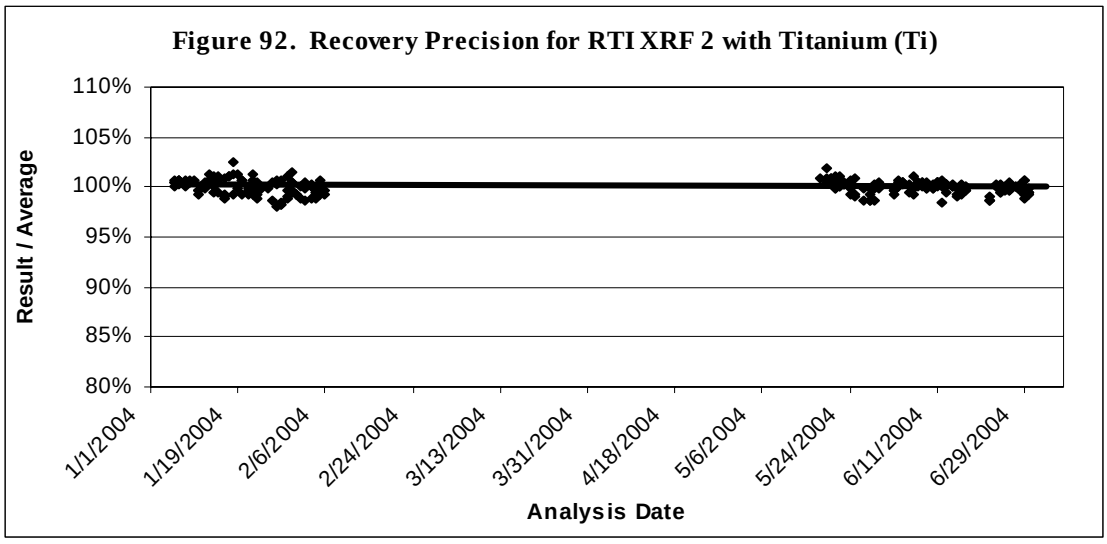


Figure 92. Recovery Precision for RTI XRF 2 with Titanium (Ti)
110%
105%
100%
95%
90%
85%
80%
Result / Average
1/1/2004
1/19/2004
2/6/2004
2/24/2004
3/13/2004
3/31/2004
4/18/2004
5/6/2004
5/24/2004
6/11/2004
6/29/2004
Analysis Date

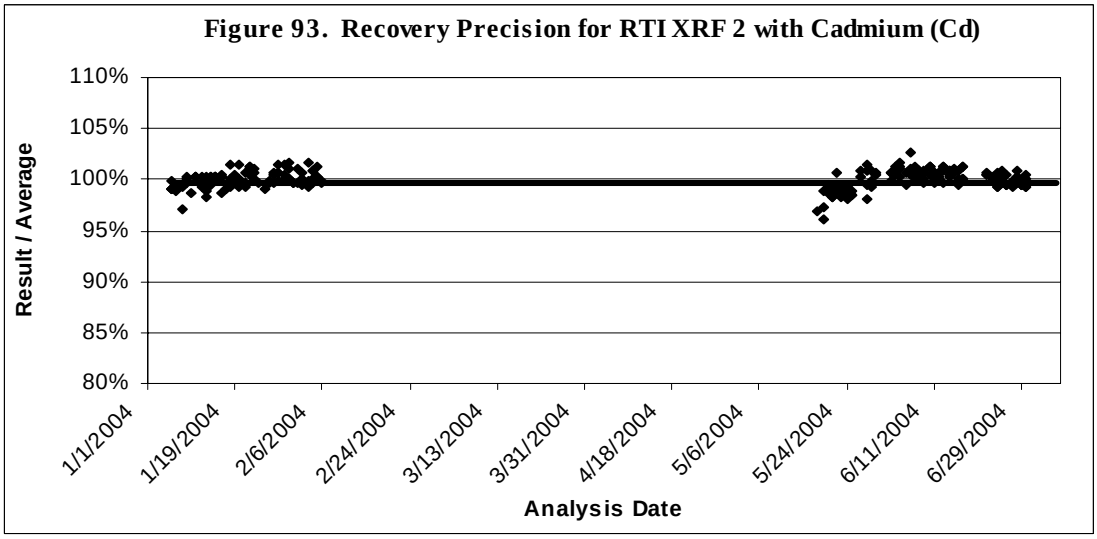


Figure 93. Recovery Precision for RTI XRF 2 with Cadmium (Cd)
110%
105%
100%
95%
90%
85%
80%
Result / Average
1/1/2004
1/19/2004
2/6/2004
2/24/2004
3/13/2004
3/31/2004
4/18/2004
5/6/2004
5/24/2004
6/11/2004
6/29/2004
Analysis Date

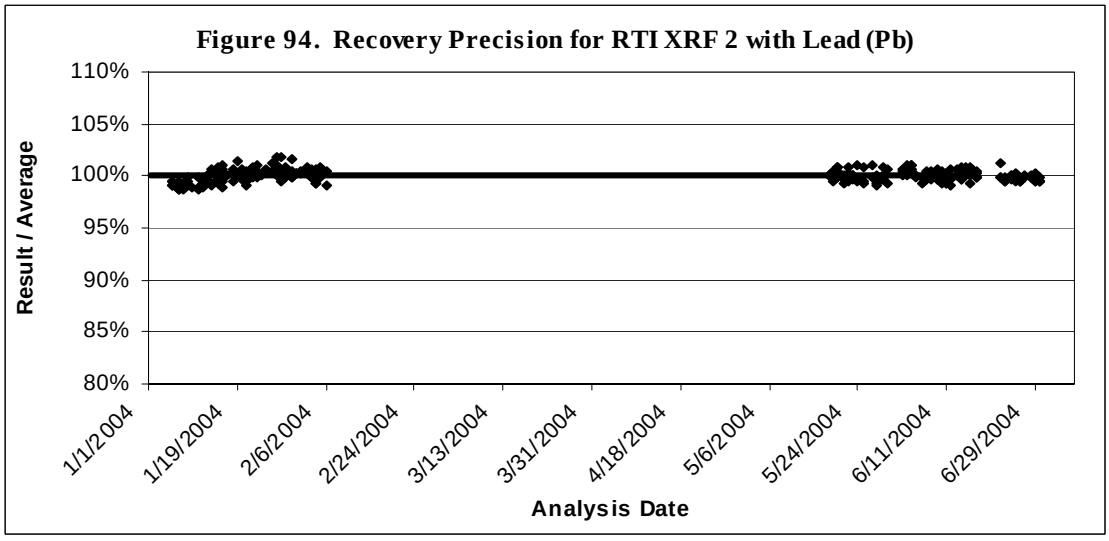


Figure 94. Recovery Precision for RTI XRF 2 with Lead (Pb)
110%
105%
100%
95%
90%
85%
80%
Result / Average
1/1/2004
1/19/2004
2/6/2004
2/24/2004
3/13/2004
3/31/2004
4/18/2004
5/6/2004
5/24/2004
6/11/2004
6/29/2004
Analysis Date

Figure 95. Recovery Precision of Aluminum (Al) in NIST SRM1832 with RTI XRF 1

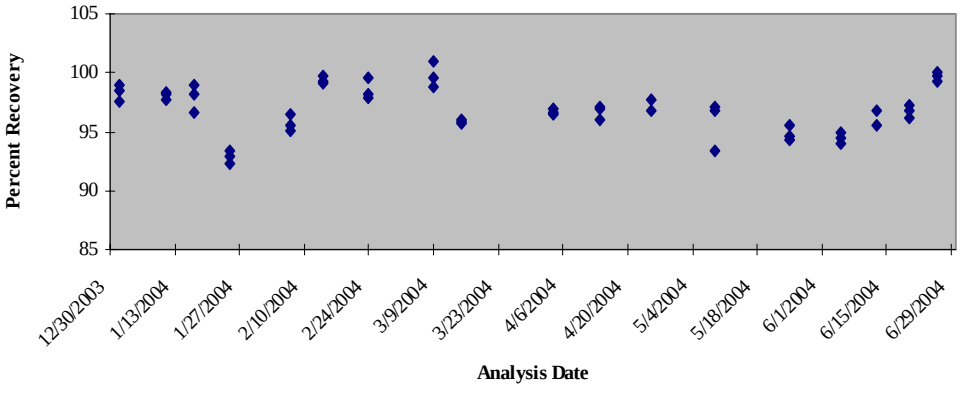


Figure 96. Recovery Precision of Silicon (Si) in NIST SRM 1832 with RTI XRF 1

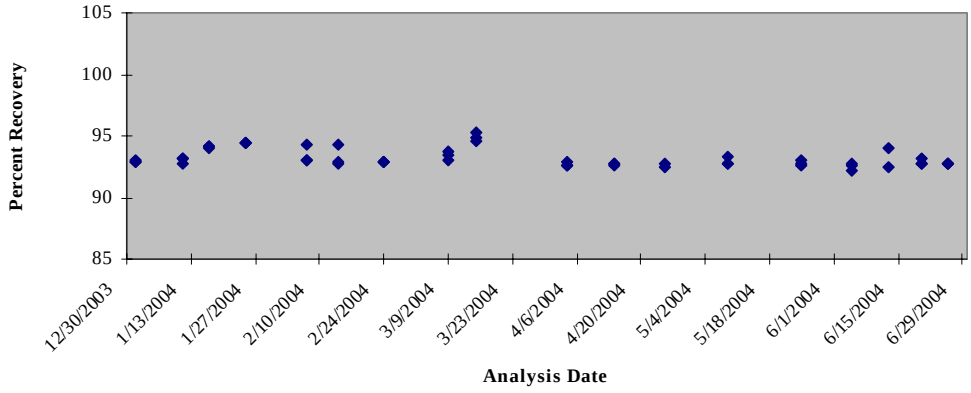


Figure 97. Recovery Precision of Silicon (Si) in NIST SRM1833 with RTI XRF 1

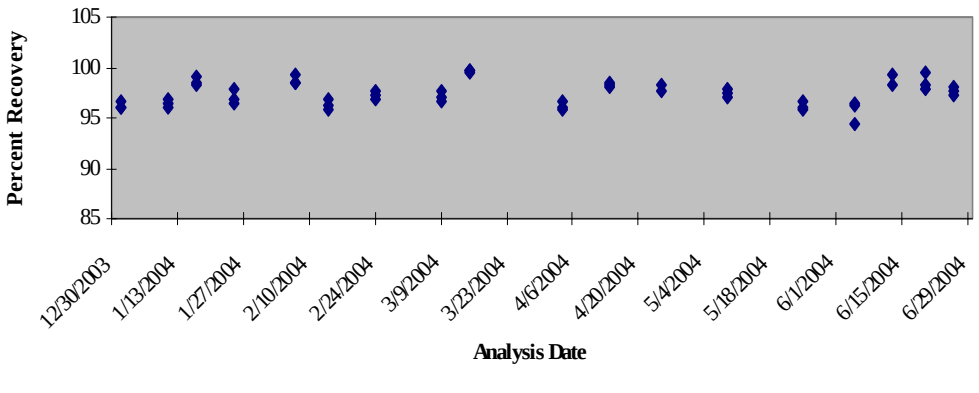


Figure 98. Recovery Precision of Potassium (K) in NIST SRM 1833 with RTI XRF 1

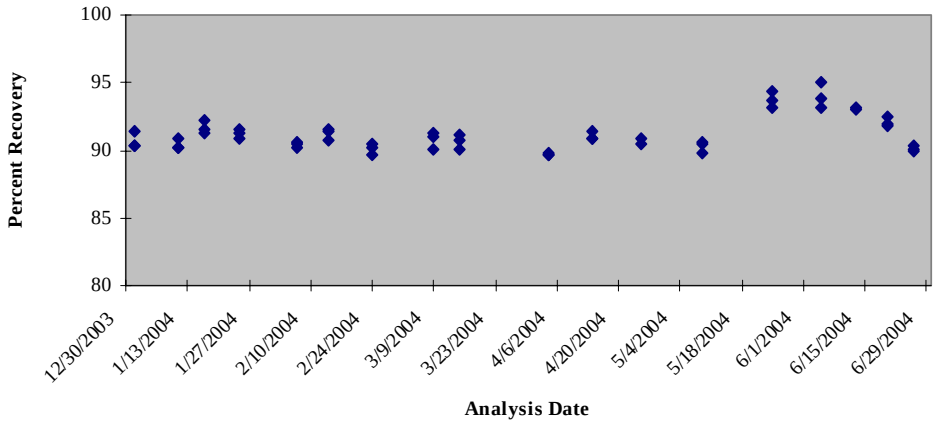


Figure 99. Recovery Precision of Calcium (Ca) in NIST SRM 1832 with RTI XRF 1

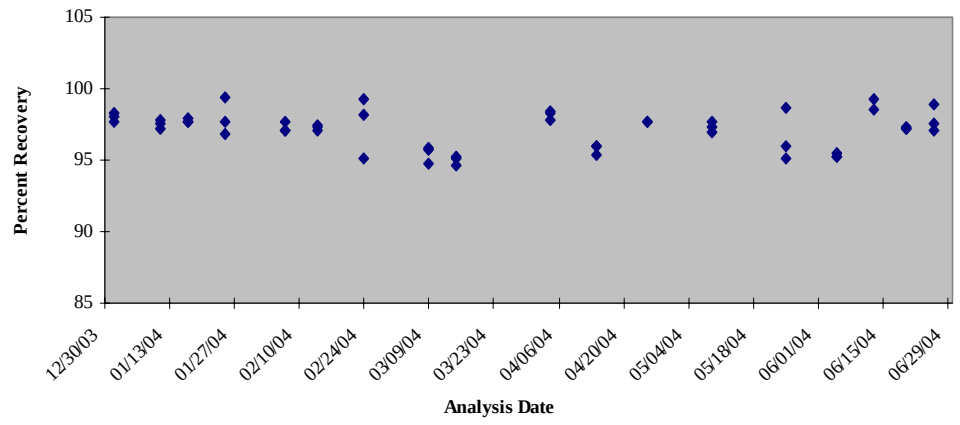


Figure 100. Recovery Precision of Titanium (Ti) in NIST SRM 1833 with RTI XRF 1

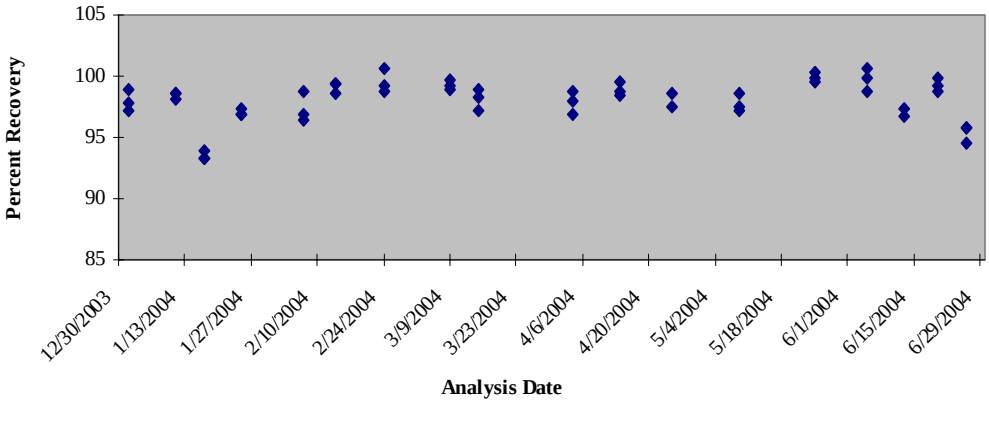


Figure 101. Recovery Precision of Vanadium (V) in NIST SRM 1832 with RTI XRF 1

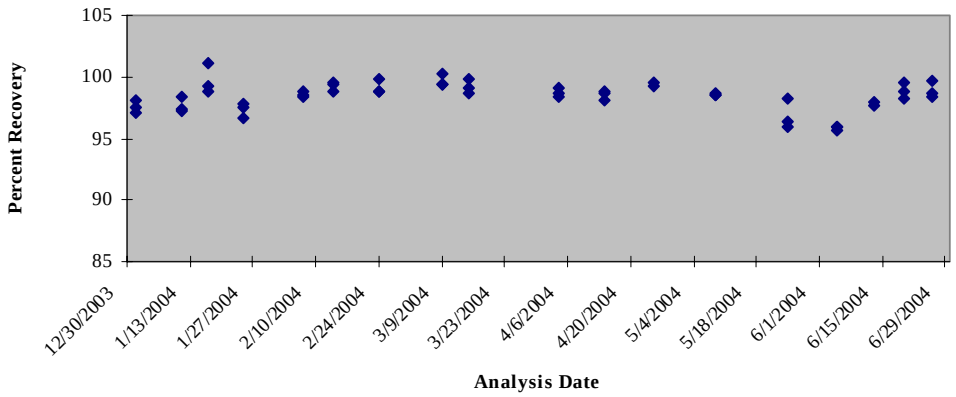


Figure 102. Recovery Precision of Manganese (Mn) in NIST SRM 1832 with RTI XRF 1

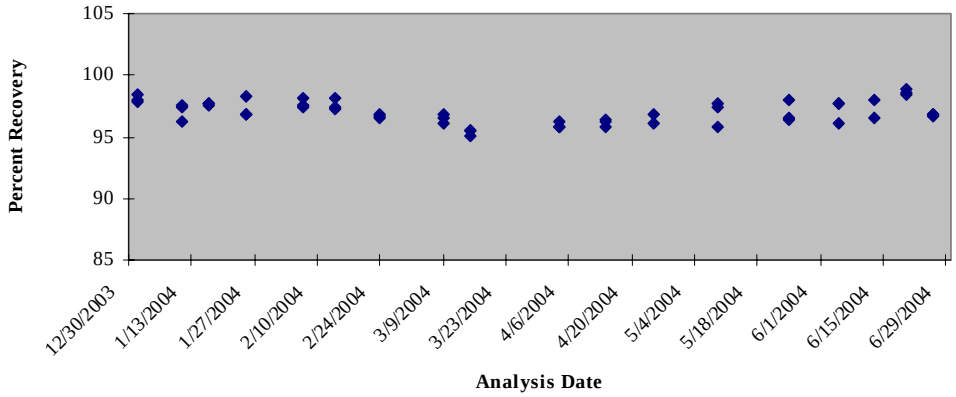


Figure 103. Recovery Precision of Cobalt (Co) in NIST SRM 1832 with RTI XRF 1

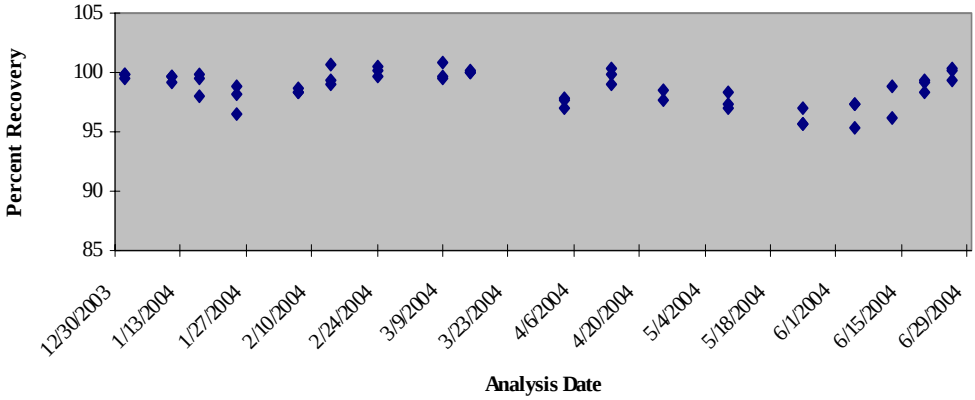


Figure 104. Recovery Precision of Iron (Fe) in NIST SRM 1833 with RTI XRF 1

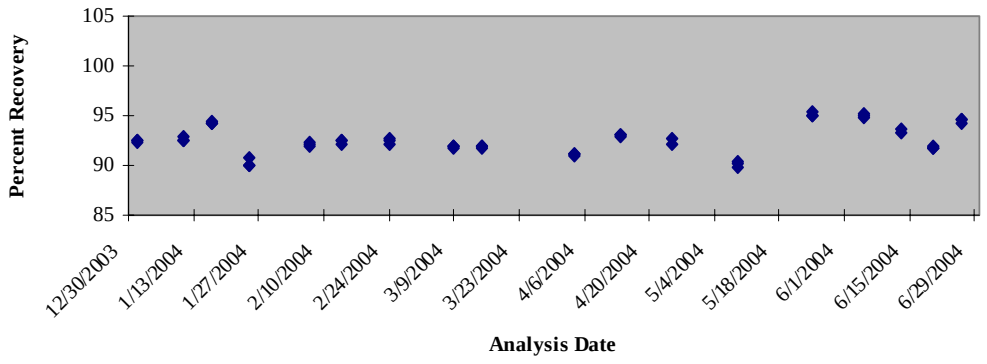


Figure 105. Recovery Precision of Copper (Cu) in NIST SRM 1832 with RTI XRF 1

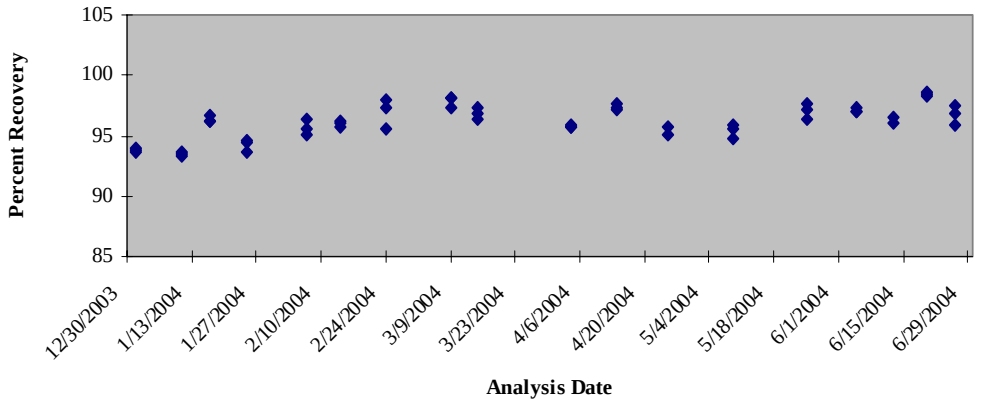


Figure 106. Recovery Precision of Zinc (Zn) in NIST SRM 1833 with RTI XRF 1

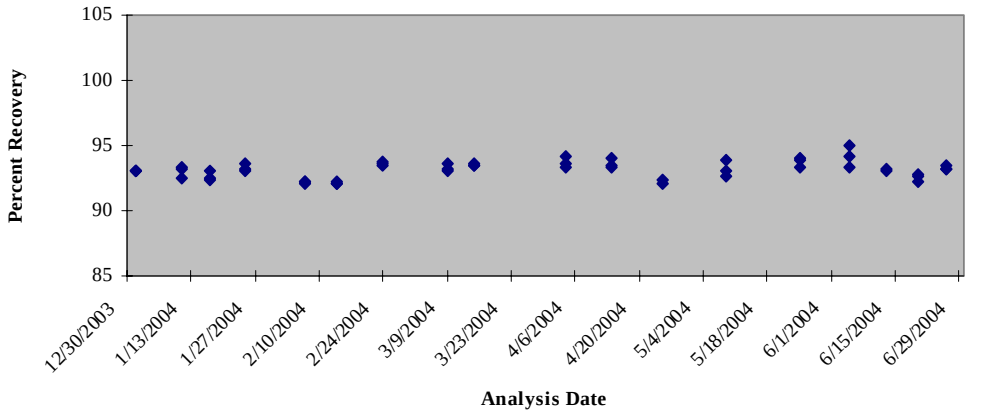


Figure 107. Recovery Precision of Lead (Pb) in NIST SRM 1833 with RTI XRF 1

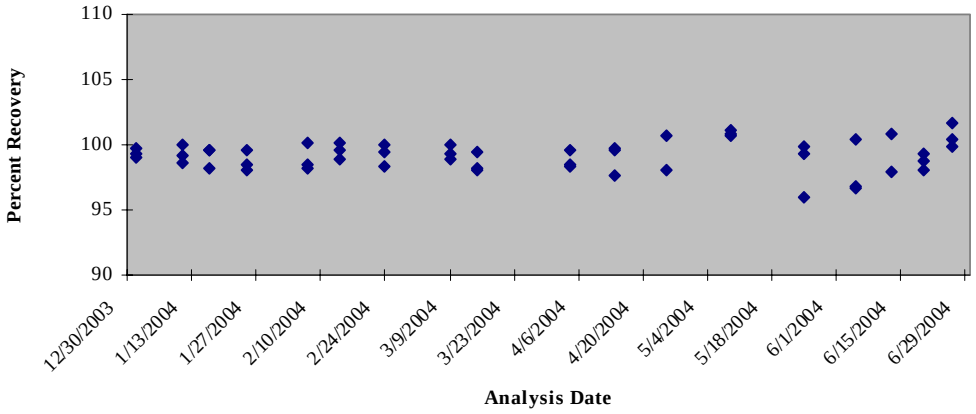


Figure 108. Recovery Precision of Aluminum (Al) in NIST SRM 1832 with RTI XRF 2

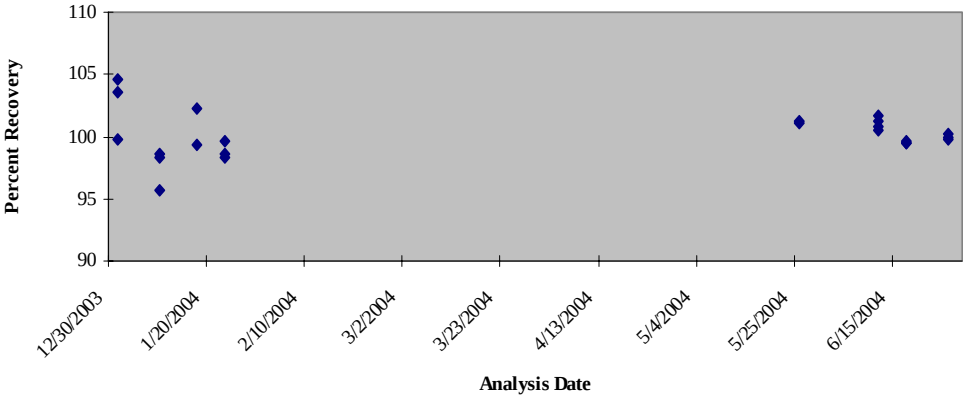


Figure 109. Recovery Precision of Silicon (Si) in NIST SRM 1832 with RTI XRF 2

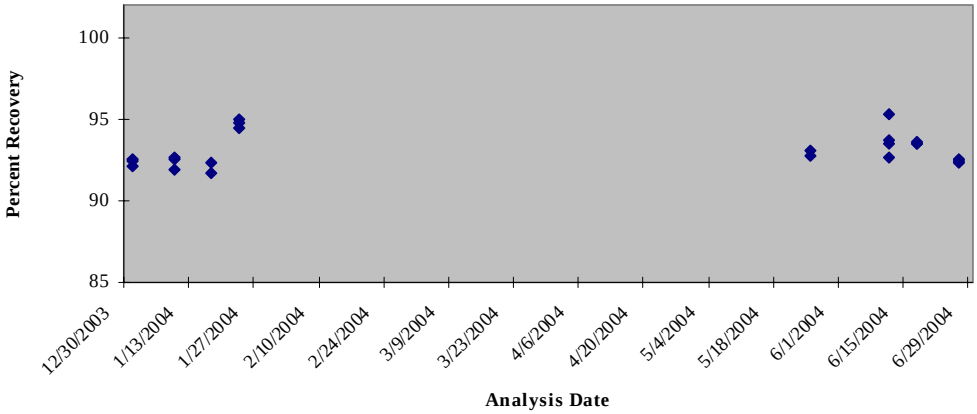


Figure 110. Recovery Precision of Silicon (Si) in NIST SRM 1833 with RTI XRF 2

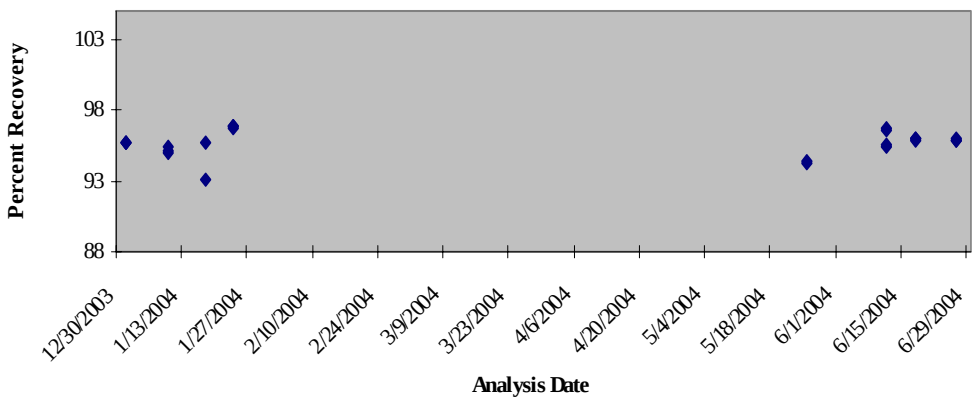


Figure 111. Recovery Precision of Potassium (K) in NIST SRM 1833 with RTI XRF 2

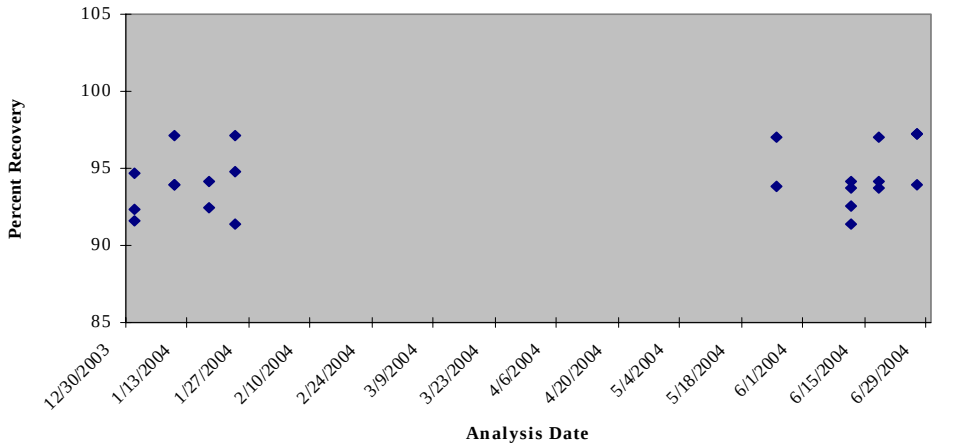


Figure 112. Recovery Precision of Calcium (Ca) in NIST SRM 1832 with RTI XRF 2

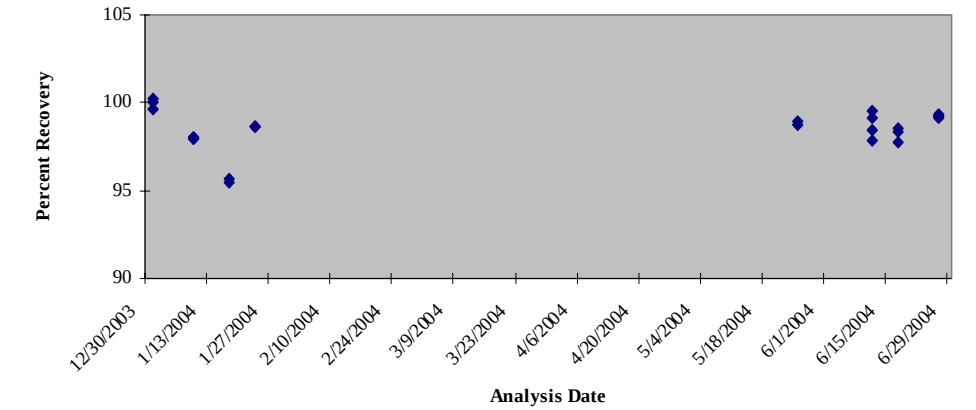


Figure 113. Recovery Precision of Titanium (Ti) in NIST SRM 1833 with RTI XRF 2

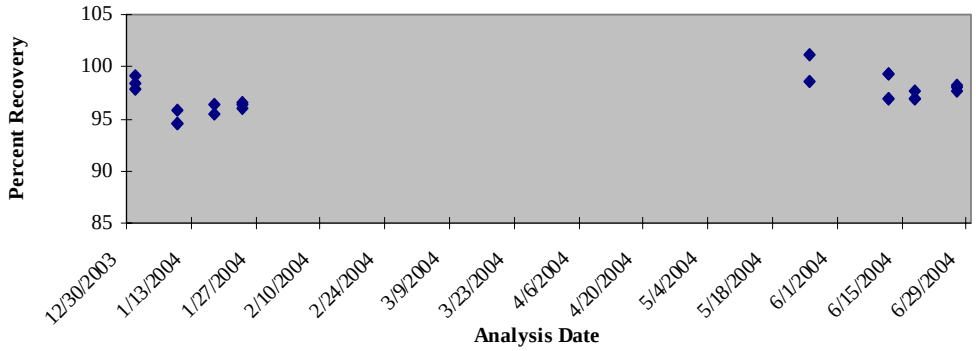


Figure 114. Recovery Precision of Vanadium (V) in NIST SRM 1832 with RTI XRF 2

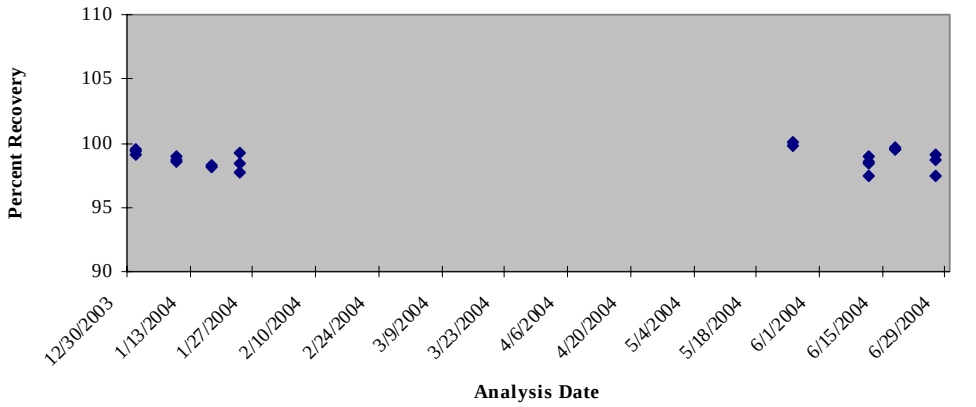


Figure 115. Recovery Precision of Manganese (Mn) in NIST SRM 1832 with RTI XRF 2

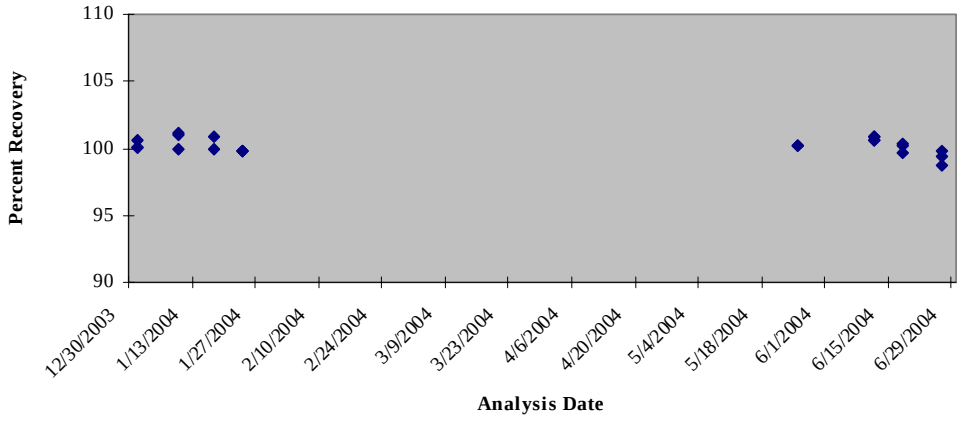


Figure 116. Recovery Precision of Cobalt (Co) in NIST SRM1832 with RTI XRF 2

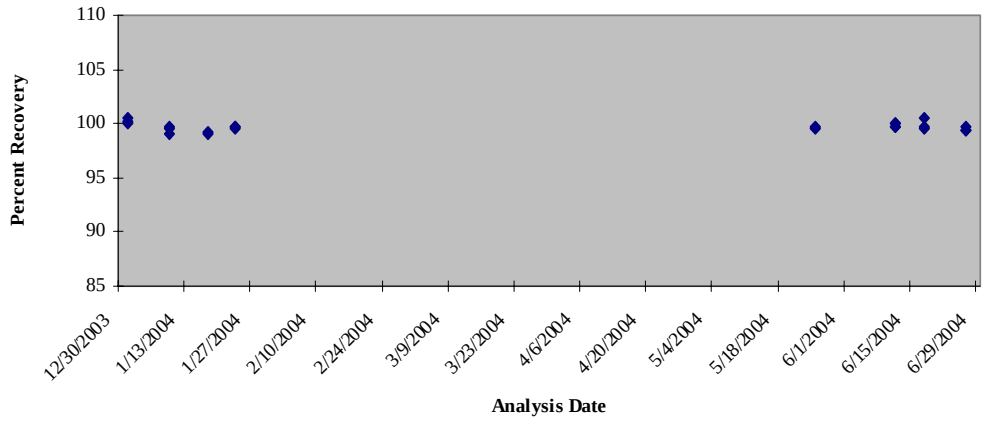


Figure 117. Recovery Precision of Iron (Fe) in NIST SRM1833 with RTI XRF 2

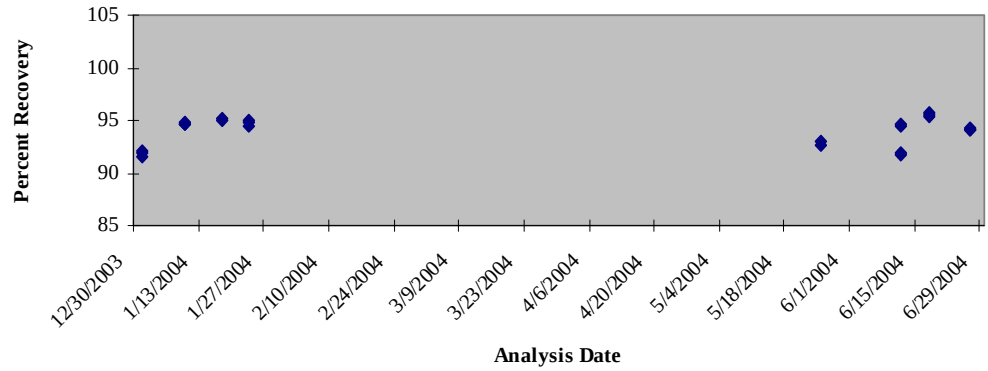


Figure 118. Recovery Precision of Copper (Cu) in NIST SRM1832 with RTI XRF 2

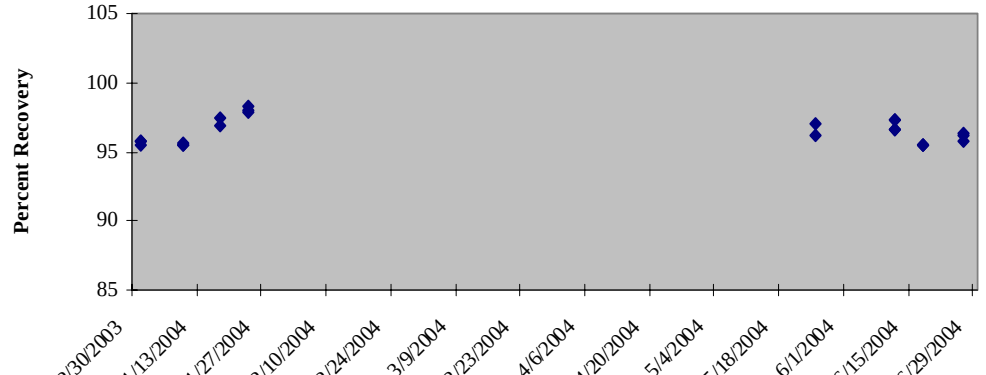


Figure 119. Recovery Precision of Zinc (Zn) in NIST SRM 1833 with RTI XRF 2

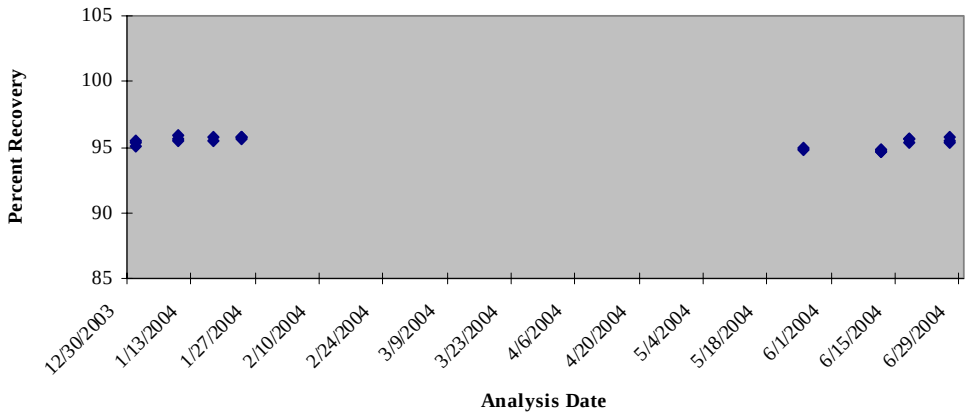


Figure 120. Recovery Precision of Lead (Pb) in NIST SRM 1833 with RTI XRF 2

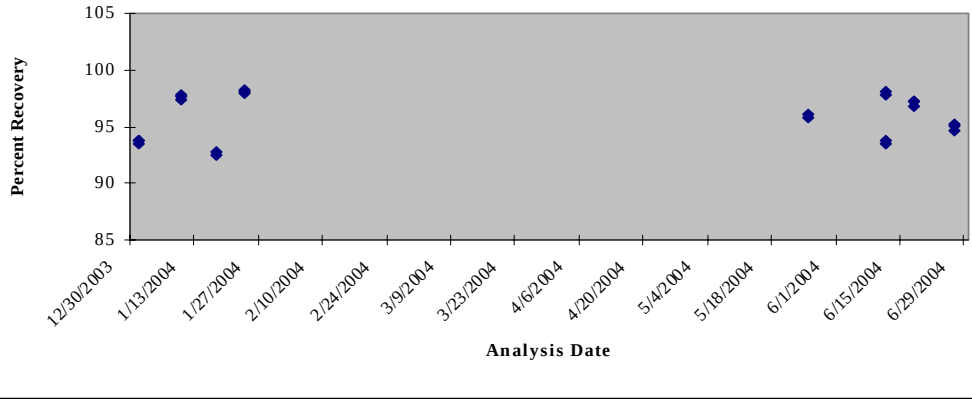


Figure 121. Results of Replicate Silicon (Si) Analysis with RTI XRF 1

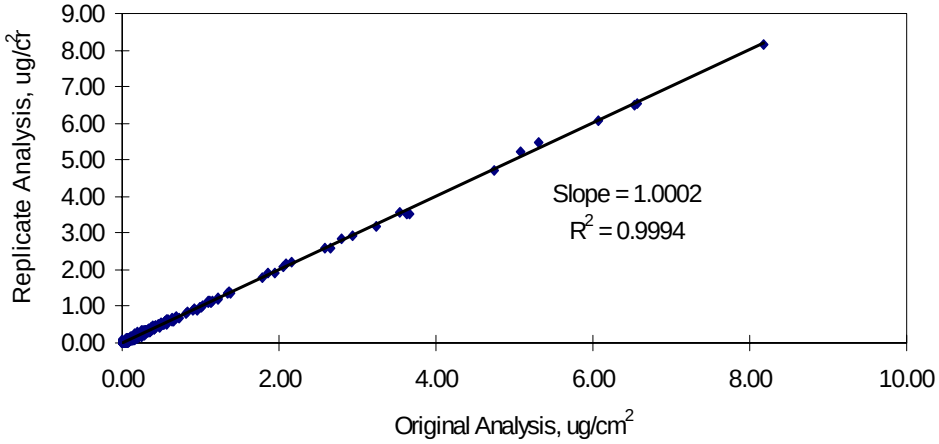


Figure 122. Results of Replicate Sulfur (S) Analysis with RTI XRF 1

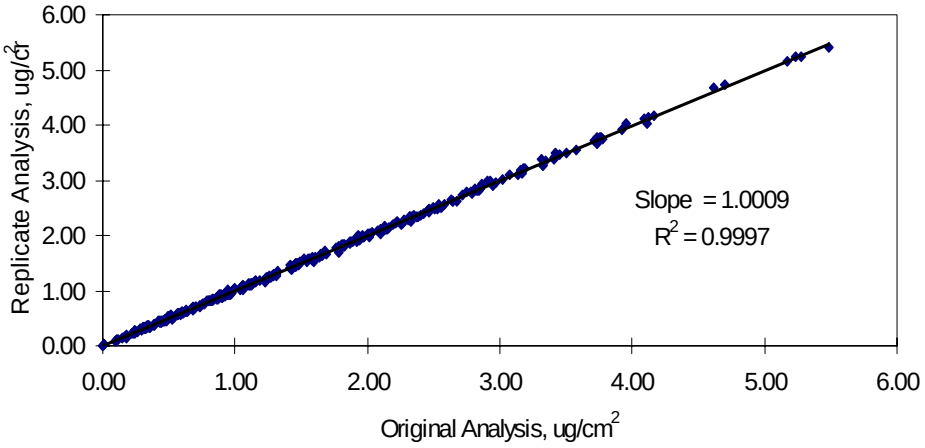


Figure 123. Results of Replicate Potassium (K) Analysis with RTI XRF1

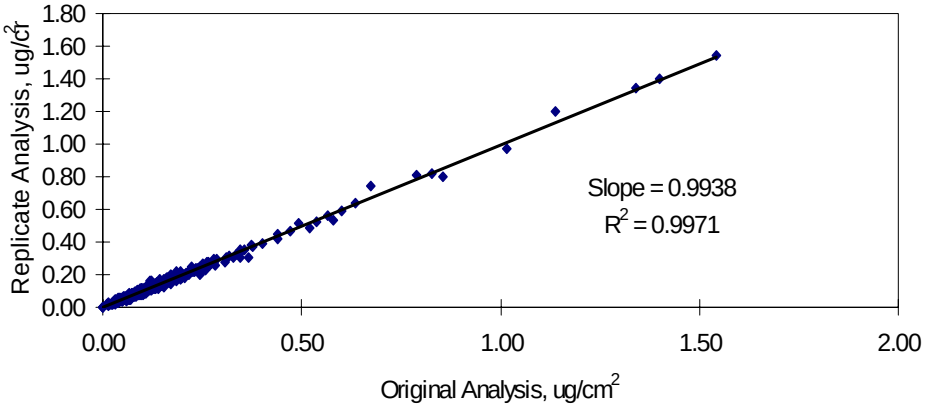


Figure 124. Results of Replicate Calcium (Ca) Analysis with RTI XRF1

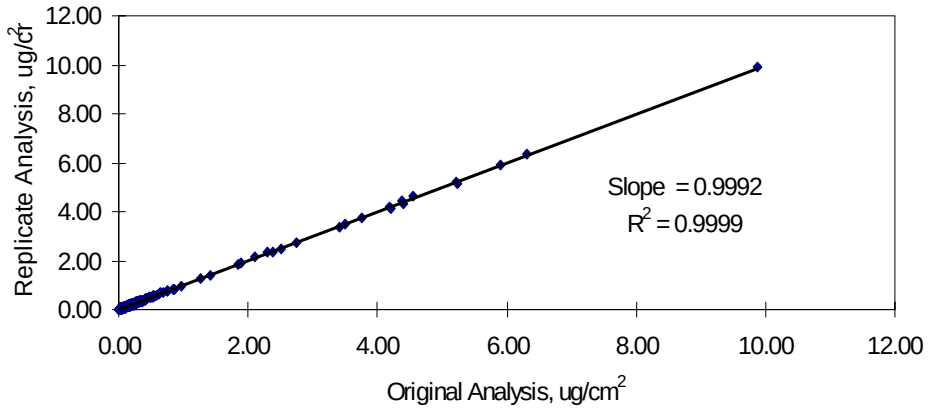


Figure 125. Results of Replicate Iron (Fe) Analysis with RTI XRF 1

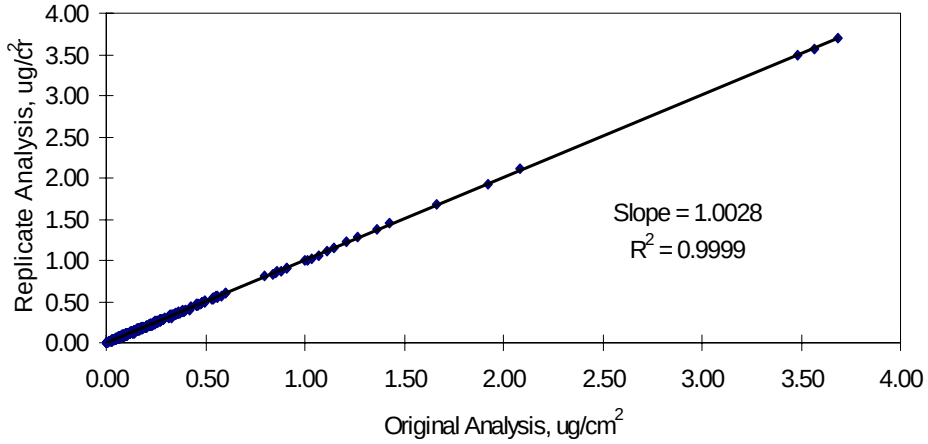


Figure 126. Results of Replicate Zinc (Zn) Analysis with RTI XRF 1

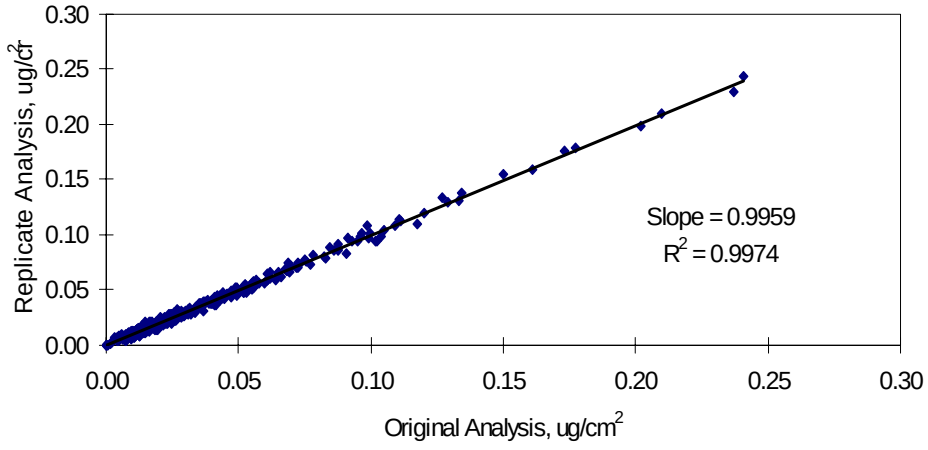


Figure 127. Results of Replicate Silicon (Si) Analysis with RTI XRF 27

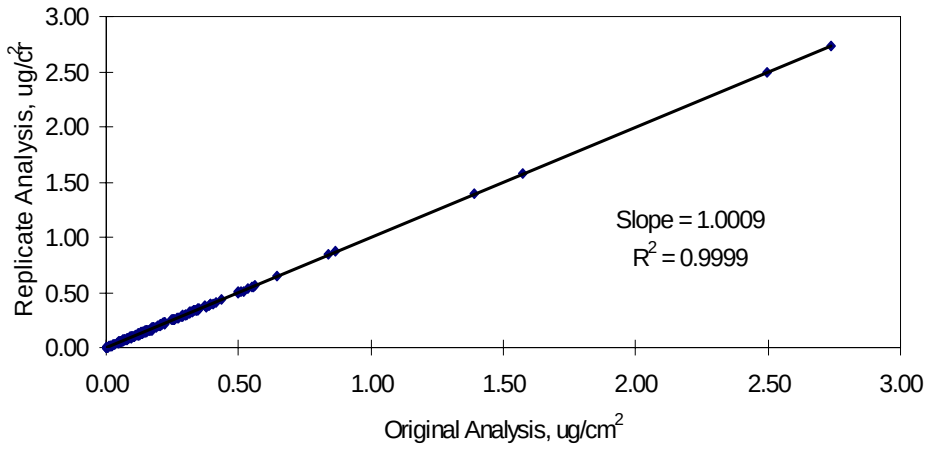


Figure 128. Results of Replicate Sulfur (S) Analysis with RTI XRF 2

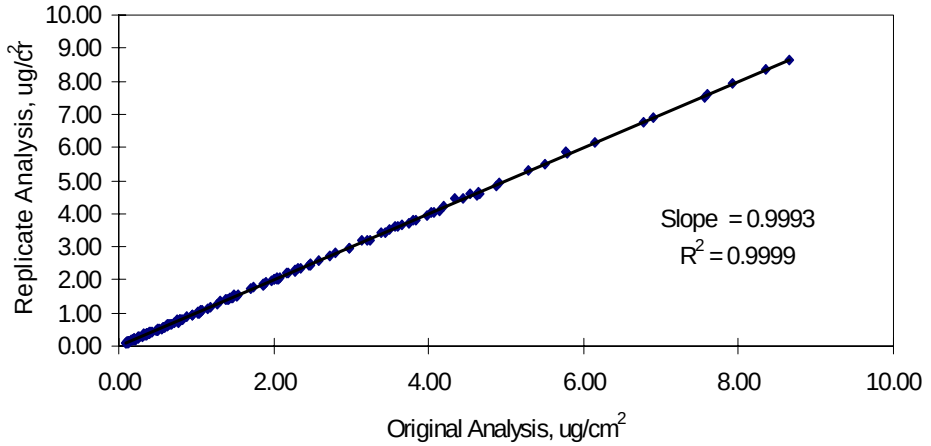


Figure 129. Results of Replicate Potassium (K) Analysis with RTI XRF 2

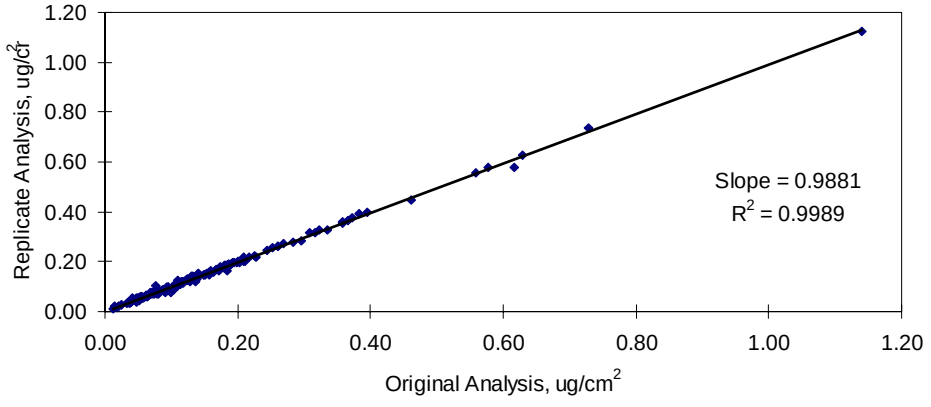


Figure 130. Results of Replicate Calcium (Ca) Analysis with RTI XRF2

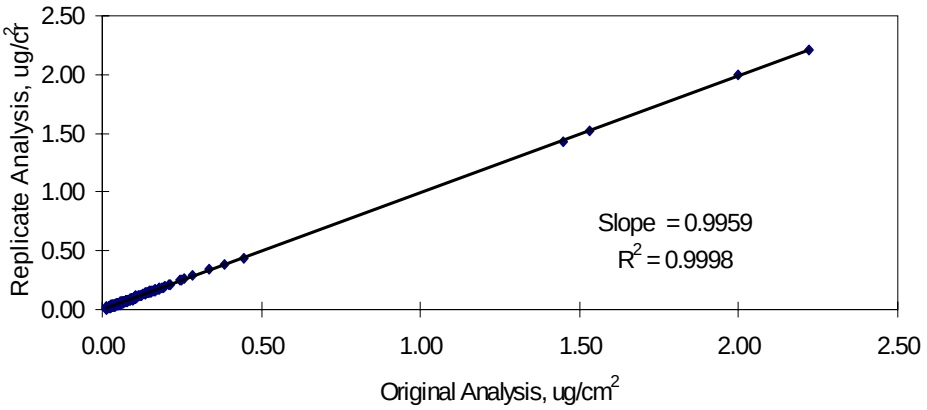


Figure 131. Results of Replicate Iron (Fe) Analysis with RTI XRF 2

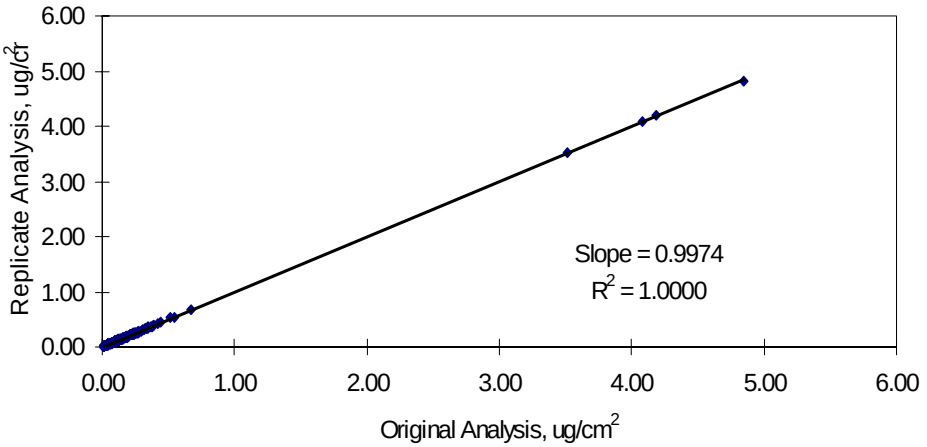
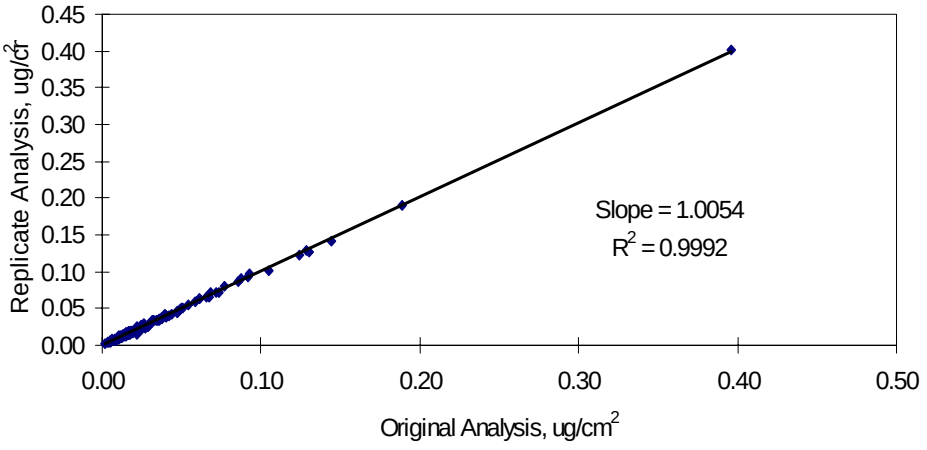


Figure 132. Results of Replicate Zinc (Zn) Analysis with RTI XRF 2

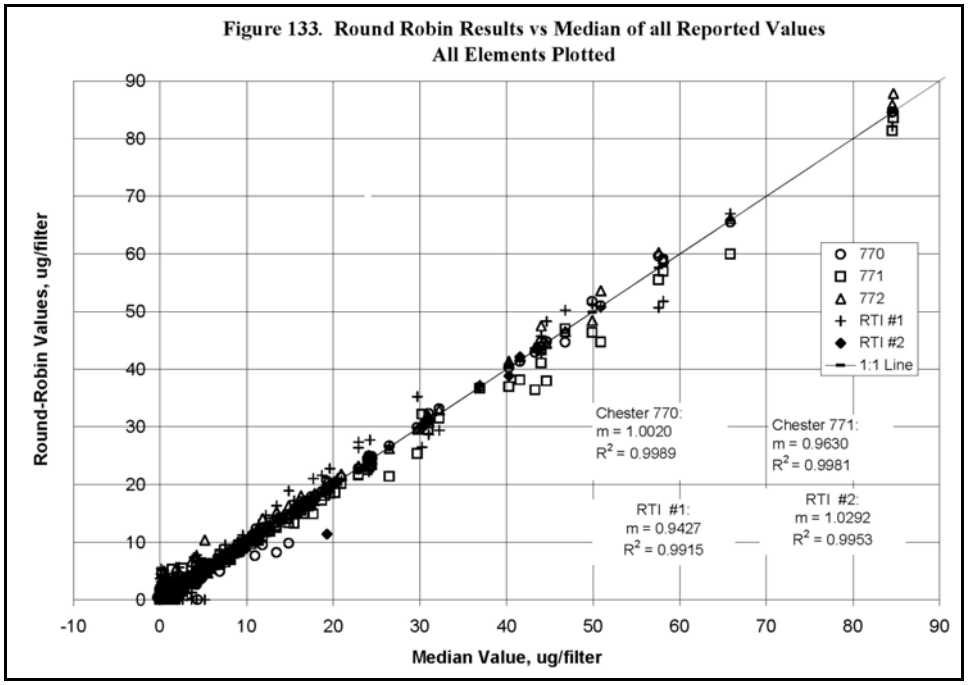


2.4.3.3 Corrective Actions – No changes were made in the analytical procedures used by the RTI XRF laboratory. However, during the six-month period there were several instrument hardware failures and a software failure after the software had been upgraded. The instruments failures at times did require instrument re-calibration, but none of the data were affected. In regards to the software failure, it only affected the significant digits when outputting the data and not the actual analysis of the data for XRF 2.

2.4.4 Round-Robin Intercomparison Results

Four different XRF instruments have been approved for use with this program. Before being accepted for use by the STN Program, each instrument was put through a series of acceptance tests using NIST reference materials and exposed STN filters. The Round-Robin program is a filter exchange whose purpose is to verify equivalency of the four instruments on an ongoing basis. To do this, exposed filters from the STN archive are being circulated among the laboratories by RTI. A total of one hundred and twenty (120) round-robin filters have been used thus far during the Speciation program. The uncertainty value for each analyte was not considered in the overall evaluation of the round robin data.

Figure 133 shows the round-robin analyses vs. the median of all observations. That is, the measured values for the 48 elements for each filter/element combination on the four instruments plotted against the median value (median value is calculated from the results for each of the four instruments). The median is used in an effort to get the best consensus value for each filter/element combination. Linear correlation equations for each instrument vs. the median value are shown, along with correlation coefficients (R-square). All four instruments have a slope greater than 0.940, which indicates good agreement between the instruments.



2.5 Sample Handling and Archiving Laboratory (SHAL)

2.5.1 Facilities

RTI has leased a 10,000 square foot facility located at 1000 Parliament Court in Durham, NC and dedicated the facility to the PM2.5 speciation SHAL laboratory. The space is approximately 3.5 miles from the main RTI campus and allows easy transfer of filters between the SHAL and the analytical laboratories. The area is a secured facility with access limited to those personnel working directly on the speciation project.

The sample handling area within the SHAL is a 4,000 square foot space equipped with fourteen workstations for the assembly and disassembly of the various filter modules. Each workstation contains a PC connected to a dedicated server and a barcode reader for inputting data into the database. As a set of speciation filters is processed, the worker immediately enters the information for the sampling event into the speciation database. This allows the information for the sampling event and tracking information for the shipment of the samples to be input directly at the time of handling. The use of barcoded labels and paperwork allows for the entry of data with minimal typographical errors.

Other features of the sample handling area include ten foot high shelving along two walls for the storage of client modules, custom built tables for the loading/unloading of the sample filters, refrigerators and freezers for storage of filters at the proper temperature, and additional space for future program needs.

The SHAL laboratory also includes a 6,000 foot warehouse area separate from the sample handling area. The warehouse area has a loading dock with pneumatic lift to accommodate different sizes of trucks. The loading dock has ample space for the unloading of incoming shipments including work areas for the measurement of the temperature of the incoming sampled filter modules. Next to the loading dock is a custom built walk-in-cooler dedicated to the speciation project. The cooler measures 16' X 10' X 7' and will hold the incoming filter modules at or below 4 degrees Centigrade. The warehouse area also has additional space if needed for future project needs and ample space for storage of packaging materials and coolers.

2.5.2 Description of QC Checks Applied

Numerous QC checks are built into the SHAL procedures. These include:

- Bar-code readers are used to input identification numbers from modules, bins, containers, and data forms to virtually eliminate data transcription errors.

- Barcoded labels with identification numbers are generated by computer and the ID numbers include a check-digit.

- The training of new employees includes a reciprocal check procedure, in which other SHAL technicians check the contents of each other's coolers before they are closed for shipment.

- Periodically all SHAL personnel review the latest version of the Standard Operating Procedure. A record of the review is included in the person's training file.

- Blank filters are taken from the SHAL refrigerator and returned unopened to the laboratories for analysis. These QC filters results are being used to improve the overall quality of the program.

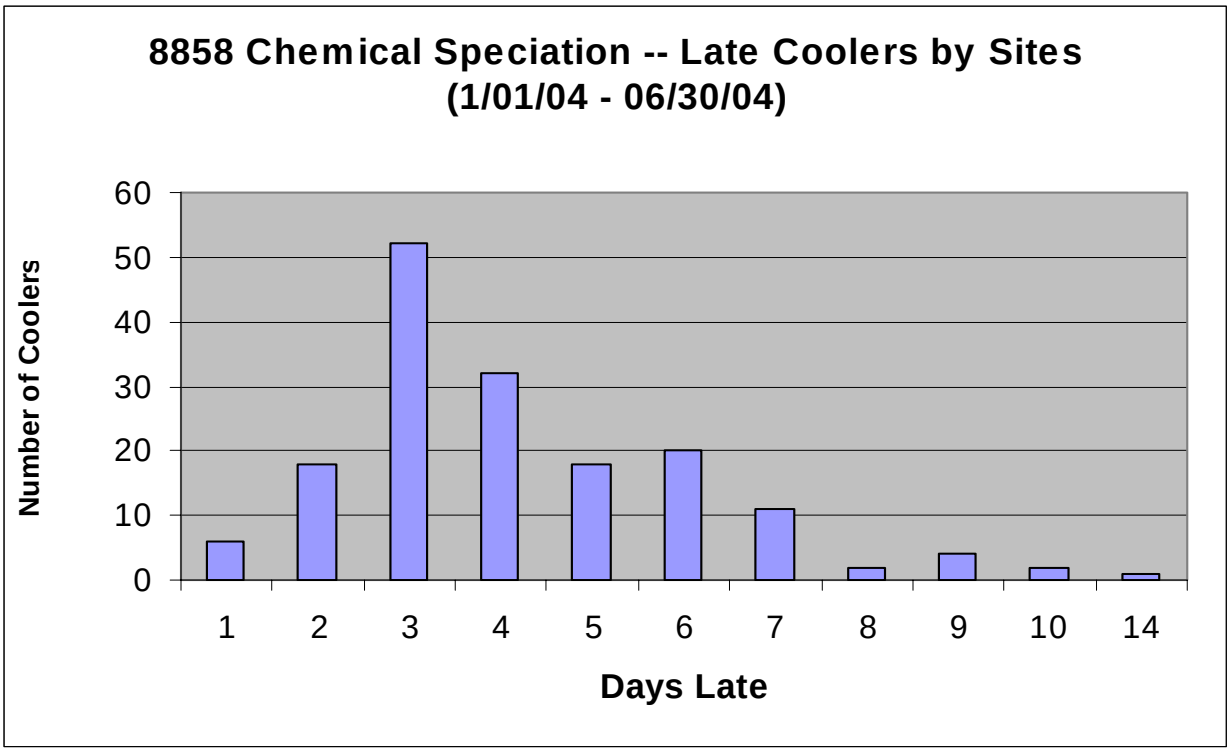
- The SHAL supervisor or his designee will periodically observe a SHAL worker performing the handling of filter modules. A checklist of correct tasks has been prepared for each type of module. The checklist is used by the supervisor during the observation of the worker handling the filters and modules. Completed checklists are kept by the SHAL supervisor. Workers are briefed following the observation of any findings. A summary of the observations for the period January 1 to June 30, 2004 is shown in the following table.

Module Type	Number Observed	Findings	Findings Reviewed With Worker
MET ONE	125	6	6
Andersen	15	1	1
Texas R&P FRM	14	3	3
URG	12	0	0
R&P Spec	17	0	0

2.5.3 Corrective Actions Taken

Problem: Coolers arriving late at the RTI SHAL laboratory delay the processing and analysis of filters and may even cause a missed sampling event if RTI cannot repack new filters into the modules and ship them to the site in time for the next sampling event. Late arriving coolers are typically due to late returns by the site or delays in transit by the carrier. A summary of late arriving coolers for the time frame of January 1 to June 30, 2004 is presented below as **Figure 134**.

Corrective Action: Late arriving coolers are usually caused by delays in the field or by Federal Express. Whenever a site has a backlog of missed shipments, it is impossible for RTI to ship a new set of modules on schedule. The DOPO is notified and the missed exposure is flagged as "scheduled but not collected" (AF).



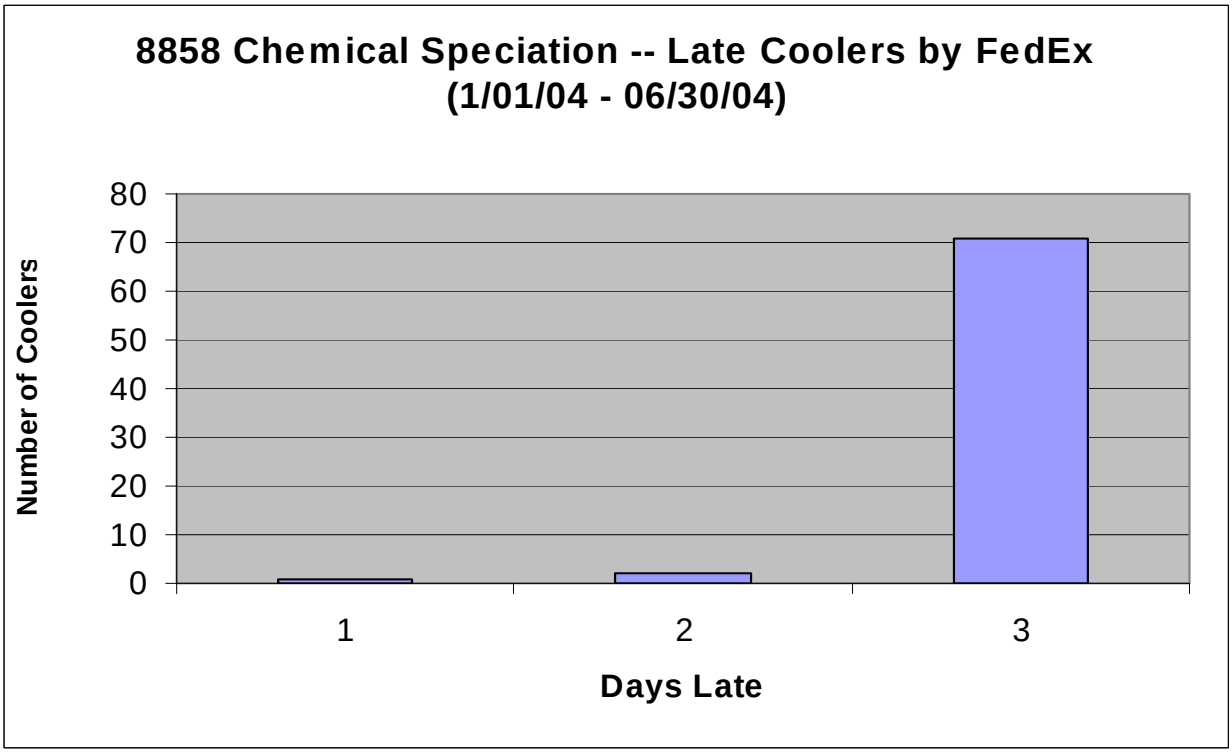


Figure 134. Graphs showing number of coolers and days late via site and Federal Express.

Problem: The SHAL found a number of tared Teflon filters with stamped unique identifying numbers that did not agree with the unique identifying number on the filter's petri slide.

Corrective Action: All incoming Teflon filters will be examined upon arrival at the SHAL laboratory to make sure the number on the petri slide matches the stamped number on the filter itself. When a Teflon filter is identified with a non-matching number on the petri slide, that filter will be sent back to the Gravimetric Laboratory to be relabeled and reweighed.

Problem: Due to illness of a SHAL employee, the SHAL refrigerator/freezer temperature logs lapsed between 4/6/04 and 6/4/04.

Corrective Action: Upon discovery of the lapse, the logs were started again. The SHAL supervisor or his designee is now reviewing the logs weekly.

Problem: Due to washing of nylon filters in the ions laboratory, the SHAL laboratory was receiving nylon filters with excessive curling. This curling made it difficult to load these filters into the R&P 2300 modules. QA review of monthly data indicated that some of the R&P 2300 modules containing nylon filters were leaking due to improper sealing of the module around the curled nylon filter.

Corrective Action: As an interim solution, the SHAL laboratory instituted a visual check of all assembled R&P 2300 modules containing nylon filters to make sure a good seal was present. In the meantime, RTI is investigating an alternate filter which would not require washing prior to use.

2.5.4 Splitting of Quartz Filters

As directed by EPA, in March of 2004, RTI began to analyze the quartz filters from eleven of the PM2.5 Speciation sites by two different analytical methods. The eleven sites selected were: Allen Park (MI), Beacon Hill (WA), Com Ed (IL), Deer Park (TX), Fresno - First Street (CA), IS 52 (NY), Lawrenceville (PA), North Birmingham (AL), Phoenix Supersite (AZ), Riverside - Rubidoux (CA) and South DeKalb (GA). Each quartz filter from the eleven sites would be analyzed by the RTI STN method and the DRI IMPROVE method.

To accomplish this, each filter would be split in half in the SHAL laboratory with one half being sent to the RTI OC/EC Laboratory for analysis by the STN method and the other half being sent to DRI for analysis by the IMPROVE method. The splitting of the quartz filters was accomplished using a custom made aluminum jig. The sampled quartz filter was placed into a recessed well in the jig and a sharp blade was run across the filter using a plastic guide to correctly split the filter into two equal halves.

All split quartz filters were kept frozen in the SHAL until transferred to the appropriate laboratory. One overnight shipment of filters was sent from RTI to DRI each week. These filters were packaged in a small cooler with frozen blue ice packs to keep the filters cold during transit.

2.6 Denuder Refurbishment Laboratory

The Denuder Refurbishment Laboratory is located in RTI Building No. 3, laboratory 220. The purpose of the laboratory is to clean and refurbish the coatings on acid-gas-removing denuders used in samplers of chemical speciation networks operated by EPA and various State and local agencies which utilize the RTI/EPA contract. The laboratory follows these protocols:

- Procedure for Coating Annular Denuders with Magnesium Oxide
- Standard Operating Procedure for Coating and Extracting Annular Denuders with Sodium Carbonate
- Procedures for Coating R & P Speciation Sampler "ChemComb" Denuders with Sodium Carbonate
- Standard Operating Procedure for Coating Annular Denuders with XAD-4 Resin.

Denuders for the Andersen and URG speciation samplers are being cleaned and then re-coated with magnesium oxide. They are replaced at the sites at 3-month intervals. The last denuder replacement cycles occurred in January and April 2004 ; the next scheduled change-out will occur in July 2004.

MetOne speciation sampler aluminum honeycomb denuders are also coated with magnesium oxide. Because the MetOne denuders are part of the sampling module and six sets of modules are in circulation to each site, these denuders are refurbished at 18-month intervals. RTI is able to remove MgO from denuders using a dilute hydrochloric acid solution. As needed, RTI orders uncoated aluminum honeycomb denuder substrates from MetOne, cleans them with solvent and deionized water, and then coats them with magnesium oxide. The change-out occurs whenever the MetOne denuder assembly has been in use for 18 months.

R & P ChemComb™ glass honeycomb denuders are cleaned and coated with sodium carbonate/glycerol. R & P denuders are replaced after each 24-hour sampling use.

No XAD-4 resin coated denuders (for removal of organic vapors) were ordered by EPA/OAQPS during the reporting interval.

The only significant problem encountered in the reporting period of operation has been the occasional receipt of broken or loose glass denuders.

As personnel assignments changed, additional workers were trained in the techniques of denuder refurbishment. Hands-on training was conducted according to the several SOPs for denuder refurbishment.

2.7 Data Processing

2.7.1 Operational Summary

Two major changes were made to improve program efficiency and data quality:

- Introduction of a new database and application for gravimetry data.
- Transfer of database operations to a new server

These changes are described below.

2.7.2 Operational Changes and Improvements

2.7.2.1 New database and application for gravimetry laboratory - Previously, the gravimetry laboratory had used Excel spreadsheets to store their weighing (pre and post) information. A new database application and database were created to store this information in a central location and to make operations more efficient and improve data quality. The new application improves efficiency by:

- facilitating data entry and data review
- facilitating matching of pre- and post- weights
- facilitating transfer of preweight information (used for XRF sample background correction) to laboratories
- facilitating transfer of filter information (used for QC checking during assembly) between the gravimetry laboratory and the SHAL.

In addition, the new application improves data quality by eliminating hand matching of pre and post weight data and by providing easier access to long-term data for evaluating control trends.

2.7.2.2 New database server - Database activities were moved to a new server that is operated by RTI's Ragland Computer Center (RCC). This new server has significantly more memory and a faster processor. Together, this provides for faster operations and allows us to perform more intricate queries for quality review. Transfer of operations to RCC's server facilities provided enhanced operational support, including include continuous server monitoring, automated backup, and continuous emergency power.

2.7.3 Problems and Corrective Actions

No significant problems or corrective actions for data processing occurred during the period.

2.8 Quality Assurance and Data Validation

2.8.1 QA Activities

QA activities directly related to data validation are described in the PM2.5 Chemical Speciation Laboratory QAPP (January 2004), and include the following:

- Review of monthly data reports sent to the state monitoring agencies and EPA
  - Verification of data attribution to the correct site, POC, and date
  - Review of report formats
  - Troubleshooting when discrepancies are found
  - Running manual and partially-automated range checks
  - Reviewing the results of fully-automated validation checks
  - Application of Level 1 outlier screening criteria.
- Review of each data batch before it is sent to AIRS
  - Verification of data attribution to the correct site, POC, and date
  - Verification that changes requested by the state monitoring agencies have been correctly made by the Data Processing personnel
  - Review of data format to be sure that records and individual fields are of the correct length.
- Troubleshooting of sample and data problems that cross the boundaries between laboratories, the SHAL, and/or the data processing function.

2.8.2 Data Validation Procedures

The full scope of the Level 0 and Level 1 procedures carried out by RTI before data are delivered to the state monitoring agencies each month are described in the Laboratory QAPP (January 2004).

The data validation procedures described in previous QA Reports continue to be performed as described there and in the Laboratory QAPP. Some of the screening procedures have been automated to speed the monthly review process; however all questionable data identified by automated screening continue to be reviewed by a data validation staff member.

Some additional validation checks have been added to improve tracking of changes between batches. These include summaries by batch of the number of records that contain AIRS null value codes and AIRS validity status codes. These checks allow QA review of trends and to spot sudden changes in the performance of the validation checks.

Because the EPA has recently expressed interest in reporting blank samples to AQS, RTI is making extra effort to resolve problems with the blank data such as "swaps" between exposed and unexposed filters due to handling or data entry. Whenever filter swaps cannot be resolved with high confidence, the affected filter(s) will be invalidated.

2.8.3 Corrective Actions

Current and previously reported problems are discussed in this section. Where a Corrective Action Request (CAR) has been issued, the CAR number is provided. Recent CARs are summarized in the following table.

CAR #	Title	Date Opened	Date Closed
001	Mismatched Teflon Filters & Bar Codes	1/21/04	1/23/04
002	Secondary Channel Negative Temp Reported as Zero	3/24/04	3/31/04
003	Lab Blank w/Excessive Weight Change	3/26/04	3/30/04
004	Data Validation Turn Around Time	3/11/04	4/1/04
005	Training Issue in Grav Lab	5/19/04	7/16/04
006	Nylon Filters Curling in R&P Modules	6/17/04	OPEN
007	Gap in Refrigerator/Freezer Monitor Logs	6/7/04	6/17/04

2.8.3.1 Current Issues –

Mismatched Teflon Filters and Bar Codes (CAR 1)

In September 2003 approximately nine Teflon filters were found to be in the incorrect petri slide according to the number printed on the filter itself. The label on the petri slide did not agree with the imprinted printed number. These errors were tracked down by SHAL and gravimetric laboratory personnel and fixed on an ad hoc basis. Affected data for exposed filters (filters used as blanks or routine samples) were carefully evaluated to be sure that they had been assigned to the correct event.

Because of persistent problems of this type, RTI has just instituted new procedures designed to intercept discrepancies of this type before the filters are used for sampling. This will involve manual checks of both the labels and the filters as they enter the gravimetric lab or the SHAL, respectively. These checks are continuing in both the SHAL and Grav lab, and are effective in identifying occasional filter misidentification. The problem was documented in CAR 001, issued in January 2004.

Secondary Channel Negative Temp Reported as Zero (CAR 2)

Due to reporting changes required by the new contract, temperatures less than zero were reported to the states as zero for channels other than the Teflon filter channel. Only temperatures less than zero were affected. Only the plain text report (RTF file) was affected. Neither the spreadsheets nor the AQS data were affected by this problem.

The RTF reporting software has been corrected so that negative temperatures in future reports will be correct. In addition, at least one RTF file will be reviewed manually during monthly data validation to scan for this or any other problem that may have occurred with the reporting software or data.

Lab Blank with Excessive Weight Change (CAR 3)

The Grav Lab identified a lab blank that gave weight changes in the range of -30 micrograms upon re-weighing. This exceeded the ±15 microgram QC limit for lab blanks. It was thought that this might be evidence of contamination during initial tare weighing: probably a bit of "fluff" or dust that was initially on the filter, but which came off subsequently.

Procedures were revised so that each weighing session is assigned its own lab blank so that the grav lab will be better able to track contamination issues and the lab blank QC check will be better applied to a discrete set of samples weighed on one date. If the re-weight recorded for any of the lab blanks differs from the tare weight by more than 15 micrograms, all filters tared with that lab blank will be re-weighed and the filters will be flagged appropriately The grav lab supervisor will amend the gravimetry SOP to more clearly define a weighing session and the steps to be taken to designate filters for use as lab blanks. In addition, it was noted that grav lab staff must adhere to the regular monthly cleaning schedule to minimize contamination.

Data Validation Turn Around Time (CAR 4)

During screening of data for the March 15 data delivery, it was noticed that an unusually large number of sulfur/sulfate ratios were out of limits for a particular sampling date. This was traced to a problem in one of the RTI XRF instruments' method files that made the sulfur results approximately 25% low. No other elements were affected. The problem with the method file was corrected and the sulfur data were calculated.

A meeting was held on 3/16/04. A need for earlier feedback on the results of Level-1 checks with the laboratories was identified. Under the existing data handling procedures, the Level-1 checks are not run until the data set is nearly complete, typically 3-5 days prior to the due date of the data. If systematic problems are found in a lab's data, there is little time for corrections to be done before the data are due to EPA. An additional issue is whether the labs are doing enough Level 0 QC checks, and whether these checks are being reviewed adequately.

Training Issue in Grav Lab (CAR 5)

Problem: A number of anomalous mass results were noticed in the gravimetric data in mid-May. In each case, the common factor was found to be a particular weighing technician who had transferred in January 2004 to the Grav Lab from another position at RTI. After the normal training period of several months, the employee had been allowed to work on his own without close supervision. (Requirements for the work performed are found in the attached job description.) The first problem identified appeared to be mixing up filters so that the weighing data did not correspond to the filter numbers entered into the computerized weighing station. Typically, a series of 10 to 20 filters would be offset by one or two positions in the database.

Short Term Solution: After the anomalous data were discovered and the source of the problem was identified, the laboratory supervisor took steps to ensure that the employee received mentoring and supervision by a more experienced technician. However, after several weeks

working under close supervision, other procedural problems were identified and it was decided that the employee should be reassigned to the job which he had previously performed satisfactorily prior to his transfer into the Grav Lab.

It was possible to identify and fix most of the data that had been misassigned due to misordering of filters, since the errors were generally a consistent offset in filter numbering within a series of 10 to 20 filters that had been weighed sequentially. Data for filters that could not be reassigned unambiguously were invalidated.

Long Term Solution: In cases of lateral transfer of employees into the Grav Lab from other RTI operations, all pre-qualification steps must be followed, including interview and evaluation of credentials to ensure that the minimum requirements stated in the attached job description are met. The Grav Lab training program will be expanded to include ongoing external QC checks of a new employee's results by a second person. The SOP for the Grav Lab will be revised to reflect this change in training procedure.

Nylon Filters Curling in R&P Modules (CAR 6)

It was found that a number of nylon filter results from a set of collocated R&P2300 samplers were unusual. One sample of the pair would be lower or higher than the other, indicating a possible leak. In addition, an unusual number of sulfur/sulfate ratio outliers were found in batches SS outliers in batches 52, 53 and 54 for the R&P samplers.

Investigation found that the R&P 2300 filter holder was sometimes not holding the nylon filters securely, resulting in a leak. Washing the nylon filters in triplicate was causing increased curl compared with unwashed filters. The R&P filter modules were slightly different than other types of modules and were more difficult to close, resulting in occasional gaps allowing air to leak past the filter.

(1) Near-term solution - A SHAL supervisor will inspect all outgoing R&P2300 nylon filters to be sure that they are securely in place in the module.

(2) Longer term solution - The IC laboratory will investigate the feasibility of switching to a different type of filter that does not require washing in order to meet acceptance limits for the ions (1 microgram per filter for sodium, potassium, ammonium, nitrate, and sulfate). This investigation is continuing, and a proposal will be submitted to EPA.

Possibly the fumes in June. We looked at the data and no high values were seen for modules assembled on that date.

Gap in Refrigerator/Freezer Monitoring Logs (CAR 7)

Due to illness of the employee who had been assigned to maintain the logs for the refrigerators and freezers in the SHAL, the daily temperature monitoring logs lapsed between 4/6/04 and 6/4/04. The refrigerators and freezers are used to store unsampled filters for a period of up to several weeks. Sampled filters removed from incoming modules may be stored for a short period of time (typically no more than a day) before they are sent to the labs for analysis.

When the problem was identified by the SHAL supervisor, the logs were restarted immediately. The SHAL supervisor will check that logbook at least once per week, and responsibility for checking the temperatures will be distributed among different staff members.

Since no mechanical problems with the refrigerators and freezers in the SHAL were noted during the period when logs were not being recorded, RTI does not believe that any data were affected.

Prior Issues

Issue: R&P Sampler Inlet Dirty

Inspection by an operator in the field indicated that impactor grease, which was visible through the module inlet, appeared dirty. This report raised a concern because opening any STN module in the field is strongly discouraged since it can lead to filter damage or contamination. However, when the operator was contacted, it was determined that the module had not been opened to conduct the inspection. The R&P sampler is different from all the other sampler types because a viscous silicone grease is used to coat the impactor plate. RTI's procedure for renewing the grease before each new usage does not require complete replacement of the grease; instead, only the contaminated spot in the middle of the plate is removed, additional grease is added as needed, and the surface is smoothed over with a straightedge. In this process, some visible contaminants can remain within the layer of grease; however, it is very unlikely that this visible discoloration will contaminate the sample.

RTI's operational response was to institute a policy that all R&P sampler modules should be checked by senior personnel before they are sealed. This inspection policy is continuing (as of 7/2004).

Issue: Blank Values not Printed in Monthly Text Report in Batch 47

Due to an error in data processing the report which lists all the data in a text (RTF) format omitted the trip and field blank masses in batch 47, delivered in December 2003. Reports in other formats were not affected by this processing error.

The data were reprocessed and reposted on RTI's web site. Reports for batch 48 were manually checked to verify that the problem did not reoccur. Future batch reports will be spot-checked to be sure that formats are correct on the RTF reports. Spot checking of RTF reports is continuing (as of 7/2004).

Issue: Blank Values Flagged incorrectly on Batches 44 and 45

Due to an error in AIRS code processing introduced by new requirements for reporting blank data to AQS (formerly AIRS), the "AM" null value code was erroneously assigned to all Trip and Field Blanks. This affected the RTF files and mass summary spreadsheets and prevented values from being printed for blanks in either report.

To address this problem, RTI cleared the erroneous "AM" codes and reran and reposted the data reports for delivery batches 44 and 45. No data reported to AQS were affected, and all the correct blank values and other flags were correct in the spreadsheet files that are reported to the states.

The data were regenerated, the reports reposted on the web site, and the states were notified of the re-posting of the RTF files. No further instances have been noted as of 7/2004.

2.8.3.2 Prior Issue: MetOne Date/Clock Problem March 2003 –

A leap year problem was seen with the internal date for the MetOne SASS units that sampled in early March 2003. Fourteen of the 50 SASS units reported elapsed sample times of 48 hours instead of the normal 24. A software bug in the sampler was found to be the problem. The SHAL was on the alert for a potential reoccurrence of the problem in February/March 2004, but no problems were seen.

3.0 Data Validity and Completeness

3.1 Summary of Scheduled Samples

Routine samples were scheduled on 1-in-6 and 1-in-3 day schedules during the reporting period for this report, delivery batches 48 through 54. **Table 26** summarizes the delivery batch by delivery date covered by this report. To avoid confusion, RTI does not report partial results for any exposure session, but waits until all the analysis results are complete before an event is reported.

Table 26. Delivery Batches by Delivery Date

Delivery Batch ID	Report Date	Earliest Sample	Latest Sample	Number of Samples
48	1/15/2004	11/17/2003	12/11/2003	1786
49	2/15/2004	12/14/2003	1/13/2004	1844
50	3/12/2004	1/16/2004	2/15/2004	2116
51	4/12/2004	2/12/2004	3/10/2004	1510
52	5/13/2004	3/10/2004	4/12/2004	2039
53	6/11/2004	4/15/2004	5/15/2004	2120
54	7/14/2004	5/15/2004	6/14/2004	1987

Turnaround times from sample receipt remained steady during the reporting period, as shown in **Table 27**. Turnaround time is defined as the elapsed time from receipt of a cooler at the SHAL for a completed event, and the reporting of the data from that event.

Table 27. Data Turnaround Times

Delivery Batch	Date	Turnaround Time (days)	Number of Events
48	1/15/2004	41	1748
49	2/15/2004	42	1802
50	3/12/2004	37	2066
51	4/12/2004	40	1469
52	5/13/2004	41	2039
53	6/11/2004	38	2120
54	7/14/2004	39	1987

3.2 Trip, Field, and SHAL Blanks

The number of blanks run during this period are summarized in **Table 28**. Blank data are not currently submitted to AIRS, but are reported to the state monitoring agencies and to EPA for statistical analysis. RTI will report blank data to AIRS whenever a format for reporting is finalized by EPA. As required by the QAPP, trip blanks are being scheduled at a frequency of one per 30 regular exposure events, and field blanks are scheduled at a rate of one per 10 regular exposures. However, use of the "alternate schedule" at sites where operators do not work on weekends has resulted in a larger proportion of Trip Blanks than required by the QAPP. Some routine samples that are not run are converted to additional Trip Blanks or Field Blanks provided that the site operator indicates that the correct SOP has been followed. Other unexposed samples are designated "unsampled blanks" when it is not clear what protocol the operator followed.

Table 28. Number of Blanks Reported in Batches 48 through 54

Delivery Batch	Sample Type	Number of Samples
48	FIELD BLANK	284
48	ROUTINE	1396
48	TRIP BLANK	68
49	FIELD BLANK	171
49	ROUTINE	1585
49	TRIP BLANK	46
50	FIELD BLANK	287
50	ROUTINE	1642
50	TRIP BLANK	137
51	FIELD BLANK	138
51	ROUTINE	1307
51	TRIP BLANK	24
52	FIELD BLANK	313
52	ROUTINE	1672
52	TRIP BLANK	54
53	FIELD BLANK	144
53	ROUTINE	1715
53	TRIP BLANK	261
54	FIELD BLANK	302
54	ROUTINE	1615
54	TRIP BLANK	70

Table 29a summarizes the Trip and Field Blank results for the reporting period. Levels are comparable with those seen previously. The comparatively high values for Organic Carbon, which are typically around 10 micrograms per filter, are thought to be due to adsorption of VOCs from the air.

Table 29b shows averages for SHAL blanks, which are blank filters that are simply sent to the SHAL and returned to the laboratory, but are not mounted in modules or sent to the sites. Because of the low number of total samples, the SHAL blanks are not broken out by delivery batch. Compared with the Field and Trip Blanks, the SHAL blanks have lower background values for most analytes, particularly gravimetric mass and organic carbon, which may reflect real differences in the opportunity for filter contamination between the Trip/Field blanks and the SHAL blanks. Organic and Elemental Carbon are analyzed by two different laboratories, RTI and DRI, which perform the STN method and Improve method, respectively. Since the filters sent to DRI are in transit for several days longer than the filters analyzed by RTI, it is not surprising that the background levels are slightly higher.

Table 29a. Trip and Field Blanks Average for the Reporting Period (µg/filter)

Trip Blanks Analysis	Analyte	Batch Number						
		48	49	50	51	52	53	54
Mass - PM2.5	Particulate matter 2.5u	9.83	11.18	7.07	9.00	10.48	11.24	8.56
OC/EC - STN	Organic carbon	10.01	9.18	9.16	10.22	9.91	10.49	10.63
OC/EC - STN	Elemental carbon	0.16	0.07	0.07	0.21	0.18	0.07	0.29
Sulfate - PM2.5	Sulfate	0.12	0.27	0.50	0.35	0.50	0.50	0.41
Nitrate - PM2.5	Nitrate	0.65	0.69	0.87	0.76	0.64	0.70	0.60
Cations - PM2.5 (NH4, Na, K)	Sodium	0.03	0.12	0.08	0.03	0.14	0.36	0.12
Cations - PM2.5 (NH4, Na, K)	Ammonium	0.00	0.00	0.00	0.00	0.08	0.01	0.04

Field Blanks Analysis	Analyte	Batch Number						
		48	49	50	51	52	53	54
Mass - PM2.5	Particulate matter 2.5u	8.87	11.45	8.61	7.88	11.38	8.74	11.88
OC/EC - STN	Organic carbon	10.13	11.20	10.72	11.07	11.93	11.57	12.94
OC/EC - STN	Elemental carbon	0.14	0.23	0.08	0.33	0.23	0.20	0.31
Sulfate - PM2.5	Sulfate	0.18	0.53	0.36	0.43	0.51	0.64	0.42
Nitrate - PM2.5	Nitrate	0.58	0.99	0.69	0.65	0.50	0.69	0.55
Cations - PM2.5 (NH4, Na, K)	Sodium	0.10	0.32	0.08	0.14	0.16	0.19	0.17
Cations - PM2.5 (NH4, Na, K)	Ammonium	0.00	0.00	0.00	0.00	0.01	0.01	0.00

Table 29b. SHAL Blanks Average for the Reporting Period (µg/filter)

ANALYSIS	ANALYTE	Filter Type	Average	Std Dev	N
Cations - PM2.5 (NH4, Na, K)	Ammonium	Nylon	0.000	0.000	51
Cations - PM2.5 (NH4, Na, K)	Potassium	Nylon	0.000	0.000	51
Cations - PM2.5 (NH4, Na, K)	Sodium	Nylon	0.013	0.041	51
Nitrate - PM2.5	Nitrate	Nylon	0.584	0.979	53
Sulfate - PM2.5	Sulfate	Nylon	0.186	0.302	53
Cations - PM2.5 (NH4, Na, K)	Ammonium	Teflon	0.000	0.000	51
Cations - PM2.5 (NH4, Na, K)	Potassium	Teflon	0.000	0.000	51
Cations - PM2.5 (NH4, Na, K)	Sodium	Teflon	0.052	0.109	51
Nitrate - PM2.5	Nitrate	Teflon	0.780	0.815	56
Sulfate - PM2.5	Sulfate	Teflon	0.352	0.338	56
OC/EC - STN	Elemental carbon	Quartz	0.039	0.113	65
OC/EC - STN	Organic carbon	Quartz	3.717	1.902	65
OC/EC - Improve*	Elemental carbon	Quartz	0.169	0.605	23
OC/EC - Improve*	Organic carbon	Quartz	5.353	3.444	23
Mass - PM2.5	Particulate matter 2.5u	Teflon	1.554	4.319	56

*Improve analyses performed by DRI

3.3 Data Completeness by Site

Table 30 shows the percentage of routine exposure records in each delivery batch group that were valid (i.e., not invalidated with an AIRS Null Value Code) relative to the number of records for scheduled events for that batch. Blank cells indicate that no analyses were scheduled for a site during a particular delivery batch interval. Percentages less than 80 are usually the result of a sample being out of service or one or more exposures being missed because of problems at the site or problems with the shipping.

Table 30. Summary of Percent Valid AIRS Data by Delivery Batch

Location	AIRS Code	POC	Percentage by Delivery Batch						
			46	47	48	49	50	51	52
20th St. Fire Station	120861016	5	100	100	100	100	100	100	100
5 Points	391530023	5	100	100	80	100	85	100	100
Air Monitoring, VA DEQ	517600020	5	76	100	100	100			
Aldine	482010024	5	29	92	88	84	90	100	100
Allen Park	261630001	5	100	100	99	100	100	100	100
Alpine	480430002	5	99	79	100	83	100	75	85
Alton	171192009	5	100	100	100	100	99	100	100
APCD (Barret)	211110048	5	100	100	100	100	100	100	100
Arendtsville	420010001	5	100	100	100	80	100	100	100
Army Reserve Center	191130037	5	100	100	100	100	100	100	100
Arnold	290990012	5	100	100	100	100	90	89	100
Ashland Health Department	210190017	5	100	100	100	85	78	100	100
Athens	130590001	5	28	85	100	100	88	100	85
Augusta	132450091	5	98	76	92	79	80	80	100

Table 30. (Continued)

Location	AIRS Code	POC	Percentage by Delivery Batch						
			46	47	48	49	50	51	52
Bakersfield-California Ave	060290014	5	87	91	100	91	70	79	80
Bakersfield-California Ave (Collocated)	060290014	6	80	91	100	100	90	78	100
Bates House (USC)	450790019	5	100	100	100	100	100	100	80
Bayland Park	482010055	5	71	100	100	98	80	89	99
Beacon Hill	530330080	6	100	91	100	91	100	89	98
Bethune School	040138006	5	80	100	100	100	100	100	100
Big Bend National Park	480430101	5	92	80	91	89	100	59	100
Bismarck Residential	380150003	5	100	100	100	100	100	100	99
Blair Street	295100085	6	100	100	100	100	100	100	100
Blair Street	295100085	6	100	100	100	100	100	100	100
Bonne Terre	291860005	5	100	100	90	99	90	92	82
Bountiful	490110004	5	100	100	100	100	100	100	100
Bowling Green-Kereiakes Park	212270007	5	100	100	100	60	50	82	100
Bristol	515200006	5	100	100	100	100	100	100	100
Buffalo	360290005	6	100	100	100	96	100	100	100
Buncombe County Board of Education	370210034	5	100	100	100	100	100	80	62
Burlington	500070012	5	100	91	100	100	100	89	100
Camden	340070003	5	13	0		0	88	100	100
Canal St. Post Office	360610062	5	100	100	92	34	34	84	99
Canton Health Dept.	391510020	5	100	100	100	96	83	100	100
Capitol	220330009	5	68	78	86	91	100	100	99
Chamizal	481410044	5	83	100	80	100	99	100	98
Channelview	482010026	5	74	0	68	84	100	79	100
Cherry Grove (1)	370330001	5	0	0	0	82			
Chester	340273001	5	91	100	100	90	75	88	100
Chester (PA)	420450002	5	100	100	100	100	100	100	100
Chesterfield	450250001	5	78	100	100	99	100	100	100
Chickasaw	010970003	5	100	100	100	100	100	100	100
Chicopee	250130008	5	20	100	84	99	78	100	89
Children's Park	040191028	5	100	100	100	100	100	100	100
Chiwaukee Prairie Site	550590019	5	100	100	85	100	100	100	100
Clio	010050002	5	95	100	100	98	93	97	90
Columbus	132150011	5	98	80	100	100	100	100	100
Com ED	170310076	5	100	100	98	75	90	98	100
Commerce City	080010006	5	100	100	100	100	88	100	100
Conroe Airport	483390078	5	70	91	89	100	92	90	92
Courthouse Annex-Libby	300530018	5	100	100	99	80	83	100	80
Covington - University College	211170007	5	100	80	100	85	100	100	100
CPW	450190049	5	100	100	100	91	100	91	100
Criscuolo Park	090090027	5						100	80

Table 30. (Continued)

Location	AIRS Code	POC	Percentage by Delivery Batch						
			46	47	48	49	50	51	52
Crossett	050030005	5	100	80	100	80	49	0	0
Dallas Convention Center	481130050	5	99	91	80	89	100	100	37
Dearborn	261630033	5	100	85	65	82	97	100	100
Decatur	011030011	5	100	80	80	100	80	100	100
Deer Park	482011039	6	83	87	100	99	100	100	100
Deer Park (Collocated)	482011039	7	74	71	100	82	91	89	99
Del Norte	350010023	5				100	86	100	83
Dona Park	483550034	5	100	100	100	100	100	100	100
Douglas	130690002	5	85	69	71	80	100	63	80
Dover	100010003	5	80	100	100	75	100	100	100
Duwamish	530330057	6	100	100	100	65	96	100	100
East Charleston	320030560	5	100	100	100	85	100	100	100
El Cajon	060730003	5	89	67	100	100	100	100	100
Elizabeth Lab	340390004	5	99	100	100	90	100	100	89
Ellis County WMA	400450890	5	100	100	100	100	100	100	100
Ellyson	120330004	6	100	100	100	100	100	100	100
Elmwood	421010136	5	100	100	100	100	100	98	100
Erie	420490003	5	80	100	100	98	100	100	100
Essex	240053001	5	67	0					
Evansville - Mill Road	181630012	5	100	100	80	100	100	100	100
Fargo NW	380171004	5	100	100	100	100	99	100	100
Florence	421255001	5	79	100	80	98	83	100	100
Florence Special	421255001	5	79	100	80	98	83	100	100
Fort Meade	240030019	5	100	100	100	100	100	100	99
Fort Wayne CAAP	180030004	5	100	100	100	100	100	100	100
Francis Elementary School	440071010	5	40	100	100	100	67	100	79
Freemansburg	420950025	5	100	100	100	100	100	100	100
Fresno - First Street	060190008	5	76	90	99	90	82	88	100
G.T. Craig	390350060	5	89	91	100	100	100	100	77
G.T. Craig - Collocated	390350060	6	89	100	100	100	100	100	88
Galveston Airport	481670014	5	65	100	90	92	100	100	92
Garden St.	020200018	5	100	100	100	100	90	100	100
Garinger High School	371190041	5	89	100	100	100	100	99	99
Gary litri	180890022	5	100	100	100	100	100	100	100
General Hospital	390870010	5	100	84	98	100	100	100	100
Georgetown (Andersen)	530330032	6	100	79	100	100	88	100	100
Grand Junction - Powell Building	080770017	5	100	100	100	100	100	100	100
Grand Rapids	260810020	5	100	100	100	80	100	100	80
Greensburg	421290008	5	99	99	100	98	100	76	100
Greensburg Special	421290008	5	99	99	100	98	100	76	100
Grenada	280430001	5	100	100	100	80	100	100	100

Table 30. (Continued)

Location	AIRS Code	POC	Percentage by Delivery Batch						
			46	47	48	49	50	51	52
Guaynabo	720610005	5	80	82	89	91	90	100	91
Guiding Hands School	390530003	5	100	80	100	80	83	100	80
Gulfport	280470008	5	100	100	83	100	100	75	89
Guthrie	471570047	5	100	100	99	100	90	100	100
Hammond Purdue	180892004	5				100	100	100	100
Hamshire	482450022	5	100	86	91	100	92	100	99
Harrisburg	420430401	5	100	100	65	98	100	100	100
Hattie Avenue	370670022	5	100	100	100	100	100	100	100
Hattiesburg	280350004	5	99	100	100	100	100	100	100
Hawthorne	490353006	5	99	100	100	91	100	100	100
Hazard - Perry County Horse Park	211930003	5	100	100	100	100	100	100	100
Hazelwood	420030021	5	100						
Hazelwood Special	420030021	5	100						
Head Start	390990014	5	100	100	80	100	100	100	100
Hendersonville	471650007	5	100	100	100	100	100	100	100
Henrico Co.	510870014	5				100	100	100	100
Hickory	370350004	5	100	100	63	80	83	75	100
Hinton	481130069	5	99	100	100	96	100	100	100
Holland	260050003	5	100	100	100	100	100	75	100
Houghton Lake	261130001	5	100	100	100	100	100	100	80
Huntsville Old Airport	010890014	5	100	100	82	100	100	100	100
IL - Decatur	171150013	5	100	98	98	100	100	100	100
IS 52	360050110	5	100	82	100	90	97	78	99
Jackson Hinds Co.	280490018	5	100	100	100	100	60	50	80
Jefferson Elementary (10th and Vine)	191630015	5	100	84	90	100	73	63	91
JFK Center	202090021	5	100	100	100	90	88	100	100
Kalamazoo	260770008	5	100	100	80	100	100	100	80
Karnack	482030002	5	99	93	100	100	100	100	100
Kaufman	482570005	5	100	100	100	67	80	84	100
Kelo	460990006	5	100	80	85	100	100	75	100
Kingsport	471631007	5	100	100	100	100	100	75	100
Lake Forest Park	530330024	6	100	80	100	100	100	100	100
Lancaster	420710007	5	100	100	100	80	50	100	80
Laurel	280670002	5	100	100	80	100	100	100	80
Lawrence County	470990002	5	100	100	100	75	100	100	100
Lawrenceville	420030008	6	90	100	100	100	100	100	100
Lawrenceville Special	420030008	6	90	100	100	100	100	100	100
Lenoir Community College	371070004	5	80	80	100	100	100	100	100
Lewis	120571075	5	100	100	100	100			
Lexington (NC)	370570002	5					100	100	80
Lexington Health Department	210670012	5	100	100	100	100	100	100	80

Table 30. (Continued)

Location	AIRS Code	POC	Percentage by Delivery Batch						
			46	47	48	49	50	51	52
Liberty (MO)	290470005	5	80	100	99	100	100	67	100
Liberty (PA)	420030064	6	100	100	80	42	80	80	100
Lindon	490494001	5	100	100	100	100	100	100	100
Lockeland School	470370023	5	80	100	100	100	100	100	100
London-Laurel County	211250004	5	100	80	100	100	100	100	100
Lorain	390933002	5	85	100	85	65	67	100	100
LPH	390610042	5	85	100	100				
Lubbock	483030001	5	100	100	100	100	22		100
Luna Pier	261150005	5	100	100	80	100	100	100	100
Luray Airport	511390004	5				100	100	100	100
Macon	130210007	5	83	64	78	80	100	100	100
Mae Drive	482011034	5	75	100	100	100	100	100	100
Manchester	330110020	5	100	100	83	100	98	100	100
Manitowoc, Woodland Dunes site	550710007	5	100	100	85	100	100	100	100
Maple Canyon	390490081	6	100	100	100	100	100	75	80
Mauriceville	483611100	5	100	100	100	99	91	79	85
Mayville Hubbard Township site	550270007	5	100	100	100	91	100	100	100
McDonald Observatory	482430004	5	100	85	100	100	100	100	100
McMillan Reservoir	110010043	5	89	99	100	100	100	100	89
Mendenhall (2)	370810013	5	0	0	20	100	100	100	60
Mesa County Health Department	080770003	5	100						
Middletown	390171004	5	100	100	100	100	100	100	100
Midlothian Tower	481390015	5	100	100	100	100	100	100	100
Millbrook	371830014	5	90	100	100	100	90	89	100
Mille Lacs	270953051	5	90	91	89	100	100	99	100
Mingo	292070001	5	60	27	56	17			
Missoula County Health Dept.	300630031	5	100	100	100	100	100	100	100
MLK	100032004	5	60	100	100	80	17	100	100
MN - Rochester	271095008	5	100	100	100	100	100	100	82
MOMS	011011002	5	100	100	100	60	100	100	100
Nampa NNC	160270004	5	100	100	100	100	100	100	100
Naperville	170434002	5					100	100	100
New Brunswick	340230006	5	89	100	100	90	100	99	100
New Brunswick (Collocated)	340230006	6	75	100	100	100	100	100	80
New Garden	420290100	5	100	100	82	100	100	100	100
NLR Parr	051190007	5	100	100	100	80	100	75	96
North Birmingham	010730023	5	100	100	100	100	100	90	100
North Los Angeles	060371103	5	100	100	100	100	100	75	80
Northbrook	170314201	5	100	100	100	100	100	100	98
NY Botanical Gardens	360050083	6	100	100	100	100	100	100	100
OCUSA Campus	401091037	5	83	100	100	80	100	100	100

Table 30. (Continued)

Location	AIRS Code	POC	Percentage by Delivery Batch						
			46	47	48	49	50	51	52
Olive Street	530330048	6	100	100	100	100	100	100	100
Owensboro - KY Wesleyan College	210590014	5	80	100	100	80	100	100	92
Padre Island National Seashore	482730314	5	84	100	100	80	100	100	100
Paducah Middle School	211451004	5	100	100	100	100	100	100	100
Pearl City	150032004	5	100	100	79	100	100	100	100
Peoria Site 1127	401431127	5	100	100	89	91	90	100	100
PerkinstownCASNET	551198001	5	80	100	80	100	100	100	100
Perry County	420990301	5	100	100	100	100	100	100	100
PHILA - AMS Laboratory	421010004	7	100	100	92	100	100	100	93
Philips	270530963	5	100	100	100	88	88	100	100
Phoenix Supersite	040139997	7	83	100	100	100	100	100	91
Pinnacle State Park	361010003	5	73	91	89	64	90	89	83
Platteville	081230008	5	80	100	83	100	100	100	100
Pleasant Green (Central MO)	290530001	5	100	100	100	96	100	100	39
Portland N. Roselawn	410510246	6	100	90	100	100	100	100	91
Portsmouth	330150014	5	100	100	100	100	100	92	99
Providence	010731009	5	80	100	100	100	100	100	100
Public Health Building	191530030	5	100	100	100	100	80	100	100
Queens College	360810124	6	100	100	100	88	99	100	89
RBD	080410011	5	0	100	80	100	100	100	100
Reno	320310016	5	100	100	100	100	90	100	100
Riverside-Rubidoux	060658001	5	90	100	89	100	100	100	91
Riverside-Rubidoux (Collocated)	060658001	6	90	100	89	100	100	100	91
Roanoke	517700014	5	96	100	100	100	100	100	100
Rochester Fire Headquarters	360556001	5	100	100	78	100	88	89	20
Rome	131150005	5	100	100	80	80	100	100	100
Roxbury (Boston)	250250042	5	100	100	100	91	99	100	100
Roxbury (Boston) - collocated	250250042	6	100	100	85	100	100	82	100
Sacramento - Del Paso Manor	060670006	5	90	98	100	100	100	98	100
San Jose - Jackson Street	060850005	5	98	100	99	100	98	96	95
Sault Ste Marie	260330901	5	100	91	99	82	100	90	100
Savannah	130510017	5	100	100	96	35	96	95	99
Scranton	420692006	5	100	100	100	100	100	100	100
Searcy	051450001	5	100	100	98	80	100	100	100
SER-DNR Headquarters	550790026	5	93	91	100	100	100	100	100
Shenandoah High School	180650003	5	85	100	100	80	100	100	100
Shreveport Airport	220150008	5	84	98	100	66	100	100	82
Simi Valley	061112002	5	100	100	100	78	100	100	100
South Bend CAAP	181411008	5				91	100	100	100
South Charleston Library	540391005	5			100	99	100	75	100
South DeKalb	130890002	5	100	100	100	100	80	100	100

Table 30. (Continued)

Location	AIRS Code	POC	Percentage by Delivery Batch						
			46	47	48	49	50	51	52
Southwick Community Center	211110043	5	100	100	100	100	83	100	100
Spring Hill Elementary School	470931020	5	100	80	80	0	100	99	100
Springfield Pumping Station	170310057	5	98	100	93	96	83	100	100
St Theo	390350038	6	97	100	99	100	83	100	100
St. Croix - USVI	780010012	5	0	100	100	100	100	100	100
St. Paul Harding	271230871	5	100	100	100	100	100	75	100
State College	420270100	5	100	100	100	100	100	100	99
State Street	090091123	5	94	91	100	100	67	100	
Sun Metro	481410053	5	100	100	100	100	80	75	100
Sydney	120573002	5				100	99	100	100
Taft	390610040	5			100	100	100	100	100
Tallahassee Community College	120730012	5	100	100	80	100	100	100	100
Taylors Fire Station	450450009	5	100	100	100	80	83	100	100
Toledo Airport	390950026	5	85	65	85	100	100	100	100
TRNP - NU	380530002	5	100	100	100	100	100	100	100
Urban League	440070022	5	100	100	100	100	100	100	80
UTC	470654002	5	100	100	100	100	100	100	40
Washington Park	180970078	5	100	100	100	100	100	100	100
Waukesha, Cleveland Ave. Site	551330027	5	80	100	100	98	100	100	100
West 43rd Ave	040134009	5	100	100	100	38	80	100	100
West Phoenix	040130019	5							75
Whiteface	360310003	5	90	82	89	71	71	36	48
Wichita Dept. of Environmental Health	201730010	5	39	100	100	82	67	82	80
Wilbur Wright Middle School	391130031	5	100	80	75	60	40	100	100
William Owen Elem. School	370510009	5	80	100	98	100	100	100	100
Woolworth St	310550019	5	64	57	66	49	75	0	85
WV - Guthrie Agricultural Center	540390011	5			90	100	90	89	80
Wylam	010732003	5	100	100	100	100	100	100	100
York	421330008	5	100	100	100	100	100	100	98
Ypsilanti	261610008	5	100	100	100	100	100	100	100

NOTES:
1) Cherry Grove data in report batches 46 to 48 were invalidated by site due to sampling problems.
2) Mendenhall data in report batches 46 to 48 were invalidated by site due to sampling problems.