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

October 1, 2000 through March 31, 2001

Prepared for:
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Contents

Section **Page**

Contents (continued)

Section **Page**

List of Tables

List of Figures

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). Establishment of a 1500-site mass measurements network and a 300-site chemical speciation monitoring network is now under way.

The ambient air data from the 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) will consist of a core set of 54 trends analysis sites and some 250 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.

Research Triangle Institute (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. This 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. As of March 31, 2001, RTI is providing support for 75 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 will not be performed initially; however, these analyses may be included later in the full STN program.

3. Assembling validated sets of data from the analyses, preparing of data reports to 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 are now coming on line. As of March 31, 2001, we are providing support to 75 sites which include the 54 STN sites. This QA report covers the collection and analysis of samples, from October 1, 2000 through March 31, 2001.

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 this past year. 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 using ion chromatography; and (4) determination of organic carbon, elemental carbon, carbonate carbon, and total carbon 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

No significant corrective actions have been taken.

2.0 Laboratory Quality Control Summaries

2.1 Gravimetric Laboratory

2.1.1 Personnel and Facilities

The Earth and Mineral Sciences Department's (EMSD's) responsibilities for the Chemical Speciation project have not changed since the Gravimetric Laboratory's previous QA report. The personnel of the Gravimetric Laboratory has changed since the previous QA report. Although the personnel transition and training provided a challenge to the department, the quality of EMSD's contribution to the Chemical Speciation project was not lessened. Personnel changes have allowed the department to improve in-house training of new gravimetric analysts. Changes in personnel are summarized in Table 1.

No changes in facilities have occurred since the previous QA report. With the expiration of the chamber's one-year warranty, RTI Facilities and Maintenance Department personnel assumed responsibility for repair and maintenance activities. RTI has purchased a heavier drive motor for the weigh chamber's dehumidifier, but it has not yet been installed. It is hoped that the installation of this drive motor will decrease chamber downtime. Weigh chamber problems and corrective actions taken in response to those problems are summarized in Table 1. No filters or analytical equipment were damaged as a result of facility problems; however, weigh chamber downtime has increased the difficulty of completing analysis of filters within the 10-day expiration period.

2.1.2 Description of Quality Control Checks Applied

Quality Control checks applied to the gravimetric analysis of Teflon® filters for the PM2.5 STN are summarized in Table 2. The QC checks have been developed from guidance provided in Section 2.12 of the *EPA Quality Assurance Handbook for Air Pollution Measurement Systems, Volume II, Ambient Air Specific Methods* (Guidance Document 2.12), and from our experience in providing federal reference method (FRM) laboratory support to various consulting firms, states, U.S. territories, and EPA since the inception of the compliance (mass) monitoring portion of the nationwide PM2.5 network.

2.1.3 Statistical Summary of Quality Control Results

There have been no changes in the types or frequency of QC checks applied to the gravimetric analysis of filters for the PM2.5 Chemical Speciation Trends Network. QC data for the laboratory are summarized in Tables 3 and 4.

Table 1. Gravimetry Laboratory - Corrective Actions in Response to Personnel Changes and Facility Problems.

Duration of Problem	Nature of Problem	Corrective Action
Early October, 2000	Two experienced analysts left Gravimetric Laboratory	Late October, 2000 - Two inexperienced analysts joined staff and began in-house training. May, 2001 - Experienced analyst rejoined staff of Gravimetric Laboratory. **Note:** "Inexperienced analysts" have completed in-house training and are working independently, and "experienced analyst" will be "refreshed" in Gravimetric Laboratory practices.
10/9/00	Low relative humidity (RH)	10/09/00 - RTI HVAC personnel replaced blown fuse in chamber's control panel.
01/16/01 - 01/25/01	High temperature	01/16/01 - 01/24/01 - RTI HVAC personnel determined that actuator on chill water valve had malfunctioned; RTI HVAC and Security personnel closely monitored chamber so that HVAC personnel could adjust valve as necessary while waiting for replacement parts to arrive. 01/25/01 - RTI HVAC personnel replaced actuator. **Note:** Filters were conditioned during this period in the weigh chamber maintained by RTI's Center for Engineering and Environmental Technology (CEET).
02/08/01	High temperature	02/08/01 - RTI Facilities and Maintenance/HVAC personnel working on the Building 11 Bay 6 air handler accidentally tripped the weigh chamber's system; system was reset upon investigation by RTI HVAC personnel.
02/25/01 - 03/02/01	High RH, High temperature	03/02/01 - RTI HVAC personnel replaced: 1) the drive motor on the dehumidifier, which had been previously replaced on 07/19/00, and 2) the alarm controller board, which was destroyed by a wiring problem. 03/13/01 - RTI HVAC personnel located and ordered a heavier drive motor, better suited to the current application of the chamber's desiccant system. (The heavier motor has not been installed as of this writing.)
03/19/01	High RH	03/19/01, early a.m. - RTI HVAC personnel restarted the dehumidifier drive motor, replaced on 03/02/01, but RH did not fall as expected. 03/19/01, mid-morning - RTI HVAC personnel determined that a blower motor in the rear of the dehumidifier had malfunctioned, a filter in the area was clogged, heaters may have malfunctioned, and recommended contacting the installation contractor. 03/21/01 - Installation contractor replaced blower motor. 03/22/01 - Installation contractor repaired/replaced fuse links. **Note:** During this period, filters were conditioned in CEET's chamber.

Table 2. Gravimetric Analysis of PM2.5 Filters - QC Checks.

QC Check	Frequency	Requirements	Comments
Working standard reference weights (mass reference standards)	After every 10th filter (at least one working standard - preferable to weigh standards bracketing weight of filter)	Verified value ± 3 µg	Reference - Guidance Document 2.12, Section 7.0, Filter Preparation and Analysis Calibrated annually at the NCDA&CS Standards Laboratory in Raleigh, NC Verified via primary standards maintained by EQSD
Blanks			Reference - Guidance Document 2.12, Section 7.0, Filter preparation and Analysis
▸ Laboratory (filter) blanks	At least one lab blank every weigh session	Initial weight ± 15 µg	Assigned by Gravimetric Laboratory for determination of contamination in the weighing environment
▸ Lot (stability filter) blanks	At least three filters from every new (manufacturer's) filter lot	Initial weight ± 5 µg (Guidance Document 2.12 suggests ± 15 µg)	Assigned by Gravimetric Laboratory for determination of period that filters from lot must be conditioned before tare weighing
▸ Field (filter) blanks	See below	See below	See below
Balance Audits	Semiannually	Satisfactory per RTI HERL audit checklist	Performed by personnel from EQSD
Replicates	Every 10th filter	Initial weight ± 15 µg	Reference - Guidance Document 2.12, Section 7.0, Filter Preparation and Analysis
Calibrations			
▸ Working Mass Standards	Annually		Performed by NCDA&CS Standards Laboratory in Raleigh, NC
▸ Balance	Auto (internal) calibration daily External calibration annually or as needed		Balances have internal calibration weights and are self-calibrating via an auto-calibrate function. RTI maintains a service contract with Mettler Toledo for annual inspection, calibration, and preventive maintenance of the balances. Mettler Toledo is also contacted on an as-needed basis for adjustment or repair.
▸ RH/T Data Logger	Annually	± 2% RH ± 0.25°C	Performed by Dickson Calibration Services
Field (filter) blanks	At least three field blanks every weigh session	Initial weight ± 30 µg	Reference - Guidance Document 2.12, Section 7.0, Filter preparation and Analysis Assigned by field for determination of contamination occurring during sampling **Field blanks are not identified to gravimetric laboratory staff.**

Table 3. Sample Throughput for the Gravimetric Laboratory.

Number of Filters	Previous QA Report	This QA Report
Tared	2441 Jan. 24 - Sept.1, 2000	2626 Sept. 1, 2000 - Feb. 23, 2001
Retained by Grav Lab for use as Lab Blanks	33 (1.4%)	27 (1.0%)
Initially Transferred to SHAL to be Loaded into Sampler Modules	2408	2599
Returned to Grav Lab for Retaring - Exceeded 30-Day Sampling Window in SHAL	N/A	205
Reconditioned and Retared	N/A	169 (remaining 36 stored for future use)
Total Transferred to and Retained by SHAL for Sampler Modules (Incl. Retared)	2408	2563
Returned to Grav Lab by SHAL for Final Weighing	2311 (96.0% return rate) Feb. 23 - Oct. 6, 2000	2235 (87.2% return rate) Sept. 18, 2000 - March 29, 2001
Voided	2 (<0.1%)	3 (0.1%)
Flagged by Grav Lab for Exceeding 10-day Holding Time in Lab	N/A	129 (5.8%)
Weighed After XRF Analysis	N/A	25 (1.1%)

Table 4. Summary of QC Checks Applied in the Gravimetric Laboratory.

QC Check	Requirements	QC Checks Applied to RTI Laboratory	Laboratory Mean	Comments
Working standard reference weights (mass reference standards)	Verified value ± 3 µg (Verified by North Carolina Department of Agriculture (NCDA) Standards Laboratory)	100-mg Verified Value = 99.968 mg (NCDA11/00)	99.967 mg ± 0.004 mg number of weighings = 602	Laboratory means fall within required range.
		200-mg (A) Verified Value = 199.987 mg (NCDA 11/00)	199.984 mg ± 0.002 mg number of weighings = 454	
		200-mg (B) Verified Value = 200.004 mg (NCDA 11/99)	200.005 mg ± 0.003 mg number of weighings = 75	
Laboratory (Filter) Blanks	Initial weight ±15 µg	178 total weighings of 27 laboratory blanks	5 µg ± 6 µg	2 of the 178 replicates (1.1%) exceeded 15 µg criterion, as follows: + 34 µg - 17 µg
Lot Blanks (Lot Stability Filters)	24-hour weight change < ±5 µg	Whatman Lot 0159007 - 9 filters weighed (3 randomly selected filters from each of 3 randomly selected boxes)	24 hours = 0 µg 48 hours = 0 µg 72 hours = 1 µg 96 hours = 1 µg	Fall well within required range.
		Whatman Lot 0230006 - 6 filters weighed (3 randomly selected filters from each of 2 randomly selected boxes)	24 hours = -1 µg 48 hours = -1 µg 72 hours = 1 µg 96 hours = 1 µg	
Replicates	Initial weight ±15 µg	245 Presampled Replicates (09/01/00 - 02/23/01)	-1 µg*	Max = 6 µg; well within required range
		249 Postsampled Replicates (09/24/00 - 03/29/01)	-1 µg*	Max = −9 µg; well within required range

*Average difference between replicate weight and initial weight of replicate filters.

Table 4 (continued)

QC Check	Requirements	QC Checks Applied to RTI Laboratory	Laboratory Mean	Comments
Calibrations				
• Working Mass Reference Standards	Annually	Last Calibrated by NCDA November 15, 2000	N/A	Laboratory made change to Teflon-tipped forceps for handling mass standards.
• Balance	Auto (internal) calibration daily	Daily	N/A	
	External calibration annually or as needed	Last Inspected and calibrated by Mettler Toledo July 20, 2000	N/A	Balance accuracy was verified by Ms. Ann Marie Carleton of EPA Region 2 during a technical systems audit on October 5, 2000.
• RH/T Data Logger	Annually	Purchased new data logger February 2001, calibrated by Dickson	N/A	
Audits				
• Balance (internal)	Semiannually	Last performed by RTI QA October 11, 2000	N/A	Included environmental evaluation, level test, scale-clarity test, zero-adjustment test, off-center (corner load error) test, precision test, and accuracy test; balance performed adequately.
• Technical Systems (external)		Ann Marie Carleton, EPA Region 2, October 5, 2000	N/A	Found no major deficiencies
		Dr. Steven Gibson, TNRCC, November 29, 2000	N/A	Found no major deficiencies; recommendations are discussed in Table 5.
		EPA-NAREL, EPA-NERL, and EPA-OAQPS, December 5, 2000	N/A	Found no major deficiencies; recommendations are discussed in Table 5.

2.1.4 Data Validity Discussion

Filters were assigned appropriate Chemical Speciation Data Flags due to problems arising in the Gravimetric Laboratory. The analyses of 129 returned filters (~5.8%) were flagged as a result of laboratory holding times exceeding the 10-day limit. Final filter weights for 25 filters (~1.1%) were obtained after the filters had been transferred to and processed by SHAL. The final weights for the nondestructively analyzed filters were appropriately flagged.

Only two replicate weighings of laboratory blanks exceeded the laboratory's 15 μg acceptance criterion, one through weight gain and one through weight loss. These excursions may have resulted from the filters not being placed on the polonium strips to minimize static charge or from initial weighing during brief environmental fluctuations in the laboratory. Filters weighed during these weigh sessions were appropriately flagged.

Excessive holding times resulted mainly from insufficient laboratory staffing and weigh chamber malfunction. Corrective actions have been implemented to alleviate both problems and increase the efficiency of the Gravimetric Laboratory. An additional analyst will join the laboratory staff in May 2001. Also, the installation of the heavier drive motor on the weigh chamber's dehumidifier will decrease weigh chamber downtime. Corrective action taken in response to other laboratory errors consists of additional analyst training.

2.1.4.1 Invalidated Data - Three of the filters returned to the Gravimetric Laboratory (~0.1%) were voided by the SHAL due to an error in the SHAL.

2.1.5 Audits, Performance Evaluations, and Accreditations

In addition to numerous informal walk-through examinations, the Gravimetric Laboratory has been evaluated in five separate formal procedures since October 2000. These evaluations have been performed by both state and federal regulatory agencies. They are summarized in Table 5. The EPA systems and performance audits findings and recommendations are given in Appendix A.

2.2 Ion Analysis Laboratory

2.2.1 Facilities

Ion chromatographic analyses are performed by personnel from CEMQA's Environmental and Industrial Chemistry Department (EICD). Five ion chromatographic systems were used for performance of the measurements. These are described in Table 6. The use of the systems was determined by the workload. A new Dionex Model 600 was recently purchased to meet the work load anticipated with the expansion of the STN.

Table 5. Audits, Performance Evaluations, and Accreditations.

Responsible Agency	Date/Activity	Recommendation	RTI Response
EPA Region 2	October 5, 2000 - Technical Systems Audit for State/Territory FRM Analysis	No deficiencies noted.	N/A
EPA-NAREL	October and November 2000 - Performance Evaluation Sample Analysis	No deficiencies noted - good agreement for all mass measurements performed at RTI and at NAREL.	N/A
Texas Natural Resource Conservation Commission	November 29, 2000 - Technical Systems Audit for Analysis of FRM Samples through the Speciation Contract Laboratory	Laboratory should document traceability of measurements to national standards.	Reference weights used by RTI QA to check the laboratory's microbalance are traceable to NIST standards. The Laboratory Supervisor will verify that calibration notes generated during in-house calibrations include the necessary traceability information.
		Laboratory should prepare an SOP for Receipt and Log-In of PM2.5 Filters.	Although this recommendation has little impact on the analysis of samples for the PM2.5 Speciation Trends Network, project-specific sample handling procedures are being prepared for each of the laboratory's clients.
EPA-NAREL, EPA-NERL, EPA-OAQPS	December 5, 2000 - Technical Systems Audit for Speciation Network Laboratory	Written criteria for temperature and humidity control in the weigh chamber should be made available which is reasonable and appropriate for good data quality.	Laboratory is reevaluating its written criteria for temperature and humidity control in response to the audit team's observations.
		Laboratory should purchase a second device to monitor the official temperature and RH inside the weigh chamber. A second device would serve as back-up since each device needs to be recertified periodically.	Laboratory purchased a second calibrated Dickson data logger in February 2001.
Louisiana Department of Environmental Quality	February 27, 2001 - Granted accreditation by Louisiana Environmental Laboratory Accreditation Program	Accreditation for the performance of the "Reference Method for the Determination of Fine Particulate Matter as PM2.5 in the Atmosphere (gravimetry)" - LELAP Certificate Number 04017.	N/A

Table 6. 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, NO3
2	Model 500 (S2A)	SO_4, NO3
3	Model 500 (S3A)	SO_4, NO3
4	DX-500 (D5C)	Na, NH4, K
5	DX-600 (D6C)	Na, NH4, K
6	DX-600 (D6A)	SO_4, NO3

2.2.2 Description of QC Checks Applied

QC checks for ion analyses are summarized in Table 7. 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) a QC sample containing concentrations of each ion in the mid- to high-range of the calibration standard concentrations, (2) a 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.

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 measures differs by more than 10 percent from the known value, the problem is identified and corrected. Any field samples are then analyzed.

Table 7. 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

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 8 shows recoveries for NO_3^- with low, medium, and high concentration QC samples for the four instruments used for anion analysis. Average recoveries for 12 combinations of level and instrument ranged from 98.5% to 102.2% over the six month period. Table 9 shows recoveries for NO_3^- with low and medium-high QA samples for the four instruments used for anion analysis. Average recoveries for eight combinations of level and instrument ranged from 97.9% to 104.4% over the six month period.

Table 10 shows recoveries for SO_4^{2-} with low, medium, and high QC samples for the four instruments used for anion analysis. Average recoveries for the 12 combinations of level and instrument ranged from 98.8% to 100.9% over the six month period. Table 11 shows recoveries for SO_4^{2-} with low and medium-high QA samples for the four instruments used for analysis. Average recoveries for the eight combinations of level and instrument ranged from 97.7% to 103.5% over the six month period.

Table 12 shows absolute relative percent different (ARPD) values for replicate measurements of nitrate and sulfate at concentrations >0.050 ppm. The ARPD value is used rather than a signed value in that the ARPD value reflects the combination of bias and precision. The maximum average ARPD value for the four instruments used over the six month period was 4.1% for nitrate and 1.2% for sulfate. Table 13 shows ARPD values for replicate measurements of nitrate and sulfate at concentrations <0.050 ppm (approximately the limit of quantitation). The maximum ARPD value was 15.5% for nitrate and 15.3% for sulfate.

Table 14 shows average percent recovery for nitrate and sulfate spikes for the four instruments over the six month period. The values for nitrate ranged from 98.8% to 101.0%, while the values for sulfate ranged from 99.5% to 100.2%.

Table 15 presents filter blank and reagent blank values for nitrate for the four instruments used over the six month period. As noted, the highest average value for filter blanks was 0.0196 ppm (25 mL extract), the highest average reagent blank deionized water was 0.0265 ppm, and the highest average reagent blank eluent was 0.0061 ppm. Table 16 presents these same values for sulfate. As noted, the highest average value for filter blank was 0.0347 ppm (25 mL extract), the highest average reagent blank deionized water was 0.0148 ppm, and the highest average reagent blank reagent was 0.0426 ppm.

Table 8. Average Percent Recovery for Low, Medium, and High Level Nitrate QC Samples.

Analyte: Nitrate Percent Recovery
Type: QC-LOW, 0.6 ppm
Inst: S1A

Date:	**Oct-00**	**Nov-00**	**Dec-00**	**Jan-01**	**Feb-01**	**Mar-01**	**Total**
Average	98.6%				99.0%		98.9%
Std Dev					0.8%		0.8%
N	1				12		13
Min	98.6%				97.7%		97.7%
Max	98.6%				99.8%		99.8%

Analyte: Nitrate Percent Recovery
Type: QC-LOW, 0.6 ppm
Inst: S2A

Date:	**Oct-00**	**Nov-00**	**Dec-00**	**Jan-01**	**Feb-01**	**Mar-01**	**Total**
Average	99.2%						99.2%
Std Dev	1.7%						1.7%
N	8						8
Min	97.4%						97.4%
Max	102.2%						102.2%

Analyte: Nitrate Percent Recovery
Type: QC-LOW, 0.6 ppm
Inst: S3A

Date:	**Oct-00**	**Nov-00**	**Dec-00**	**Jan-01**	**Feb-01**	**Mar-01**	**Total**
Average	99.2%	99.4%	99.3%	98.8%	98.8%	98.3%	98.9%
Std Dev	0.6%	1.0%	0.8%	0.6%	1.4%	1.3%	1.1%
N	7	15	11	18	6	26	83
Min	98.6%	97.9%	97.9%	98.0%	96.8%	96.0%	96.0%
Max	100.2%	102.2%	100.3%	100.0%	101.0%	101.8%	102.2%

Analyte: Nitrate Percent Recovery
Type: QC-LOW, 0.6 ppm
Inst: D6A

Date:	**Oct-00**	**Nov-00**	**Dec-00**	**Jan-01**	**Feb-01**	**Mar-01**	**Total**
Average			98.6%		98.9%		98.7%
Std Dev			1.1%		0.1%		0.9%
N			5		2		7
Min			96.9%		98.8%		96.9%
Max			99.8%		99.0%		99.8%

Table 8 (continued).

Analyte:	Nitrate		Percent Recovery				
Type:	QC-MED, 1.5 ppm						
Inst:	S1A						
Date:	**Oct-00**	**Nov-00**	**Dec-00**	**Jan-01**	**Feb-01**	**Mar-01**	**Total**
Average	98.5%				99.2%		99.1%
Std Dev	0.3%				0.9%		0.9%
N	2				14		16
Min	98.3%				97.4%		97.4%
Max	98.7%				100.5%		100.5%

Analyte:	Nitrate		Percent Recovery				
Type:	QC-MED, 1.5 ppm						
Inst:	S2A						
Date:	**Oct-00**	**Nov-00**	**Dec-00**	**Jan-01**	**Feb-01**	**Mar-01**	**Total**
Average	99.4%						99.4%
Std Dev	0.8%						0.8%
N	12						12
Min	98.1%						98.1%
Max	101.1%						101.1%

Analyte:	Nitrate		Percent Recovery				
Type:	QC-MED, 1.5 ppm						
Inst:	S3A						
Date:	**Oct-00**	**Nov-00**	**Dec-00**	**Jan-01**	**Feb-01**	**Mar-01**	**Total**
Average	100.1%	99.5%	99.5%	98.8%	98.6%	98.8%	99.1%
Std Dev	1.4%	0.5%	0.4%	0.4%	1.0%	1.1%	0.9%
N	9	18	13	23	8	33	104
Min	98.5%	98.4%	98.7%	98.2%	96.7%	96.8%	96.7%
Max	102.4%	100.1%	100.3%	99.8%	100.0%	101.6%	102.4%

Analyte:	Nitrate		Percent Recovery				
Type:	QC-MED, 1.5 ppm						
Inst:	D6A						
Date:	**Oct-00**	**Nov-00**	**Dec-00**	**Jan-01**	**Feb-01**	**Mar-01**	**Total**
Average			99.6%		99.2%		99.5%
Std Dev			0.5%		0.6%		0.5%
N			7		3		10
Min			99.1%		98.7%		98.7%
Max			100.4%		99.8%		100.4%

Table 8 (continued).

Analyte: Nitrate Percent Recovery
Type: QC-HIGH, 6.0 ppm
Inst: S1A

Date:	Oct-00	Nov-00	Dec-00	Jan-01	Feb-01	Mar-01	Total
Average	102.0%				101.5%		101.5%
Std Dev					0.7%		0.6%
N	1				6		7
Min	102.0%				100.5%		100.5%
Max	102.0%				102.3%		102.3%

Analyte: Nitrate Percent Recovery
Type: QC-HIGH, 6.0 ppm
Inst: S2A

Date:	Oct-00	Nov-00	Dec-00	Jan-01	Feb-01	Mar-01	Total
Average	101.8%						101.8%
Std Dev	0.7%						0.7%
N	5						5
Min	101.2%						101.2%
Max	102.6%						102.6%

Analyte: Nitrate Percent Recovery
Type: QC-HIGH, 6.0 ppm
Inst: S3A

Date:	Oct-00	Nov-00	Dec-00	Jan-01	Feb-01	Mar-01	Total
Average	102.2%	101.5%	102.0%	101.1%	101.2%	101.8%	101.6%
Std Dev	0.6%	0.6%	0.3%	0.4%	0.3%	0.4%	0.6%
N	7	11	5	9	3	14	49
Min	101.4%	100.3%	101.4%	100.6%	100.9%	101.2%	100.3%
Max	103.1%	102.5%	102.3%	101.6%	101.5%	102.8%	103.1%

Analyte: Nitrate Percent Recovery
Type: QC-HIGH, 6.0 ppm
Inst: D6A

Date:	Oct-00	Nov-00	Dec-00	Jan-01	Feb-01	Mar-01	Total
Average			101.9%		101.3%		101.8%
Std Dev			0.6%				0.6%
N			3		1		4
Min			101.2%		101.3%		101.2%
Max			102.4%		101.3%		102.4%

Table 9. Average Percent Recovery for Low and Medium-High Level Nitrate QA Samples.

Analyte: Nitrate Percent Recovery
Type: QA LOW, 0.6 ppm
Inst: S1A

Date:	Oct-00	Nov-00	Dec-00	Jan-01	Feb-01	Mar-01	Total
Average	104.4%				98.8%		99.6%
Std Dev					1.1%		2.4%
N	1				6		7
Min	104.4%				97.6%		97.6%
Max	104.4%				100.6%		104.4%

Analyte: Nitrate Percent Recovery
Type: QA LOW, 0.6 ppm
Inst: S2A

Date:	Oct-00	Nov-00	Dec-00	Jan-01	Feb-01	Mar-01	Total
Average	102.9%						102.9%
Std Dev	1.3%						1.3%
N	7						7
Min	101.0%						101.0%
Max	104.7%						104.7%

Analyte: Nitrate Percent Recovery
Type: QA LOW, 0.6 ppm
Inst: S3A

Date:	Oct-00	Nov-00	Dec-00	Jan-01	Feb-01	Mar-01	Total
Average	103.5%	102.1%	98.4%	98.2%	100.3%	98.0%	99.8%
Std Dev	2.1%	2.5%	0.6%	0.6%	0.6%	0.9%	2.6%
N	7	9	5	9	3	14	47
Min	101.1%	98.6%	97.7%	97.1%	99.7%	97.1%	97.1%
Max	107.1%	104.9%	99.2%	98.9%	100.9%	100.5%	107.1%

Analyte: Nitrate Percent Recovery
Type: QA LOW, 0.6 ppm
Inst: D6A

Date:	Oct-00	Nov-00	Dec-00	Jan-01	Feb-01	Mar-01	Total
Average			97.9%		99.1%		98.2%
Std Dev			1.0%				1.0%
N			3		1		4
Min			97.2%		99.1%		97.2%
Max			99.0%		99.1%		99.1%

Table 9 (continued).

Analyte: Nitrate Percent Recovery
Type: QA MED-HIGH , 3.0 ppm
Inst: S1A

Date:	**Oct-00**	**Nov-00**	**Dec-00**	**Jan-01**	**Feb-01**	**Mar-01**	**Total**
Average	103.3%				101.3%		101.6%
Std Dev					1.1%		1.2%
N	1				6		7
Min	103.3%				100.0%		100.0%
Max	103.3%				102.9%		103.3%

Analyte: Nitrate Percent Recovery
Type: QA MED-HIGH , 3.0 ppm
Inst: S2A

Date:	**Oct-00**	**Nov-00**	**Dec-00**	**Jan-01**	**Feb-01**	**Mar-01**	**Total**
Average	103.6%						103.6%
Std Dev	1.2%						1.2%
N	5						5
Min	102.9%						102.9%
Max	105.8%						105.8%

Analyte: Nitrate Percent Recovery
Type: QA MED-HIGH , 3.0 ppm
Inst: S3A

Date:	**Oct-00**	**Nov-00**	**Dec-00**	**Jan-01**	**Feb-01**	**Mar-01**	**Total**
Average	103.6%	103.3%	101.7%	101.4%	101.0%	101.6%	101.9%
Std Dev	0.8%	1.9%	0.5%	0.6%	0.2%	0.7%	1.2%
N	3	7	6	9	3	14	42
Min	102.7%	100.3%	101.0%	100.8%	100.8%	100.0%	100.0%
Max	104.2%	104.9%	102.2%	102.8%	101.2%	102.6%	104.9%

Analyte: Nitrate Percent Recovery
Type: QA MED-HIGH , 3.0 ppm
Inst: D6A

Date:	**Oct-00**	**Nov-00**	**Dec-00**	**Jan-01**	**Feb-01**	**Mar-01**	**Total**
Average			101.0%		101.2%		101.0%
Std Dev			0.1%				0.1%
N			3		1		4
Min			100.9%		101.2%		100.9%
Max			101.1%		101.2%		101.2%

Table 10. Average Percent Recovery for Low, Medium, and High Level Sulfate QC Samples.

Analyte: Sulfate Percent Recovery
Type: QC-LOW, 1.2 ppm
Inst: S1A

Date:	**Oct-00**	**Nov-00**	**Dec-00**	**Jan-01**	**Feb-01**	**Mar-01**	**Total**
Average	99.7%				100.2%		100.2%
Std Dev					1.1%		1.0%
N	1				12		13
Min	99.7%				98.6%		98.6%
Max	99.7%				102.8%		102.8%

Analyte: Sulfate Percent Recovery
Type: QC-LOW, 1.2 ppm
Inst: S2A

Date:	**Oct-00**	**Nov-00**	**Dec-00**	**Jan-01**	**Feb-01**	**Mar-01**	**Total**
Average	99.3%						99.3%
Std Dev	1.3%						1.3%
N	8						8
Min	97.9%						97.9%
Max	101.9%						101.9%

Analyte: Sulfate Percent Recovery
Type: QC-LOW, 1.2 ppm
Inst: S3A

Date:	**Oct-00**	**Nov-00**	**Dec-00**	**Jan-01**	**Feb-01**	**Mar-01**	**Total**
Average	99.4%	99.4%	99.9%	99.2%	99.8%	98.8%	99.3%
Std Dev	1.0%	1.1%	0.7%	0.5%	1.3%	1.1%	1.0%
N	7	15	11	18	6	26	83
Min	98.4%	98.1%	98.5%	98.3%	97.5%	97.2%	97.2%
Max	101.3%	102.7%	100.8%	100.3%	101.0%	103.0%	103.0%

Analyte: Sulfate Percent Recovery
Type: QC-LOW, 1.2 ppm
Inst: D6A

Date:	**Oct-00**	**Nov-00**	**Dec-00**	**Jan-01**	**Feb-01**	**Mar-01**	**Total**
Average			98.9%		99.5%		99.1%
Std Dev			0.8%		0.8%		0.8%
N			5		2		7
Min			98.1%		98.9%		98.1%
Max			100.0%		100.1%		100.1%

Table 10 (continued).

Analyte:	Sulfate		Percent Recovery				
Type:	QC-MED, 3.0 ppm						
Inst:	S1A						
Date:	**Oct-00**	**Nov-00**	**Dec-00**	**Jan-01**	**Feb-01**	**Mar-01**	**Total**
Average	100.4%				101.0%		100.9%
Std Dev	0.2%				1.0%		1.0%
N	2				14		16
Min	100.2%				99.2%		99.2%
Max	100.5%				102.5%		102.5%

Analyte:	Sulfate		Percent Recovery				
Type:	QC-MED, 3.0 ppm						
Inst:	S2A						
Date:	**Oct-00**	**Nov-00**	**Dec-00**	**Jan-01**	**Feb-01**	**Mar-01**	**Total**
Average	100.2%						100.2%
Std Dev	0.7%						0.7%
N	12						12
Min	99.1%						99.1%
Max	101.0%						101.0%

Analyte:	Sulfate		Percent Recovery				
Type:	QC-MED, 3.0 ppm						
Inst:	S3A						
Date:	**Oct-00**	**Nov-00**	**Dec-00**	**Jan-01**	**Feb-01**	**Mar-01**	**Total**
Average	100.0%	100.1%	100.3%	99.4%	99.9%	100.0%	99.9%
Std Dev	0.9%	0.5%	0.5%	0.3%	0.6%	0.7%	0.7%
N	9	18	13	23	8	33	104
Min	99.2%	99.2%	99.4%	98.6%	98.7%	98.9%	98.6%
Max	101.8%	101.0%	101.3%	100.1%	100.5%	101.7%	101.8%

Analyte:	Sulfate		Percent Recovery				
Type:	QC-MED, 3.0 ppm						
Inst:	D6A						
Date:	**Oct-00**	**Nov-00**	**Dec-00**	**Jan-01**	**Feb-01**	**Mar-01**	**Total**
Average			100.3%		100.6%		100.4%
Std Dev			0.3%		0.4%		0.3%
N			7		3		10
Min			99.8%		100.1%		99.8%
Max			100.8%		100.9%		100.9%

Table 10 (continued).

Analyte: Sulfate Percent Recovery
Type: QC-HIGH, 12.0 ppm
Inst: S1A

Date:	**Oct-00**	**Nov-00**	**Dec-00**	**Jan-01**	**Feb-01**	**Mar-01**	**Total**
Average	98.8%				99.0%		98.9%
Std Dev					0.3%		0.2%
N	1				6		7
Min	98.8%				98.5%		98.5%
Max	98.8%				99.2%		99.2%

Analyte: Sulfate Percent Recovery
Type: QC-HIGH, 12.0 ppm
Inst: S2A

Date:	**Oct-00**	**Nov-00**	**Dec-00**	**Jan-01**	**Feb-01**	**Mar-01**	**Total**
Average	99.7%						99.7%
Std Dev	0.4%						0.4%
N	5						5
Min	99.3%						99.3%
Max	100.3%						100.3%

Analyte: Sulfate Percent Recovery
Type: QC-HIGH, 12.0 ppm
Inst: S3A

Date:	**Oct-00**	**Nov-00**	**Dec-00**	**Jan-01**	**Feb-01**	**Mar-01**	**Total**
Average	99.9%	99.6%	99.9%	99.1%	99.2%	100.3%	99.7%
Std Dev	0.4%	0.5%	0.6%	0.4%	0.5%	1.4%	0.9%
N	7	11	5	9	3	14	49
Min	99.4%	98.6%	99.0%	98.5%	98.7%	98.3%	98.3%
Max	100.3%	100.3%	100.3%	99.9%	99.6%	102.2%	102.2%

Analyte: Sulfate Percent Recovery
Type: QC-HIGH, 12.0 ppm
Inst: D6A

Date:	**Oct-00**	**Nov-00**	**Dec-00**	**Jan-01**	**Feb-01**	**Mar-01**	**Total**
Average			99.7%		99.0%		99.5%
Std Dev			0.7%				0.7%
N			3		1		4
Min			98.8%		99.0%		98.8%
Max			100.1%		99.0%		100.1%

Table 11. Average Percent Recovery for Low and Medium-High Level Sulfate QA Samples.

Analyte: Sulfate Percent Recovery
Type: QA LOW, 1.2 ppm
Inst: S1A

Date:	Oct-00	Nov-00	Dec-00	Jan-01	Feb-01	Mar-01	Total
Average	100.7%				99.8%		99.9%
Std Dev					0.7%		0.7%
N	1				6		7
Min	100.7%				98.9%		98.9%
Max	100.7%				100.8%		100.8%

Analyte: Sulfate Percent Recovery
Type: QA LOW, 1.2 ppm
Inst: S2A

Date:	Oct-00	Nov-00	Dec-00	Jan-01	Feb-01	Mar-01	Total
Average	100.0%						100.0%
Std Dev	0.4%						0.4%
N	7						7
Min	99.2%						99.2%
Max	100.3%						100.3%

Analyte: Sulfate Percent Recovery
Type: QA LOW, 1.2 ppm
Inst: S3A

Date:	Oct-00	Nov-00	Dec-00	Jan-01	Feb-01	Mar-01	Total
Average	100.4%	100.2%	98.8%	98.3%	99.6%	97.7%	98.9%
Std Dev	0.7%	0.6%	0.7%	0.6%	0.3%	0.4%	1.2%
N	7	9	5	9	3	14	47
Min	99.7%	99.2%	97.7%	97.6%	99.2%	97.2%	97.2%
Max	101.3%	100.9%	99.4%	99.1%	99.9%	98.5%	101.3%

Analyte: Sulfate Percent Recovery
Type: QA LOW, 1.2 ppm
Inst: D6A

Date:	Oct-00	Nov-00	Dec-00	Jan-01	Feb-01	Mar-01	Total
Average			98.1%		98.5%		98.2%
Std Dev			0.6%				0.5%
N			3		1		4
Min			97.6%		98.5%		97.6%
Max			98.7%		98.5%		98.7%

Table 11 (continued).

Analyte: Sulfate Percent Recovery
Type: QA MED-HIGH, 6.0 ppm
Inst: S1A

Date:	Oct-00	Nov-00	Dec-00	Jan-01	Feb-01	Mar-01	Total
Average	103.5%				101.6%		101.9%
Std Dev					1.1%		1.2%
N	1				6		7
Min	103.5%				100.2%		100.2%
Max	103.5%				103.2%		103.5%

Analyte: Sulfate Percent Recovery
Type: QA MED-HIGH, 6.0 ppm
Inst: S2A

Date:	Oct-00	Nov-00	Dec-00	Jan-01	Feb-01	Mar-01	Total
Average	101.9%						101.9%
Std Dev	0.5%						0.5%
N	5						5
Min	101.6%						101.6%
Max	102.7%						102.7%

Analyte: Sulfate Percent Recovery
Type: QA MED-HIGH, 6.0 ppm
Inst: S3A

Date:	Oct-00	Nov-00	Dec-00	Jan-01	Feb-01	Mar-01	Total
Average	102.2%	101.9%	102.2%	101.7%	101.2%	101.9%	101.9%
Std Dev	0.9%	0.6%	0.6%	0.7%	0.2%	0.8%	0.7%
N	3	7	6	9	3	14	42
Min	101.2%	101.0%	101.2%	101.1%	101.0%	101.1%	101.0%
Max	102.9%	102.5%	102.7%	103.4%	101.4%	104.2%	104.2%

Analyte: Sulfate Percent Recovery
Type: QA MED-HIGH, 6.0 ppm
Inst: D6A

Date:	Oct-00	Nov-00	Dec-00	Jan-01	Feb-01	Mar-01	Total
Average			101.8%		101.4%		101.7%
Std Dev			0.3%				0.3%
N			3		1		4
Min			101.5%		101.4%		101.4%
Max			102.1%		101.4%		102.1%

Table 12. Absolute Relative Percent Difference for Replicate Nitrate and Sulfate Measurements at Concentrations > 0.050 ppm

Analyte:	Nitrate		Conc>	0.050			
Type:	Replicate						
Instrument:	S1A						
Date:	**Oct-00**	**Nov-00**	**Dec-00**	**Jan-01**	**Feb-01**	**Mar-01**	**Total**
Average	4.1%				1.1%		1.4%
Std Dev	3.5%				1.0%		1.6%
N	2				17		19
Min	1.6%				0.1%		0.1%
Max	6.6%				3.0%		6.6%

Analyte:	Nitrate		Conc>	0.050			
Type:	Replicate						
Instrument:	S2A						
Date:	**Oct-00**	**Nov-00**	**Dec-00**	**Jan-01**	**Feb-01**	**Mar-01**	**Total**
Average	0.6%						0.6%
Std Dev	0.5%						0.5%
N	11						11
Min	0.0%						0.0%
Max	1.7%						1.7%

Analyte:	Nitrate		Conc>	0.050			
Type:	Replicate						
Instrument:	S3A						
Date:	**Oct-00**	**Nov-00**	**Dec-00**	**Jan-01**	**Feb-01**	**Mar-01**	**Total**
Average	0.4%	0.2%	0.6%	0.3%	1.3%	0.7%	0.5%
Std Dev	0.4%	0.2%	0.5%	0.4%	1.5%	0.8%	0.8%
N	7	17	13	20	9	35	101
Min	0.0%	0.0%	0.1%	0.0%	0.0%	0.0%	0.0%
Max	1.2%	0.5%	1.9%	1.4%	3.8%	3.9%	3.9%

Analyte:	Nitrate		Conc>	0.050			
Type:	Replicate						
Instrument:	D6A						
Date:	**Oct-00**	**Nov-00**	**Dec-00**	**Jan-01**	**Feb-01**	**Mar-01**	**Total**
Average			0.4%		1.1%		0.6%
Std Dev			0.4%		1.3%		0.8%
N			8		3		11
Min			0.0%		0.1%		0.0%
Max			1.3%		2.6%		2.6%

Table 12 (continued).

Analyte:	Sulfate			Conc>	0.050		
Type:	Replicate						
Instrument:	S1A						
Date:	**Oct-00**	**Nov-00**	**Dec-00**	**Jan-01**	**Feb-01**	**Mar-01**	**Total**
Average	1.2%				1.3%		1.3%
Std Dev	1.4%				2.1%		2.0%
N	2				16		18
Min	0.3%				0.0%		0.0%
Max	2.2%				8.6%		8.6%

Analyte:	Sulfate			Conc>	0.050		
Type:	Replicate						
Instrument:	S2A						
Date:	**Oct-00**	**Nov-00**	**Dec-00**	**Jan-01**	**Feb-01**	**Mar-01**	**Total**
Average	0.8%						0.8%
Std Dev	1.1%						1.1%
N	13						13
Min	0.0%						0.0%
Max	3.8%						3.8%

Analyte:	Sulfate			Conc>	0.050		
Type:	Replicate						
Instrument:	S3A						
Date:	**Oct-00**	**Nov-00**	**Dec-00**	**Jan-01**	**Feb-01**	**Mar-01**	**Total**
Average	0.7%	0.3%	0.5%	1.3%	1.2%	0.5%	0.7%
Std Dev	1.0%	0.2%	1.0%	2.9%	1.8%	0.8%	1.5%
N	7	14	14	17	8	34	94
Min	0.1%	0.0%	0.0%	0.0%	0.2%	0.0%	0.0%
Max	2.9%	0.7%	3.3%	10.0%	5.1%	3.3%	10.0%

Analyte:	Sulfate			Conc>	0.050		
Type:	Replicate						
Instrument:	D6A						
Date:	**Oct-00**	**Nov-00**	**Dec-00**	**Jan-01**	**Feb-01**	**Mar-01**	**Total**
Average			0.2%		0.5%		0.2%
Std Dev			0.2%		0.2%		0.2%
N			9		3		12
Min			0.0%		0.3%		0.0%
Max			0.4%		0.7%		0.7%

Table 13. Absolute Relative Percent Difference for Replicate Nitrate and Sulfate Measurements at Concentrations < 0.050 ppm

Analyte: Nitrate Conc< 0.050
Type: Replicate
Instrument: S1A

Date:	Oct-00	Nov-00	Dec-00	Jan-01	Feb-01	Mar-01	Total
Average					15.5%		15.5%
Std Dev							
N					1		1
Min					15.5%		15.5%
Max					15.5%		15.5%

Analyte: Nitrate Conc< 0.050
Type: Replicate
Instrument: S2A

Date:	Oct-00	Nov-00	Dec-00	Jan-01	Feb-01	Mar-01	Total
Average	9.8%						9.8%
Std Dev	9.2%						9.2%
N	3						3
Min	1.4%						1.4%
Max	19.7%						19.7%

Analyte: Nitrate Conc< 0.050
Type: Replicate
Instrument: S3A

Date:	Oct-00	Nov-00	Dec-00	Jan-01	Feb-01	Mar-01	Total
Average			5.6%	4.2%		2.2%	3.7%
Std Dev				7.3%		1.6%	5.3%
N			1	5		3	9
Min			5.6%	0.1%		0.3%	0.1%
Max			5.6%	16.9%		3.2%	16.9%

Analyte: Nitrate Conc< 0.050
Type: Replicate
Instrument: D6A

Date:	Oct-00	Nov-00	Dec-00	Jan-01	Feb-01	Mar-01	Total
Average			0.5%				0.5%
Std Dev							
N			1				1
Min			0.5%				0.5%
Max			0.5%				0.5%

Table 13 (continued).

Analyte: Sulfate Conc< 0.050
Type: Replicate
Instrument: S1A

Date:	Oct-00	Nov-00	Dec-00	Jan-01	Feb-01	Mar-01	Total
Average					2.1%		2.1%
Std Dev					2.2%		2.2%
N					2		2
Min					0.5%		0.5%
Max					3.6%		3.6%

Analyte: Sulfate Conc< 0.050
Type: Replicate
Instrument: S2A

Date:	Oct-00	Nov-00	Dec-00	Jan-01	Feb-01	Mar-01	Total
Average	3.2%						3.2%
Std Dev							
N	1						1
Min	3.2%						3.2%
Max	3.2%						3.2%

Analyte: Sulfate Conc< 0.050
Type: Replicate
Instrument: S3A

Date:	Oct-00	Nov-00	Dec-00	Jan-01	Feb-01	Mar-01	Total
Average		5.4%	0.4%	32.8%		5.5%	15.3%
Std Dev		4.0%		73.8%		2.9%	44.8%
N		5	1	7		6	19
Min		1.6%	0.4%	0.7%		2.5%	0.4%
Max		11.6%	0.4%	200.0%		10.0%	200.0%

Analyte: Sulfate Conc< 0.050
Type: Replicate
Instrument: D6A

Date:	Oct-00	Nov-00	Dec-00	Jan-01	Feb-01	Mar-01	Total
Average							
Std Dev							
N							
Min							
Max							

Table 14. Average Percent Recovery for Nitrate and Sulfate Spikes

Analyte: Nitrate
Type: Spike
Instrument: S1A

Date:	Oct-00	Nov-00	Dec-00	Jan-01	Feb-01	Mar-01	Total
Average	99.6%				100.5%		100.4%
Std Dev					1.1%		1.1%
N	1				14		15
Min	99.6%				98.4%		98.4%
Max	99.6%				102.0%		102.0%

Analyte: Nitrate
Type: Spike
Instrument: S2A

Date:	Oct-00	Nov-00	Dec-00	Jan-01	Feb-01	Mar-01	Total
Average	98.8%						98.8%
Std Dev	0.7%						0.7%
N	12						12
Min	97.5%						97.5%
Max	99.8%						99.8%

Analyte: Nitrate
Type: Spike
Instrument: S3A

Date:	Oct-00	Nov-00	Dec-00	Jan-01	Feb-01	Mar-01	Total
Average	101.0%	99.7%	100.5%	99.5%	100.1%	99.6%	99.8%
Std Dev	2.5%	0.8%	0.5%	0.8%	1.4%	1.8%	1.4%
N	7	16	12	23	7	30	95
Min	98.5%	98.1%	99.5%	97.8%	97.6%	96.5%	96.5%
Max	105.1%	100.9%	101.3%	100.9%	101.7%	103.6%	105.1%

Analyte: Nitrate
Type: Spike
Instrument: D6A

Date:	Oct-00	Nov-00	Dec-00	Jan-01	Feb-01	Mar-01	Total
Average			99.7%		100.3%		99.9%
Std Dev			0.8%		1.2%		0.9%
N			7		3		10
Min			98.8%		99.0%		98.8%
Max			101.2%		101.3%		101.3%

Table 14 (continued).

Analyte:	Sulfate						
Type:	Spike						
Instrument:	S1A						
Date:	**Oct-00**	**Nov-00**	**Dec-00**	**Jan-01**	**Feb-01**	**Mar-01**	**Total**
Average	100.1%				100.2%		100.2%
Std Dev					1.3%		1.3%
N	1				14		15
Min	100.1%				97.3%		97.3%
Max	100.1%				101.9%		101.9%

Analyte:	Sulfate						
Type:	Spike						
Instrument:	S2A						
Date:	**Oct-00**	**Nov-00**	**Dec-00**	**Jan-01**	**Feb-01**	**Mar-01**	**Total**
Average	99.9%						99.9%
Std Dev	0.7%						0.7%
N	12						12
Min	98.3%						98.3%
Max	100.8%						100.8%

Analyte:	Sulfate						
Type:	Spike						
Instrument:	S3A						
Date:	**Oct-00**	**Nov-00**	**Dec-00**	**Jan-01**	**Feb-01**	**Mar-01**	**Total**
Average	99.5%	99.7%	100.3%	99.5%	100.2%	100.1%	99.9%
Std Dev	1.1%	1.0%	0.8%	0.7%	0.8%	1.5%	1.1%
N	7	16	12	23	7	30	95
Min	98.1%	98.2%	98.7%	98.2%	99.2%	97.3%	97.3%
Max	101.3%	102.0%	102.1%	100.4%	101.5%	103.6%	103.6%

Analyte:	Sulfate						
Type:	Spike						
Instrument:	D6A						
Date:	**Oct-00**	**Nov-00**	**Dec-00**	**Jan-01**	**Feb-01**	**Mar-01**	**Total**
Average			100.1%		100.2%		100.2%
Std Dev			0.5%		1.1%		0.7%
N			7		3		10
Min			99.0%		98.9%		98.9%
Max			100.6%		100.9%		100.9%

Table 15. Filter and Reagent Blanks Values for Nitrate.

Analyte: Nitrate
Type: Filter Blank
Inst: S1A

Date:	Oct-00	Nov-00	Dec-00	Jan-01	Feb-01	Mar-01	Total
Average					0.0038		0.0038
Std Dev					0.0076		0.0076
N					9		9
Min					0.0000		0.0000
Max					0.0185		0.0185

Analyte: Nitrate
Type: Filter Blank
Inst: S2A

Date:	Oct-00	Nov-00	Dec-00	Jan-01	Feb-01	Mar-01	Total
Average							
Std Dev							
N							
Min							
Max							

Analyte: Nitrate
Type: Filter Blank
Inst: S3A

Date:	Oct-00	Nov-00	Dec-00	Jan-01	Feb-01	Mar-01	Total
Average		0.0066	0.0196	0.0000	0.0000	0.0078	0.0071
Std Dev		0.0099	0.0191	0.0000	0.0000	0.0142	0.0125
N		9	3	3	3	12	30
Min		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
Max		0.0202	0.0381	0.0000	0.0000	0.0351	0.0381

Analyte: Nitrate
Type: Filter Blank
Inst: D6A

Date:	Oct-00	Nov-00	Dec-00	Jan-01	Feb-01	Mar-01	Total
Average							
Std Dev							
N							
Min							
Max							

Table 15 (continued).

Analyte: Nitrate
Type: Reagent Blank DI H2O
Inst: S1A

Date:	Oct-00	Nov-00	Dec-00	Jan-01	Feb-01	Mar-01	Total
Average	0.0265				0.0095		0.0116
Std Dev	0.0047				0.0116		0.0123
N	2				14		16
Min	0.0232				0.0000		0.0000
Max	0.0298				0.0263		0.0298

Analyte: Nitrate
Type: Reagent Blank DI H2O
Inst: S2A

Date:	Oct-00	Nov-00	Dec-00	Jan-01	Feb-01	Mar-01	Total
Average	0.0027						0.0027
Std Dev	0.0086						0.0086
N	10						10
Min	0.0000						0.0000
Max	0.0272						0.0272

Analyte: Nitrate
Type: Reagent Blank DI H2O
Inst: S3A

Date:	Oct-00	Nov-00	Dec-00	Jan-01	Feb-01	Mar-01	Total
Average	0.0000	0.0032	0.0090	0.0110	0.0063	0.0063	0.0070
Std Dev	0.0000	0.0074	0.0123	0.0155	0.0117	0.0137	0.0128
N	8	18	19	30	8	33	116
Min	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
Max	0.0000	0.0217	0.0303	0.0500	0.0277	0.0459	0.0500

Analyte: Nitrate
Type: Reagent Blank DI H2O
Inst: D6A

Date:	Oct-00	Nov-00	Dec-00	Jan-01	Feb-01	Mar-01	Total
Average			0.0000		0.0077		0.0033
Std Dev			0.0000		0.0133		0.0087
N			4		3		7
Min			0.0000		0.0000		0.0000
Max			0.0000		0.0231		0.0231

Table 15 (continued).

Analyte: Nitrate
Type: Reagent Blank Eluent
Inst: S1A

Date:	Oct-00	Nov-00	Dec-00	Jan-01	Feb-01	Mar-01	Total
Average					0.0031		0.0031
Std Dev					0.0076		0.0076
N					6		6
Min					0.0000		0.0000
Max					0.0186		0.0186

Analyte: Nitrate
Type: Reagent Blank Eluent
Inst: S2A

Date:	Oct-00	Nov-00	Dec-00	Jan-01	Feb-01	Mar-01	Total
Average	0.0000						0.0000
Std Dev	0.0000						0.0000
N	4						4
Min	0.0000						0.0000
Max	0.0000						0.0000

Analyte: Nitrate
Type: Reagent Blank Eluent
Inst: S3A

Date:	Oct-00	Nov-00	Dec-00	Jan-01	Feb-01	Mar-01	Total
Average	0.0000	0.0000	0.0000	0.0017	0.0061	0.0000	0.0009
Std Dev		0.0000	0.0000	0.0063	0.0106	0.0000	0.0044
N	1	9	6	14	3	12	45
Min	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
Max	0.0000	0.0000	0.0000	0.0237	0.0183	0.0000	0.0237

Analyte: Nitrate
Type: Reagent Blank Eluent
Inst: D6A

Date:	Oct-00	Nov-00	Dec-00	Jan-01	Feb-01	Mar-01	Total
Average			0.0000		0.0000		0.0000
Std Dev			0.0000		0.0000		0.0000
N			2		2		4
Min			0.0000		0.0000		0.0000
Max			0.0000		0.0000		0.0000

Table 16. Filter and Reagent Blank Values for Sulfate.

Analyte: Sulfate
Type: Filter Blank
Inst: S1A

Date:	Oct-00	Nov-00	Dec-00	Jan-01	Feb-01	Mar-01	Total
Average					0.0347		0.0347
Std Dev					0.0255		0.0255
N					9		9
Min					0.0000		0.0000
Max					0.0930		0.0930

Analyte: Sulfate
Type: Filter Blank
Inst: S2A

Date:	Oct-00	Nov-00	Dec-00	Jan-01	Feb-01	Mar-01	Total
Average							
Std Dev							
N							
Min							
Max							

Analyte: Sulfate
Type: Filter Blank
Inst: S3A

Date:	Oct-00	Nov-00	Dec-00	Jan-01	Feb-01	Mar-01	Total
Average		0.0035	0.0000	0.0054	0.0113	0.0049	0.0047
Std Dev		0.0070	0.0000	0.0093	0.0197	0.0115	0.0102
N		9	3	3	3	12	30
Min		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
Max		0.0180	0.0000	0.0161	0.0340	0.0327	0.0340

Analyte: Sulfate
Type: Filter Blank
Inst: D6A

Date:	Oct-00	Nov-00	Dec-00	Jan-01	Feb-01	Mar-01	Total
Average							
Std Dev							
N							
Min							
Max							

Table 16 (continued).

Analyte: Sulfate
Type: Reagent Blank DI H2O
Inst: S1A

Date:	Oct-00	Nov-00	Dec-00	Jan-01	Feb-01	Mar-01	Total
Average	0.0108				0.0061		0.0066
Std Dev	0.0152				0.0149		0.0145
N	2				14		16
Min	0.0000				0.0000		0.0000
Max	0.0215				0.0539		0.0539

Analyte: Sulfate
Type: Reagent Blank DI H2O
Inst: S2A

Date:	Oct-00	Nov-00	Dec-00	Jan-01	Feb-01	Mar-01	Total
Average	0.0000						0.0000
Std Dev	0.0000						0.0000
N	10						10
Min	0.0000						0.0000
Max	0.0000						0.0000

Analyte: Sulfate
Type: Reagent Blank DI H2O
Inst: S3A

Date:	Oct-00	Nov-00	Dec-00	Jan-01	Feb-01	Mar-01	Total
Average	0.0087	0.0076	0.0010	0.0148	0.0104	0.0087	0.0090
Std Dev	0.0057	0.0093	0.0044	0.0191	0.0147	0.0232	0.0171
N	8	18	19	30	8	33	116
Min	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
Max	0.0152	0.0235	0.0191	0.0608	0.0342	0.1158	0.1158

Analyte: Sulfate
Type: Reagent Blank DI H2O
Inst: D6A

Date:	Oct-00	Nov-00	Dec-00	Jan-01	Feb-01	Mar-01	Total
Average			0.0041		0.0000		0.0024
Std Dev			0.0082		0.0000		0.0062
N			4		3		7
Min			0.0000		0.0000		0.0000
Max			0.0165		0.0000		0.0165

Table 16 (continued).

Analyte: Sulfate
Type: Reagent Blank Eluent
Inst: S1A

Date:	Oct-00	Nov-00	Dec-00	Jan-01	Feb-01	Mar-01	Total
Average					0.0084		0.0084
Std Dev					0.0097		0.0097
N					6		6
Min					0.0000		0.0000
Max					0.0220		0.0220

Analyte: Sulfate
Type: Reagent Blank Eluent
Inst: S2A

Date:	Oct-00	Nov-00	Dec-00	Jan-01	Feb-01	Mar-01	Total
Average	0.0000						0.0000
Std Dev	0.0000						0.0000
N	4						4
Min	0.0000						0.0000
Max	0.0000						0.0000

Analyte: Sulfate
Type: Reagent Blank Eluent
Inst: S3A

Date:	Oct-00	Nov-00	Dec-00	Jan-01	Feb-01	Mar-01	Total
Average	0.0000	0.0115	0.0144	0.0092	0.0258	0.0025	0.0094
Std Dev		0.0095	0.0187	0.0148	0.0122	0.0086	0.0136
N	1	9	6	14	3	12	45
Min	0.0000	0.0000	0.0000	0.0000	0.0187	0.0000	0.0000
Max	0.0000	0.0232	0.0472	0.0470	0.0399	0.0298	0.0472

Analyte: Sulfate
Type: Reagent Blank Eluent
Inst: D6A

Date:	Oct-00	Nov-00	Dec-00	Jan-01	Feb-01	Mar-01	Total
Average			0.0100		0.0426		0.0263
Std Dev			0.0142		0.0269		0.0258
N			2		2		4
Min			0.0000		0.0236		0.0000
Max			0.0200		0.0617		0.0617

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 17 presents the average percent recovery value for sodium for both QA and QC samples for the two instruments used for these measurements. As noted, the average recovery for the QA sample ranged from 95.6% to 101.8%. The average recovery for the QC samples ranged from 98.8% to 100.4%.

Table 18 presents the average percent recovery value for ammonium for both QA and QC samples for the two instruments used for these measurements. The average recovery for the QA samples ranged from 94.7% to 102.4%. The average recovery for the QC samples ranged from 98.3% to 100.4%.

Table 19 presents the average percent recovery value for potassium for both QA and QC samples for the two instruments used for these measurements. The average recovery for the QA samples ranged from 93.4% to 100.0%. The average recovery for the QC samples ranged from 98.3% to 101.1%.

Table 20 shows ARPD values for replicate measurements of sodium, ammonium, and potassium at concentrations >0.050 ppm (approximately the limit of quantitation). As noted, the maximum ARPD for sodium for the two instruments used over the six month period is 2.6%. The corresponding values for ammonium and potassium are 1.2% and 5.2%, respectively.

Table 21 shows ARPD values for replicate measurements of sodium, ammonium, and potassium at concentrations <0.050 ppm. The maximum ARPD for the two instruments used over the six month period are 18.2%, 17.4%, and 49.1% for sodium, ammonium, and potassium, respectively.

Table 22 shows average percent recovery for spikes of sodium, ammonium, and potassium for the two instruments used over the six month period. The average recovery values ranged from 98.3% to 100.7% for sodium, 96.3% to 99.3% for ammonium, and 93.6% to 98.8% for potassium

Table 23 presents filter and reagent blank values for sodium for the two instruments used for these measurements. As noted, the highest average value for filter blank was 0.0141 ppm (25 mL extract) and the highest reagent blank deionized water was 0.0025 ppm. Table 24 presents the same values for ammonium. As noted, the highest average value for filter blank was 0.0060 ppm (25 mL extract), and the highest reagent blank deionized water was 0.0080 ppm. Table 25 presents these same values for potassium. As noted, the highest average value for filter blank was 0.0012 ppm (25 mL extract) and the highest reagent blank deionized water was 0.0017 ppm.

Table 17. Average Percent Recovery for Sodium QA and QC Samples.

Analyte: Sodium
Type: QA, 0.4 ppm
Instrument: D5C

Date:	Oct-00	Nov-00	Dec-00	Jan-01	Feb-01	Mar-01	Total
Average	98.3%	97.7%	95.6%				97.6%
Std Dev	4.3%	2.8%	0.8%				3.3%
N	11	13	4				28
Min	94.4%	95.0%	94.7%				94.4%
Max	107.0%	101.6%	96.5%				107.0%

Analyte: Sodium
Type: QA, 0.4 ppm
Instrument: D6C

Date:	Oct-00	Nov-00	Dec-00	Jan-01	Feb-01	Mar-01	Total
Average			99.8%	101.1%	101.8%	101.5%	101.2%
Std Dev			0.9%	1.3%	3.1%	2.8%	2.4%
N			9	15	14	22	60
Min			98.7%	98.9%	99.3%	98.1%	98.1%
Max			101.4%	104.2%	108.2%	109.3%	109.3%

Analyte: Sodium
Type: QC, 2.0 ppm
Instrument: D5C

Date:	Oct-00	Nov-00	Dec-00	Jan-01	Feb-01	Mar-01	Total
Average	98.8%	100.4%	100.2%				99.6%
Std Dev	4.1%	2.4%	0.6%				3.3%
N	14	10	4				28
Min	92.8%	98.0%	99.6%				92.8%
Max	105.0%	106.1%	100.8%				106.1%

Analyte: Sodium
Type: QC, 2.0 ppm
Instrument: D6C

Date:	Oct-00	Nov-00	Dec-00	Jan-01	Feb-01	Mar-01	Total
Average			99.7%	100.3%	100.1%	100.0%	100.0%
Std Dev			0.4%	0.4%	0.9%	1.2%	0.9%
N			10	15	16	24	65
Min			99.0%	99.4%	99.1%	97.6%	97.6%
Max			100.2%	101.2%	102.4%	103.1%	103.1%

Table 17 (continued).

Analyte: Sodium
Type: QA, 4.0 ppm
Instrument: D5C

Date:	Oct-00	Nov-00	Dec-00	Jan-01	Feb-01	Mar-01	Total
Average	98.4%	97.8%	96.7%				97.9%
Std Dev	2.1%	1.3%	0.7%				1.7%
N	17	15	5				37
Min	94.9%	96.1%	95.9%				94.9%
Max	102.2%	99.6%	97.5%				102.2%

Analyte: Sodium
Type: QA, 4.0 ppm
Instrument: D6C

Date:	Oct-00	Nov-00	Dec-00	Jan-01	Feb-01	Mar-01	Total
Average			99.3%	99.1%	99.3%	99.2%	99.2%
Std Dev			0.3%	0.3%	0.8%	1.3%	0.9%
N			9	16	18	27	70
Min			98.9%	98.6%	97.5%	96.9%	96.9%
Max			99.7%	99.8%	100.6%	101.1%	101.1%

Analyte: Sodium
Type: QC, 5.0 ppm
Instrument: D5C

Date:	Oct-00	Nov-00	Dec-00	Jan-01	Feb-01	Mar-01	Total
Average	100.1%	99.7%	99.3%				99.8%
Std Dev	2.2%	0.8%	0.6%				1.5%
N	10	11	4				25
Min	97.3%	98.6%	98.5%				97.3%
Max	104.7%	101.0%	99.8%				104.7%

Analyte: Sodium
Type: QC, 5.0 ppm
Instrument: D6C

Date:	Oct-00	Nov-00	Dec-00	Jan-01	Feb-01	Mar-01	Total
Average			99.4%	99.7%	100.3%	99.7%	99.8%
Std Dev			0.4%	0.3%	0.8%	0.7%	0.7%
N			6	9	10	15	40
Min			99.0%	99.2%	99.1%	98.3%	98.3%
Max			100.1%	100.1%	101.5%	100.9%	101.5%

Table 18. Average Percent Recovery for Ammonium QA and QC Samples.

Analyte:	Ammonium					
Type:	QA, 0.4 ppm					
Instrument:	D5C					
Date:	**Oct-00**	**Nov-00**	**Dec-00**	**Jan-01**	**Feb-01**	**Mar-01**	**Total**
Average	96.8%	98.5%	94.7%				97.3%
Std Dev	5.2%	3.4%	3.0%				4.2%
N	11	13	4				28
Min	90.8%	94.8%	90.7%				90.7%
Max	103.8%	104.2%	97.7%				104.2%

Analyte:	Ammonium						
Type:	QA, 0.4 ppm						
Instrument:	D6C						
Date:	**Oct-00**	**Nov-00**	**Dec-00**	**Jan-01**	**Feb-01**	**Mar-01**	**Total**
Average			102.0%	101.7%	102.4%	100.4%	101.4%
Std Dev			1.9%	1.5%	1.9%	2.4%	2.1%
N			9	15	14	22	60
Min			98.1%	98.6%	99.5%	92.0%	92.0%
Max			103.6%	105.1%	105.4%	103.7%	105.4%

Analyte:	Ammonium						
Type:	QC, 2.0 ppm						
Instrument:	D5C						
Date:	**Oct-00**	**Nov-00**	**Dec-00**	**Jan-01**	**Feb-01**	**Mar-01**	**Total**
Average	98.9%	98.7%	98.3%				98.8%
Std Dev	5.2%	1.5%	0.6%				3.7%
N	14	10	4				28
Min	92.0%	96.4%	97.6%				92.0%
Max	106.6%	101.0%	99.1%				106.6%

Analyte:	Ammonium						
Type:	QC, 2.0 ppm						
Instrument:	D6C						
Date:	**Oct-00**	**Nov-00**	**Dec-00**	**Jan-01**	**Feb-01**	**Mar-01**	**Total**
Average			99.3%	100.4%	100.2%	99.2%	99.7%
Std Dev			1.1%	0.9%	1.4%	1.2%	1.3%
N			10	15	16	24	65
Min			97.6%	98.6%	98.3%	96.9%	96.9%
Max			100.5%	102.1%	103.4%	101.9%	103.4%

Table 18 (continued).

Analyte: Ammonium
Type: QA, 4.0 ppm
Instrument: D5C

Date:	Oct-00	Nov-00	Dec-00	Jan-01	Feb-01	Mar-01	Total
Average	100.2%	97.7%	96.0%				98.6%
Std Dev	4.0%	1.2%	1.6%				3.2%
N	17	15	5				37
Min	96.3%	95.8%	93.5%				93.5%
Max	107.3%	99.6%	97.4%				107.3%

Analyte: Ammonium
Type: QA, 4.0 ppm
Instrument: D6C

Date:	Oct-00	Nov-00	Dec-00	Jan-01	Feb-01	Mar-01	Total
Average			98.7%	99.2%	99.8%	99.7%	99.5%
Std Dev			0.9%	0.9%	1.0%	1.0%	1.0%
N			9	16	18	27	70
Min			97.2%	97.3%	98.7%	98.2%	97.2%
Max			99.8%	100.8%	102.3%	102.8%	102.8%

Analyte: Ammonium
Type: QC, 5.0 ppm
Instrument: D5C

Date:	Oct-00	Nov-00	Dec-00	Jan-01	Feb-01	Mar-01	Total
Average	100.0%	99.3%	99.1%				99.6%
Std Dev	4.0%	0.4%	1.3%				2.6%
N	10	11	4				25
Min	95.3%	98.7%	97.8%				95.3%
Max	108.6%	100.1%	100.4%				108.6%

Analyte: Ammonium
Type: QC, 5.0 ppm
Instrument: D6C

Date:	Oct-00	Nov-00	Dec-00	Jan-01	Feb-01	Mar-01	Total
Average			98.5%	99.8%	100.2%	100.1%	99.8%
Std Dev			0.9%	0.6%	1.1%	1.4%	1.2%
N			6	9	10	15	40
Min			97.3%	98.9%	98.8%	97.9%	97.3%
Max			99.6%	100.9%	102.1%	104.0%	104.0%

Table 19. Average Percent Recovery for Potassium QA and QC Samples.

Analyte:	Potassium						
Type:	QA, 0.4 ppm						
Instrument:	D5C						
Date:	**Oct-00**	**Nov-00**	**Dec-00**	**Jan-01**	**Feb-01**	**Mar-01**	**Total**
Average	95.3%	98.0%	93.4%				96.3%
Std Dev	4.8%	5.4%	4.3%				5.1%
N	11	13	4				28
Min	91.7%	92.7%	89.1%				89.1%
Max	104.1%	107.8%	97.5%				107.8%

Analyte:	Potassium						
Type:	QA, 0.4 ppm						
Instrument:	D6C						
Date:	**Oct-00**	**Nov-00**	**Dec-00**	**Jan-01**	**Feb-01**	**Mar-01**	**Total**
Average			99.6%	99.8%	100.0%	99.6%	99.7%
Std Dev			1.5%	0.8%	1.6%	3.1%	2.1%
N			9	15	14	22	60
Min			97.1%	98.3%	95.5%	92.7%	92.7%
Max			101.4%	100.9%	101.9%	104.1%	104.1%

Analyte:	Potassium						
Type:	QC, 2.0 ppm						
Instrument:	D5C						
Date:	**Oct-00**	**Nov-00**	**Dec-00**	**Jan-01**	**Feb-01**	**Mar-01**	**Total**
Average	98.8%	99.8%	98.3%				99.1%
Std Dev	4.6%	1.8%	0.8%				3.4%
N	14	10	4				28
Min	92.6%	97.3%	97.3%				92.6%
Max	105.4%	102.1%	99.0%				105.4%

Analyte:	Potassium						
Type:	QC, 2.0 ppm						
Instrument:	D6C						
Date:	**Oct-00**	**Nov-00**	**Dec-00**	**Jan-01**	**Feb-01**	**Mar-01**	**Total**
Average			99.6%	100.3%	100.1%	100.3%	100.1%
Std Dev			0.6%	0.4%	0.9%	1.4%	1.0%
N			10	15	16	24	65
Min			98.7%	99.4%	99.0%	98.4%	98.4%
Max			100.2%	101.1%	101.9%	104.6%	104.6%

Table 19 (continued).

Analyte: Potassium
Type: QA, 4.0 ppm
Instrument: D5C

Date:	Oct-00	Nov-00	Dec-00	Jan-01	Feb-01	Mar-01	Total
Average	99.3%	98.0%	95.7%				98.3%
Std Dev	2.3%	1.8%	0.9%				2.3%
N	17	15	5				37
Min	96.2%	95.4%	94.6%				94.6%
Max	103.2%	100.4%	96.6%				103.2%

Analyte: Potassium
Type: QA, 4.0 ppm
Instrument: D6C

Date:	Oct-00	Nov-00	Dec-00	Jan-01	Feb-01	Mar-01	Total
Average			99.6%	99.4%	99.5%	99.4%	99.4%
Std Dev			0.5%	0.3%	0.6%	1.3%	0.9%
N			9	16	18	27	70
Min			98.8%	98.7%	98.7%	98.0%	98.0%
Max			100.4%	99.8%	100.5%	103.6%	103.6%

Analyte: Potassium
Type: QC, 5.0 ppm
Instrument: D5C

Date:	Oct-00	Nov-00	Dec-00	Jan-01	Feb-01	Mar-01	Total
Average	101.1%	99.6%	98.6%				100.1%
Std Dev	2.8%	1.1%	0.8%				2.1%
N	10	11	4				25
Min	98.3%	98.7%	97.8%				97.8%
Max	107.0%	101.5%	99.4%				107.0%

Analyte: Potassium
Type: QC, 5.0 ppm
Instrument: D6C

Date:	Oct-00	Nov-00	Dec-00	Jan-01	Feb-01	Mar-01	Total
Average			98.9%	99.6%	99.9%	100.1%	99.8%
Std Dev			0.7%	0.4%	0.6%	1.4%	1.0%
N			6	9	10	15	40
Min			98.2%	99.1%	98.8%	97.6%	97.6%
Max			100.0%	100.2%	100.9%	103.0%	103.0%

Table 20. Absolute Relative Percent Difference for Replicate Measurement of Sodium, Ammonium, and Potassium at Concentrations >0.050 ppm

Analyte:	Sodium		Conc>	0.050			
Type:	Replicate						
Inst:	D5C						
Date:	**Oct-00**	**Nov-00**	**Dec-00**	**Jan-01**	**Feb-01**	**Mar-01**	**Total**
Average	1.1%	2.0%	2.1%				1.6%
Std Dev	1.0%	1.5%	2.7%				1.4%
N	15	6	3				24
Min	0.0%	0.2%	0.2%				0.0%
Max	4.1%	4.1%	5.3%				5.3%

Analyte:	Sodium		Conc>	0.050			
Type:	Replicate						
Inst:	D6C						
Date:	**Oct-00**	**Nov-00**	**Dec-00**	**Jan-01**	**Feb-01**	**Mar-01**	**Total**
Average			1.3%	1.8%	2.0%	2.6%	2.2%
Std Dev			1.2%	3.1%	2.9%	4.2%	3.4%
N			6	8	14	25	53
Min			0.1%	0.0%	0.0%	0.1%	0.0%
Max			3.3%	9.2%	10.0%	20.8%	20.8%

Analyte:	Ammonium		Conc>	0.050			
Type:	Replicate						
Inst:	D5C						
Date:	**Oct-00**	**Nov-00**	**Dec-00**	**Jan-01**	**Feb-01**	**Mar-01**	**Total**
Average	1.2%	0.6%	0.7%				0.9%
Std Dev	1.3%	0.5%	0.6%				1.1%
N	13	13	5				31
Min	0.0%	0.0%	0.0%				0.0%
Max	5.1%	2.0%	1.4%				5.1%

Analyte:	Ammonium		Conc>	0.050			
Type:	Replicate						
Inst:	D6C						
Date:	**Oct-00**	**Nov-00**	**Dec-00**	**Jan-01**	**Feb-01**	**Mar-01**	**Total**
Average			0.1%	0.3%	0.6%	0.4%	0.4%
Std Dev			0.1%	0.3%	0.6%	0.4%	0.4%
N			12	16	18	33	79
Min			0.0%	0.0%	0.0%	0.0%	0.0%
Max			0.5%	0.9%	2.5%	1.8%	2.5%

Table 20 (continued).

Analyte:	Potassium		Conc>	0.050			
Type:	Replicate						
Inst:	D5C						
Date:	Oct-00	Nov-00	Dec-00	Jan-01	Feb-01	Mar-01	Total
Average	2.4%	1.3%	1.6%				1.8%
Std Dev	2.1%	1.1%	0.5%				1.7%
N	4	3	2				9
Min	0.1%	0.5%	1.3%				0.1%
Max	5.1%	2.5%	2.0%				5.1%

Analyte:	Potassium		Conc>	0.050			
Type:	Replicate						
Inst:	D6C						
Date:	Oct-00	Nov-00	Dec-00	Jan-01	Feb-01	Mar-01	Total
Average			1.5%	3.5%	5.2%	3.5%	3.6%
Std Dev			1.3%	2.2%	3.1%	2.4%	2.6%
N			4	5	6	3	18
Min			0.2%	0.7%	1.0%	0.8%	0.2%
Max			3.1%	6.2%	8.2%	5.1%	8.2%

Table 21. Absolute Relative Percent Difference for Replicate Measurement of Sodium, Ammonium, and Potassium at Concentrations <0.050 ppm

Analyte:	**Sodium**		**Conc<**	**0.050**			
Type:	**Replicate**						
Inst:	**D5C**						
Date:	**Oct-00**	**Nov-00**	**Dec-00**	**Jan-01**	**Feb-01**	**Mar-01**	**Total**
Average	**14.7%**	**11.6%**	**9.8%**				**11.7%**
Std Dev	**4.5%**	**20.4%**	**6.3%**				**16.6%**
N	**2**	**10**	**3**				**15**
Min	**11.5%**	**0.7%**	**2.7%**				**0.7%**
Max	**17.9%**	**67.9%**	**14.4%**				**67.9%**

Analyte:	**Sodium**		**Conc<**	**0.050**			
Type:	**Replicate**						
Inst:	**D6C**						
Date:	**Oct-00**	**Nov-00**	**Dec-00**	**Jan-01**	**Feb-01**	**Mar-01**	**Total**
Average			**7.9%**	**6.4%**	**10.1%**	**18.2%**	**11.0%**
Std Dev			**8.1%**	**3.5%**	**8.5%**	**17.4%**	**11.6%**
N			**6**	**11**	**10**	**11**	**38**
Min			**2.0%**	**0.7%**	**1.3%**	**2.1%**	**0.7%**
Max			**23.2%**	**12.3%**	**25.2%**	**55.9%**	**55.9%**

Table 21 (continued).

Analyte: Ammonium Conc< 0.050
Type: Replicate
Inst: D5C

Date:	Oct-00	Nov-00	Dec-00	Jan-01	Feb-01	Mar-01	Total
Average	7.3%	17.4%					12.3%
Std Dev							7.2%
N	1	1					2
Min	7.3%	17.4%					7.3%
Max	7.3%	17.4%					17.4%

Analyte: Ammonium Conc< 0.050
Type: Replicate
Inst: D6C

Date:	Oct-00	Nov-00	Dec-00	Jan-01	Feb-01	Mar-01	Total
Average					3.3%	8.4%	6.4%
Std Dev					2.3%	4.5%	4.4%
N					2	3	5
Min					1.6%	3.4%	1.6%
Max					4.9%	12.0%	12.0%

Analyte: Potassium Conc< 0.050
Type: Replicate
Inst: D5C

Date:	Oct-00	Nov-00	Dec-00	Jan-01	Feb-01	Mar-01	Total
Average	49.1%	8.4%	18.9%				13.4%
Std Dev	59.8%	3.2%	17.9%				12.9%
N	2	2	3				7
Min	6.9%	6.1%	4.1%				4.1%
Max	91.4%	10.7%	38.9%				91.4%

Analyte: Potassium Conc< 0.050
Type: Replicate
Inst: D6C

Date:	Oct-00	Nov-00	Dec-00	Jan-01	Feb-01	Mar-01	Total
Average			4.3%	20.0%	7.8%	11.4%	11.4%
Std Dev			4.1%	56.7%	5.6%	11.3%	25.9%
N			8	12	14	28	62
Min			1.0%	0.1%	0.5%	0.3%	0.1%
Max			12.1%	200.0%	16.3%	42.9%	200.0%

Table 22. Average Percent Recovery for Spikes of Sodium, Ammonium, and Potassium

Analyte: Sodium
Type: Spike
Inst: D5C

Date:	Oct-00	Nov-00	Dec-00	Jan-01	Feb-01	Mar-01	Total
Average	99.2%	98.9%	98.3%				98.9%
Std Dev	1.6%	0.7%	2.1%				1.4%
N	15	13	6				34
Min	95.4%	97.9%	94.4%				94.4%
Max	101.5%	100.1%	100.4%				101.5%

Analyte: Sodium
Type: Spike
Inst: D6C

Date:	Oct-00	Nov-00	Dec-00	Jan-01	Feb-01	Mar-01	Total
Average			99.0%	99.3%	99.8%	100.1%	99.7%
Std Dev			0.3%	0.8%	1.2%	1.3%	1.2%
N			11	15	19	29	74
Min			98.5%	98.0%	97.4%	97.2%	97.2%
Max			99.5%	100.6%	103.0%	102.3%	103.0%

Analyte: Ammonium
Type: Spike
Inst: D5C

Date:	Oct-00	Nov-00	Dec-00	Jan-01	Feb-01	Mar-01	Total
Average	99.3%	98.2%	96.3%				98.4%
Std Dev	2.8%	0.7%	1.6%				2.2%
N	15	13	6				34
Min	92.6%	96.9%	94.2%				92.6%
Max	102.9%	99.4%	98.3%				102.9%

Analyte: Ammonium
Type: Spike
Inst: D6C

Date:	Oct-00	Nov-00	Dec-00	Jan-01	Feb-01	Mar-01	Total
Average			97.7%	98.7%	94.3%	98.2%	97.2%
Std Dev			1.3%	1.3%	22.9%	2.2%	11.6%
N			11	15	19	29	74
Min			95.8%	95.6%	0.0%	92.6%	0.0%
Max			100.2%	100.3%	103.9%	102.3%	103.9%

Table 22 (continued).

Analyte: Potassium
Type: Spike
Inst: D5C

Date:	**Oct-00**	**Nov-00**	**Dec-00**	**Jan-01**	**Feb-01**	**Mar-01**	**Total**
Average	98.8%	97.4%	95.6%				97.7%
Std Dev	3.1%	2.3%	2.5%				2.9%
N	15	13	6				34
Min	95.2%	94.6%	91.1%				91.1%
Max	103.8%	101.9%	97.4%				103.8%

Analyte: Potassium
Type: Spike
Inst: D6C

Date:	**Oct-00**	**Nov-00**	**Dec-00**	**Jan-01**	**Feb-01**	**Mar-01**	**Total**
Average			97.7%	98.2%	93.6%	98.6%	97.1%
Std Dev			1.3%	1.2%	22.7%	2.1%	11.6%
N			11	15	19	29	74
Min			95.6%	96.2%	0.0%	96.3%	0.0%
Max			99.4%	100.2%	102.3%	106.2%	106.2%

Table 23. Filter and Reagent Blank Values for Sodium.

Analyte: Sodium
Type: Filter Blank
Instrument: D5C

Date:	Oct-00	Nov-00	Dec-00	Jan-01	Feb-01	Mar-01	Total
Average		0.0028					0.0028
Std Dev		0.0062					0.0062
N		9					9
Min		0.0000					0.0000
Max		0.0180					0.0180

Analyte: Sodium
Type: Filter Blank
Instrument: D6C

Date:	Oct-00	Nov-00	Dec-00	Jan-01	Feb-01	Mar-01	Total
Average			0.0011	0.0000	0.0141	-0.0057	0.0035
Std Dev			0.0026	0.0012	0.0185	0.0065	0.0151
N			3	3	12	12	30
Min			-0.0005	-0.0012	-0.0042	-0.0183	-0.0183
Max			0.0041	0.0011	0.0647	0.0049	0.0647

Analyte: Sodium
Type: Reagent Blank DI H2O
Instrument: D5C

Date:	Oct-00	Nov-00	Dec-00	Jan-01	Feb-01	Mar-01	Total
Average	0.0000	0.0001	-0.0002				0.0000
Std Dev	0.0000	0.0004	0.0008				0.0005
N	15	20	10				45
Min	0.0000	0.0000	-0.0024				-0.0024
Max	0.0000	0.0019	0.0000				0.0019

Analyte: Sodium
Type: Reagent Blank DI H2O
Instrument: D6C

Date:	Oct-00	Nov-00	Dec-00	Jan-01	Feb-01	Mar-01	Total
Average			-0.0021	0.0003	0.0025	-0.0008	0.0001
Std Dev			0.0053	0.0039	0.0110	0.0166	0.0116
N			11	26	23	34	94
Min			-0.0074	-0.0051	-0.0097	-0.0167	-0.0167
Max			0.0120	0.0079	0.0330	0.0624	0.0624

Table 24. Filter and Reagent Blank Values for Ammonium.

Analyte: Ammonium
Type: Filter Blank
Instrument: D5C

Date:	Oct-00	Nov-00	Dec-00	Jan-01	Feb-01	Mar-01	Total
Average		0.0000					0.0000
Std Dev		0.0000					0.0000
N		9					9
Min		0.0000					0.0000
Max		0.0000					0.0000

Analyte: Ammonium
Type: Filter Blank
Instrument: D6C

Date:	Oct-00	Nov-00	Dec-00	Jan-01	Feb-01	Mar-01	Total
Average			-0.0074	-0.0029	-0.0020	0.0060	0.0006
Std Dev			0.0015	0.0008	0.0046	0.0108	0.0087
N			3	3	12	12	30
Min			-0.0089	-0.0038	-0.0135	0.0000	-0.0135
Max			-0.0060	-0.0021	0.0024	0.0253	0.0253

Analyte: Ammonium
Type: Reagent
Blank DI H2O
Instrument: D5C

Date:	Oct-00	Nov-00	Dec-00	Jan-01	Feb-01	Mar-01	Total
Average	0.0000	0.0009	0.0015				0.0007
Std Dev	0.0000	0.0029	0.0047				0.0029
N	15	20	10				45
Min	0.0000	0.0000	0.0000				0.0000
Max	0.0000	0.0103	0.0150				0.0150

Analyte: Ammonium
Type: Reagent
Blank DI H2O
Instrument: D6C

Date:	Oct-00	Nov-00	Dec-00	Jan-01	Feb-01	Mar-01	Total
Average			-0.0060	-0.0004	0.0013	0.0080	0.0024
Std Dev			0.0066	0.0081	0.0092	0.0111	0.0104
N			11	26	23	34	94
Min			-0.0136	-0.0106	-0.0132	-0.0136	-0.0136
Max			0.0067	0.0165	0.0239	0.0382	0.0382

Table 25. Filter and Reagent Blank Values for Potassium.

Analyte: Potassium
Type: Filter Blank
Instrument: D5C

Date:	Oct-00	Nov-00	Dec-00	Jan-01	Feb-01	Mar-01	Total
Average		0.0000					0.0000
Std Dev		0.0000					0.0000
N		9					9
Min		0.0000					0.0000
Max		0.0000					0.0000

Analyte: Potassium
Type: Filter Blank
Instrument: D6C

Date:	Oct-00	Nov-00	Dec-00	Jan-01	Feb-01	Mar-01	Total
Average			0.0000	0.0000	0.0012	0.0000	0.0005
Std Dev			0.0000	0.0000	0.0041	0.0000	0.0026
N			3	3	12	12	30
Min			0.0000	0.0000	0.0000	0.0000	0.0000
Max			0.0000	0.0000	0.0143	0.0000	0.0143

Analyte: Potassium
Type: Reagent Blank DI H2O
Instrument: D5C

Date:	Oct-00	Nov-00	Dec-00	Jan-01	Feb-01	Mar-01	Total
Average	0.0000	0.0000	0.0000				0.0000
Std Dev	0.0000	0.0000	0.0000				0.0000
N	15	20	10				45
Min	0.0000	0.0000	0.0000				0.0000
Max	0.0000	0.0000	0.0000				0.0000

Analyte: Potassium
Type: Reagent Blank DI H2O
Instrument: D6C

Date:	Oct-00	Nov-00	Dec-00	Jan-01	Feb-01	Mar-01	Total
Average			0.0013	0.0017	0.0004	0.0001	0.0008
Std Dev			0.0023	0.0029	0.0014	0.0015	0.0022
N			11	26	23	34	94
Min			0.0000	0.0000	0.0000	-0.0067	-0.0067
Max			0.0057	0.0071	0.0061	0.0039	0.0071

2.2.4 Data Validity Discussion

To date, no data have been invalidated as a result of errors in the ion chromatography laboratory. Any inconsistencies that are observed in the filter samples are flagged on the ion chromatography data report when it is submitted for entry into the database. For example, on a few occasions, two 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.

2.2.5 Summary of Audit Findings and Recommendations

All audit findings and recommendations are described in Appendix A to this report.

2.2.6 Corrective Actions Taken

No analytical corrective actions were needed during this six month period.

Quartz filters, which were used by certain samplers beginning in September 2000, showed very high levels of sodium. RTI was not provided with unsampled quartz filters to use for background determination.

2.3 Organic and Elemental Carbon Laboratory

2.3.1 Description of QC Checks Applied

Quality control checks, acceptance criteria, and corrective actions for the Organic and Elemental Carbon (OC/EC) Laboratory are summarized in Table 26.

2.3.2 Statistical Summary of QC Results

The OC/EC Laboratory has two carbon analyzers designated as the New analyzer (because it is the newer of the two) and the Retrofit analyzer (because it is an old analyzer that has been retrofit to be equivalent to the New analyzer).

The method detection limit for total carbon (TC) is determined annually. Both the OC/EC carbon analyzers met the required limit of $\leq$0.5 µg C/cm^2 with MDLs of 0.13 µg C/cm^2 for the New analyzer and 0.16 µg C/cm^2 for the Retrofit analyzer on March 16, 2001.

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 on the following day.

Routine quality control 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 26. Summary of OC/EC Checks, Acceptance Criteria, and Corrective Actions

QC Element	Frequency	Acceptance Criteria	Corrective Action
Method Detection Limit	annually	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	Blank $\leq$0.3 µg/cm^2	Determine if the problem is with the filter or the instrument, and, if necessary, initiate corrective action to identify and solve any instrument problem before analyzing samples.
Three-Point Calibration	weekly	Correlation Coefficient (R^2) $\geq$0.99	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) 90% to 110% recovery, and (2) calibration peak area 90% to 110% of average for the weekly 3-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/cm^2-- Less than 10% RPD, (2) TC Values 5 - 10 µg/cm^2-- Less than 15% RPD, (3) TC Values less than 5 µg/cm^2-- Within 0.5 µg/cm^2.	Flag analysis results for that filter with non-uniform filter deposit (LFU) flag.

Figure 1 (figures start on page 66) shows measured TC for daily instrument blanks run on the New and Retrofit OC/EC analyzers. The 104 daily instrument blanks run on the New OC/EC analyzer gave a mean total FID response corresponding to 0.063 µg C/cm^2 with a standard deviation of 0.028 µg C/cm^2, and the 101 daily instrument blanks run on the Retrofit OC/EC analyzer gave a mean total FID response corresponding to 0.043 µg C/cm^2 with a standard deviation of 0.039 µg C/cm^2. None of the daily instrument blanks run on either instrument exceeded the acceptance criterion of 0.3 µg C/cm^2.

Figure 2 shows linearity (as R^2, forced-fit through the origin) for all 3-point calibrations run on both instruments. Both the New and Retro OC/EC analyzers met the $R^2 \geq 0.99$ requirement for every 3-point calibration.

Percent recovery of standards is used to make sure the instruments are functioning properly and are still calibrated correctly. Figure 3 shows percent recovery on the New OC/EC analyzer 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. Figure 4 shows the same data for the Retrofit OC/EC analyzer.

Response factors for the flame ionization detector (FID) are used to monitor FID performance. Figures 5 and 6 show FID response factors for each of the three calibrations standards and the average FID response factor for each 3-point calibration on the New and Retrofit instruments, respectively.

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 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. Figures 7 and 8 show relative percent difference of duplicate measurements versus filter concentration (µg C/cm^2) for the New and Retrofit instruments, respectively. Insets on the two figures show total number of duplicates run on each instrument and the numbers of filters that passed and that failed the appropriate duplicate criteria. Filters that failed to meet the appropriate duplicate acceptance criterion were flagged as having a nonuniform filter deposit.

2.3.3 Data Validity Discussion

2.3.3.1 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 has happened only twice and, so far, has happened only when a quartz filter was cut in half for analysis by two different laboratories.

2.3.3.2 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

A copy of the audit findings and recommendations are given in Appendix A, and RTI's responses to those findings and recommendations are given in Appendix B.

2.3.5 Corrective Actions Taken

No corrective actions were taken during the period October 1, 2000, through March 31, 2001.

2.4 X-ray Fluorescence Laboratory

2.4.1 Description of QC Checks Applied

QC elements for the analysis of elements by EDXRF, their frequency of application and control limits, and corrective actions are shown in Table 27.

Table 27. QC Procedures Used to Analyze EDXRF Elements

QC Element	Frequency	Control Limits	Corrective Action
Calibration	as needed	--	--
Calibration verification	weekly	within NIST uncertainties	recalibrate
Instrument precision	once per batch of ≤ 15	95–105% recovery	batch reanalysis
Excitation condition check	every sample	within analysis uncertainty	sample reanalysis
Sample replicate precision	10%	± 5 RPD	batch reanalysis

The two-sigma (95 percent confidence level) detection limits in units of ng/cm^2 are 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.

2.4.2 Statistical Summary of QC Results

2.4.2.1 Precision – The precision is monitored by the reproducibility of the XRF signal in counts per second. The counts for a select element 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. Figures 9 through 15 show the following:

- Precision recovery for Si(0) with Rh L - ranges between 96% and 104%
- Precision recovery for Si(1) with Ti target - ranges between 94% and 111%
- Precision recovery for Ti(2) with Fe target - ranges between 99% (with one apparent outlier) and 106%
- Precision recovery for Fe(3) with Ge target - ranges between 97% and 105%
- Precision recovery for Se(4) with Rh K - ranges between 97% and 108%
- Precision recovery for Pb(4) with Rh K - ranges between 93% and 108%
- Precision recovery for Cd(5) with filter - ranges between 94% and 104%.

2.4.2.2 Recovery - Recovery or system accuracy is determined by the analysis of a series of NIST Standard Reference Materials filters. Recovery is calculated by comparison of a measured and expected values. Figures 16 through 28 show recovery for 12 select elements spanning the range of the 48 elements normally measured. All recovery values for all elements ranged between 92% and 108%.

2.4.2.3 Replicates – Ten percent of the filters are reanalyzed and the results for select elements are compared. Figures 29 through 34 compare replicate values for six elements through regression analysis. Note that slopes are all greater than 0.999 and correlation coefficients are all greater than 0.998, indicating acceptable replication.

2.4.3 Data Validity Discussion

The data presented in Section 2.4.2 indicate no problems with the XRF data. The only problems encountered were occasional tears and/or pinholes in the filters. These were minor, and not considered to have a significant impact on the analysis results.

2.4.4 Summary of Audit Findings and Recommendations

All audit findings and recommendations are described in Appendix A to this report.

2.4.5 Corrective Actions

No changes were made in the analytical procedures used by the XRF laboratory, Chester LabNet (LabCor). No substantive corrective actions were taken,.

2.5 Sample Handling and Archiving Laboratory (SHAL)

2.5.1 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, 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. This cross-checking procedure is also used when an excessive number of packing errors is reported.

2.5.2 Corrective Actions Taken

Problem: The R&P FRM type samplers (used in Texas) frequently have sampler problems and operators miss sampling events. **Corrective Action:** RTI is now providing a Field Blank with each shipment to a site using this type of sampler. The blank filters can now be used to complete a "makeup" run if a scheduled event is missed.

Problem: Some monitoring agencies were not able to service sites on weekends due to work rules or other local factors. In response, EPA designed an "alternate schedule" in which weekend filter pickup and installation is not done; however, this requires that either a Friday or a Monday sample be missed. **Corrective Action:** The alternate schedule developed by EPA is being implemented at specified sites. Unused sample sets are being analyzed as Trip Blanks.

Problem: As some of the SHAL PC's were being upgraded, the return air bills were not printing correctly. The third party billing number to EPA's account was truncated. This problem was not discovered immediately. **Corrective Action:** RTI sent an e-mail through the DOPOs to all site operators alerting them to the problem and asking them to correct the billing number on any air bills they had in their possession. If the sites are billed for a shipment they should notify RTI who will correct the billing.

2.6 Denuder Refurbishment Laboratory

The Denuder Refurbishment Laboratory is located in RTI Building 3, Laboratory 220. The purpose of the laboratory is to clean and refurbish the coatings on various acid-gas-removing denuders used in the chemical speciation networks operated by EPA and various State and local agencies which utilize the RTI/EPA contract. The laboratory follows these protocols:

- SOP for Coating Annular Denuders with Magnesium Oxide
- SOP for Coating and Extracting Annular Denuders with Sodium Carbonate
- SOP for Coating R & P Speciation Sampler ChemComb© Denuders with Sodium Carbonate
- SOP for Coating Annular Denuders with XAD-4 Resin

2.6.1 Operational Summary

Magnesium oxide denuder refurbishments have been performed on URG and Andersen denuders. We also coated R & P brand honeycomb denuders with sodium carbonate. Thus far in the program, EPA/OAQPS has not directed RTI to provide XAD-4 resin coated denuders for removal of organic vapors.

The laboratory has refurbished frosted glass annular denuders for the Andersen RAAS speciation sampler and the URG MASS-400 speciation sampler at three-month intervals since the program began. The Met One SASS speciation sampler aluminum honeycomb denuders have not yet been refurbished since these denuders are part of the sampling module and receive only one-sixth the exposure of the annular denuders which are part of the sampler itself and are exposed to ambient air each sampling event.

The laboratory is experienced in the preparation of sodium carbonate-coated denuders for Andersen, URG, Met One, and R&P speciation samplers. Citric acid-coated denuders can also be prepared, should they be required to removal and quantification of basic gases (i.e., ammonia and amines).

2.6.2 Problems and Corrective Actions

Only one significant problem has been encountered in the denuder laboratory. Two URG downtube denuders have arrived at RTI broken. The site operator was alerted to the proper procedures for packaging and shipping. Since it could not be clearly established how and when the denuder had been broken, RTI had URG repair them at one-half the price of a new denuder, and thus promptly returned the denuders to service.

2.6.3 Quality Assurance Activities

Since no analysis of denuder extracts are presently conducted, the QA activities for denuders are confined to the following three topics.

- Obstruction-free annuluses. After coating and drying the interior, each denuder is inspected by holding it to a strong light and viewing down the tube. Thus far, only a few “bridges” of magnesium oxide coating have been noted. These bridges were removed with a thin piece of plastic film.

- Adherence of coating to surfaces. The dried coated denuder is subjected to a blast of nitrogen gas to remove non-adhering particles. The denuder is then gently tapped against a dark laboratory bench surface to ensure no visible coating particles fall out. If some do, the nitrogen gas blast and the tapping test are repeated until no particles are seen.

- Uniformity of coating. Each coated denuder is visually examined to see that all surfaces have been coated. Because it is impossible to clearly see all interior surfaces, a net weight of coating is established and compared to other coated denuder weight increases. The clean, dry denuder is first weighed to the nearest 0.01 g to establish a tare weight. After coating and drying, the denuder is reweighed to the nearest 0.01 g. The uniformity of coating from denuder to denuder is approximated by comparing the net weights of magnesium oxide applied. The typical URG downtube denuder retains 0.9 g of magnesium oxide. The typical Andersen annular denuder retains about 0.4 g of magnesium oxide. The typical R&P glass Chemcomb® denuder retains 0.014 g of sodium carbonate coating mixture. The amount retained by the Met One aluminum honeycomb denuder has not yet been determined.

2.7 Data Processing

2.7.1 Operational Summary

Data processing operations continued as described in the previous semiannual QA report. Significant milestones included the addition of new sites for the Trends network and other PM2.5 monitoring. Modifications were made to the data base programming to accommodate special sample types (e.g., "drop off" filters). Some of the data validation screens were automated, which increased efficiency of monthly data review.

2.7.2 Problems and Corrective Actions

The data processing system has continued to operate with minimal problems, although improvements and modifications continue to be made. Only one corrective action was taken that directly affects data users:

Problem: State monitoring agency personnel complained of difficulty understanding the data report (RTF file) included in the monthly data reporting. **Corrective Action:** RTI devised a new report that highlighted only the flagged data. This will be included in monthly data reporting along with the original report and the spreadsheets as soon as EPA/OAQPS has had the opportunity to review the format of the new report.

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 (December 2000), 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

- 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

- Development and application of Level 1 outlier screening criteria

- 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 (data summaries will be provided in Section 3)

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 (March 2001).

The data validation procedures described in the previous QA Report 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.

2.8.3 Problems and Corrective Actions

Most QA problems and corrective actions should be described in the operational sections of this report. Below are some additional problems and corrective actions pertaining to data validation and other areas:

Problem: The State of Texas received permission to use RTI's PM2.5 analysis program to supply gravimetric PM2.5 data for their compliance program. This was implemented using two side-by-side FRM samplers, one of which sampled on a Teflon filter, while the other sampled with a quartz filter. To avoid destroying the Teflon filters, which were used to generate the compliance data, the anion and cation analyses were performed using the quartz filter. This was done for several months until the State discovered that the sodium ion data was being biased high by the sodium background of the quartz filters. **Corrective Action:** Ion analysis of quartz filters was discontinued in June 2001. Instead, the Teflon filters will be analyzed for anions and cations.

Problem: Level 1 validation limits were developed based on statistics collected during the Minitrends study. Using these limits , the flagged data are examined manually to determine if any objective problem can be determined. However, an excessive number of samples are being flagged by the original screening criteria, resulting in unnecessary and unproductive extra work. Specific data validation codes for AIRS corresponding to these Level 1 checks also need to be reviewed and approved by EPA/OAQPS. **Corrective Action:** These validation limits and data flagging criteria for AIRS require further refinement based on input from EPA and the PM2.5 monitoring community.

Problem: Poor agreement between data gathered by chemical speciation samplers collocated with FRM samplers has been reported by some agencies. **Corrective Action:** It is not clear what the problem(s) might be. Some of the reported discrepancies involve particular sampler types. RTI is continuing to work with the manufacturers, EPA, and the monitoring agencies to identify and fix any problems having to do with sampling canister preparation and/or filter analysis.

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 8 through 15, or approximately August, 2000, through March, 2001. New sites are operated on a 1-in-6 day schedule during the first month in an attempt to minimize the impacts of startup errors. After one month, most sites are put on 1-in-3 sampling schedule unless otherwise directed. 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.

Blanks were run as shown in Table 28. Blank data are not submitted to AIRS, but are reported to the state monitoring agencies and to EPA for statistical analysis. 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. 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 29 shows the approximate data range corresponding to each delivery batch. Sample batches divide on approximately the 10th of the months shown; so, for example, Batch 8 would run from approximately August 11 through September 10. However, samples not previously delivered are also included in the next delivery batch as soon as all the data are complete.

3.2 Completeness Summaries and Frequency of AIRS Null Value Codes

AIRS Null Value Codes indicate exposures that have been invalidated either in the field, in the laboratory, or by the state monitoring agency.

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). Blank cells indicate that no analyses were scheduled for a site during a particular delivery batch interval.

Table 28. Summary of Blanks.

Blank Type	Delivery Batch	Count of Blanks
Field Blank	8	14
Field Blank	9	35
Field Blank	10	29
Field Blank	11	29
Field Blank	12	8
Field Blank	13	13
Field Blank	14	25
Field Blank	15	66
Trip Blank	9	9
Trip Blank	10	11
Trip Blank	11	3
Trip Blank	13	16
Trip Blank	14	3
Unsampled blank	8	9
Unsampled blank	9	52
Unsampled blank	10	14
Unsampled blank	11	12
Unsampled blank	12	19
Unsampled blank	13	22
Unsampled blank	14	20
Unsampled blank	15	11

Table 29. Batch Numbers by Sampling Date.

Delivery Batch Number	**Sampling Date Range** (sample batches divide on approximately the 10th of the months shown.)
8	August - September, 2000
9	August - September, 2000 (new Texas sites only)
10	September - October, 2000
11	October - November, 2000
12	November - December, 2000
13	December, 2000 - January, 2001
14	January - February, 2001
15	February - March, 2001

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

LOCATION_NAME	POC	8	9	10	11	12	13	14	15
Air Monitoring, VA DEQ	5								
Aldine	5		90.5	96.2	89.5	90.4	92.3	98.2	100.0
Allen Park	5						96.1	96.5	77.3
Alpine	5								
Bayland Park	5		100.0	100.0	90.9	100.0	76.7	74.5	90.4
Beacon Hill	6	100.0		100.0	93.5	88.1	78.8	94.0	84.6
Bismarck Residential	5			100.0	100.0				
Bismarck Residential	6	100.0							
Blair Street	6	94.6		97.6	99.4	100.0	100.0	98.2	100.0
Boyd Park	5								100.0
Burlington	5						100.0	100.0	79.1
Chamizal	5								
Channelview	5		100.0	100.0	100.0	99.8	98.2	89.5	100.0
Chicago - SE Police Station	6	99.1		100.0	100.0				
Chicopee	5							94.9	67.7
Commerce City	5								54.7
Conroe Airport	5		90.1	100.0	88.7	100.0	84.9	92.3	92.3
CPW	5								100.0
Deer Park	6	69.7		100.0	91.7	100.0	57.7	92.4	99.7
Deer Park - FRM	5		96.6	94.1					
Deer Park (Collocated)	7							100.0	100.0
Dona Park	5								100.0
East Elementary SASS	5				74.5				
Essex	5						77.3	100.0	89.2
Fresno - First Street	5			100.0	98.9	86.7	76.4	97.8	100.0
Fresno - First Street	6	100.0							
G.T. Craig	5						100.0	100.0	100.0
Galveston Airport	5		97.0	90.7	93.0	100.0	100.0	98.2	100.0
Garringer High School	5							100.0	99.7
Georgetown	5	100.0		100.0	100.0	79.2	100.0	100.0	100.0
Guaynabo	5								
Gulfport	5								
Hamshire	5		71.5	100.0	92.3	100.0	100.0	100.0	98.4
Hawthorne	5			68.5	90.9	100.0	100.0	89.9	100.0
Hawthorne	6	100.0							
Hinton	5					98.8	78.8	92.9	100.0
HRM 3#	5		96.8	100.0	87.5	94.7	89.1	100.0	98.2
IS 52	5						100.0		100.0
IS 52	6					9.4		100.0	
Jefferson Elementary (10th and Vine)	5								94.8
LaPorte Airport	5		99.0	81.9					
Lewis	5			100.0	90.9	100.0	100.0	89.6	100.0
Lewis	6	63.7							

Table 30 (continued).

LOCATION_NAME	POC	8	9	10	11	12	13	14	15
McMillan Reservoir	5								
New Brunswick	5							100.0	100.0
North Birmingham	5							100.0	100.0
NY Botanical Gardens	5	100.0							
NY Botanical Gardens	6	100.0		100.0	100.0	100.0	100.0	100.0	100.0
Osborn	5						100.0	100.0	100.0
Peoria Site 1127	5								100.0
PHILA - AMS Laboratory	6	100.0		100.0	92.3	99.2			
PHILA - AMS Laboratory	7							100.0	100.0
Philips	5							100.0	100.0
Phoenix Supersite	5	100.0							
Phoenix Supersite	7			100.0	100.0	100.0	100.0	100.0	100.0
Pinnacle State Park	6								100.0
Portland - SE Lafayette	5	100.0							
Portland - SE Lafayette	6			100.0	97.7	98.0	99.4	100.0	99.0
Queens College	6								
Rochester Fire Headquarters	5							69.8	100.0
Roxbury (Boston)	5			58.0	42.2	73.2	83.6	9.4	39.6
Roxbury (Boston)	6			54.5	48.4	71.9	96.9		
Sacramento - Del Paso Manor	5	100.0		100.0	100.0	100.0	85.9	100.0	88.7
San Jose - Fourth Street	5	100.0		100.0	100.0	100.0	100.0	87.1	99.8
SER-DNR Headquarters	5						100.0	80.9	100.0
South DeKalb	5								
Southfield	5								
Sun Metro	5						100.0	100.0	87.2
Treatment Plant SASS collocated	6				100.0				
Treatment Plant SASS	5				100.0				
Washington Park	5						97.9	100.0	100.0

Figures 1 through 34 are contained in the following pages.

Figure 1. OC/EC Instrument Blanks.

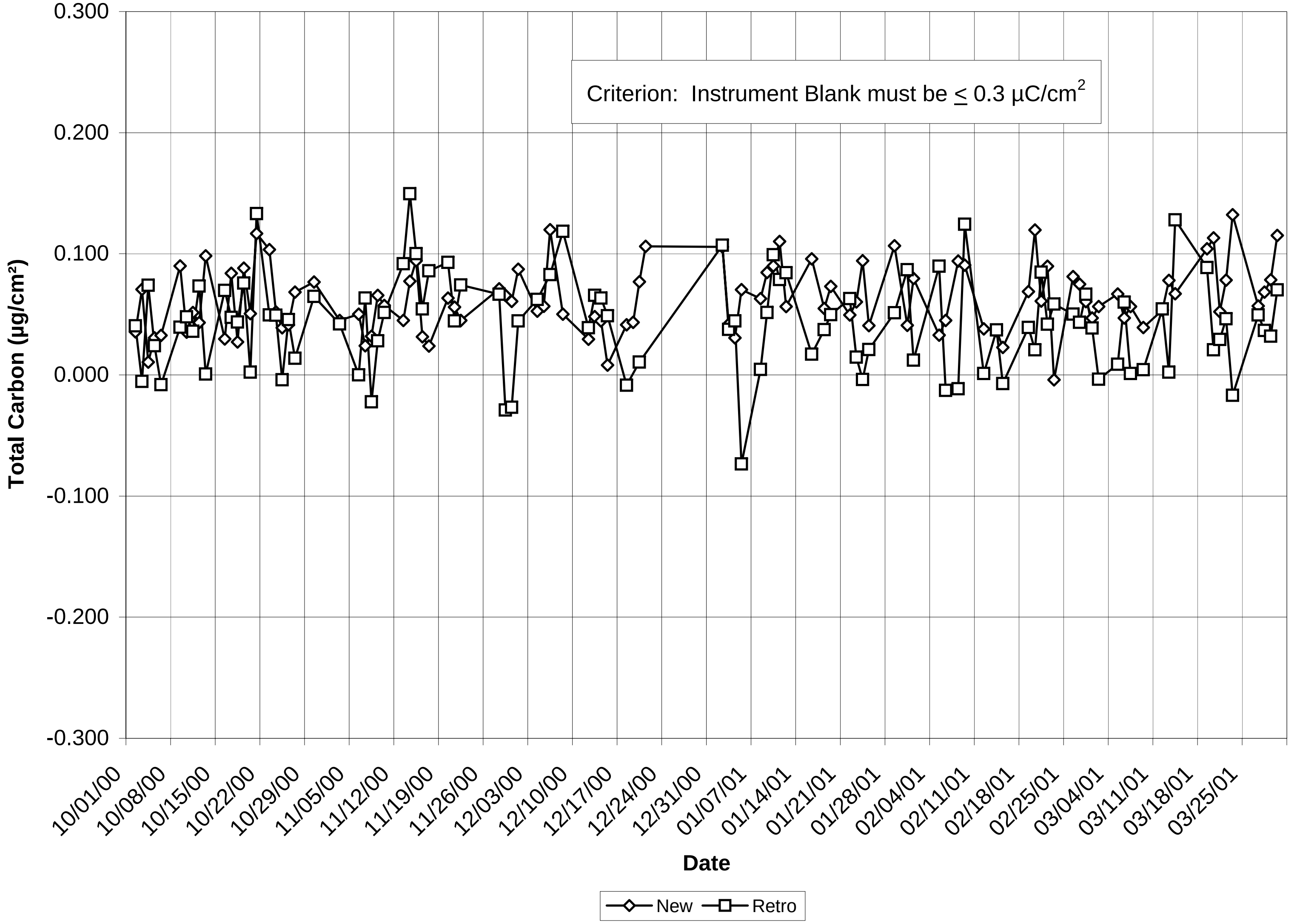


Figure 2. Linearity of Three-Point Calibrations

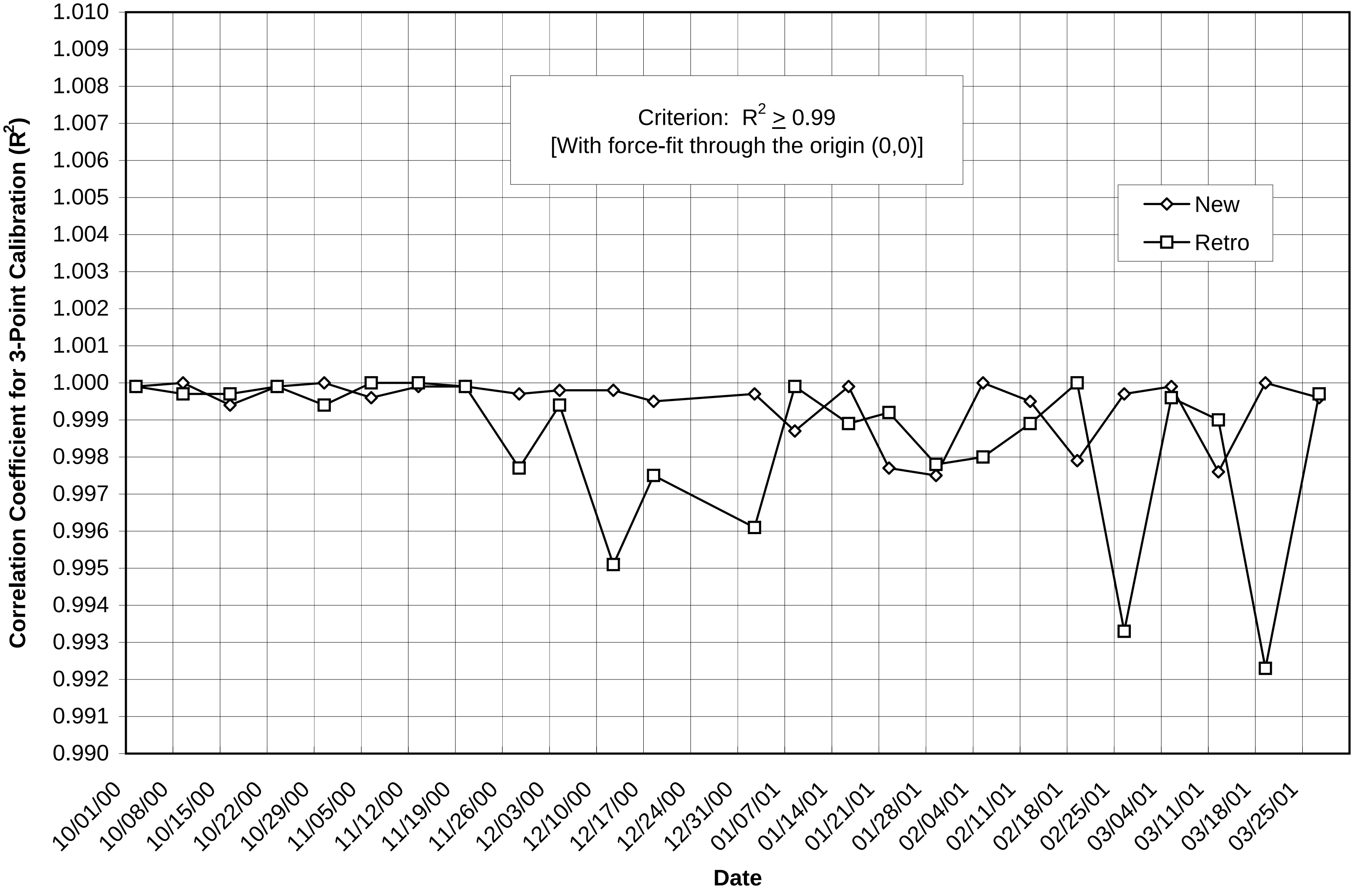


Figure 3. Percent Recoveries for Three-Point Calibration Standards on the New OC/EC Analyzer

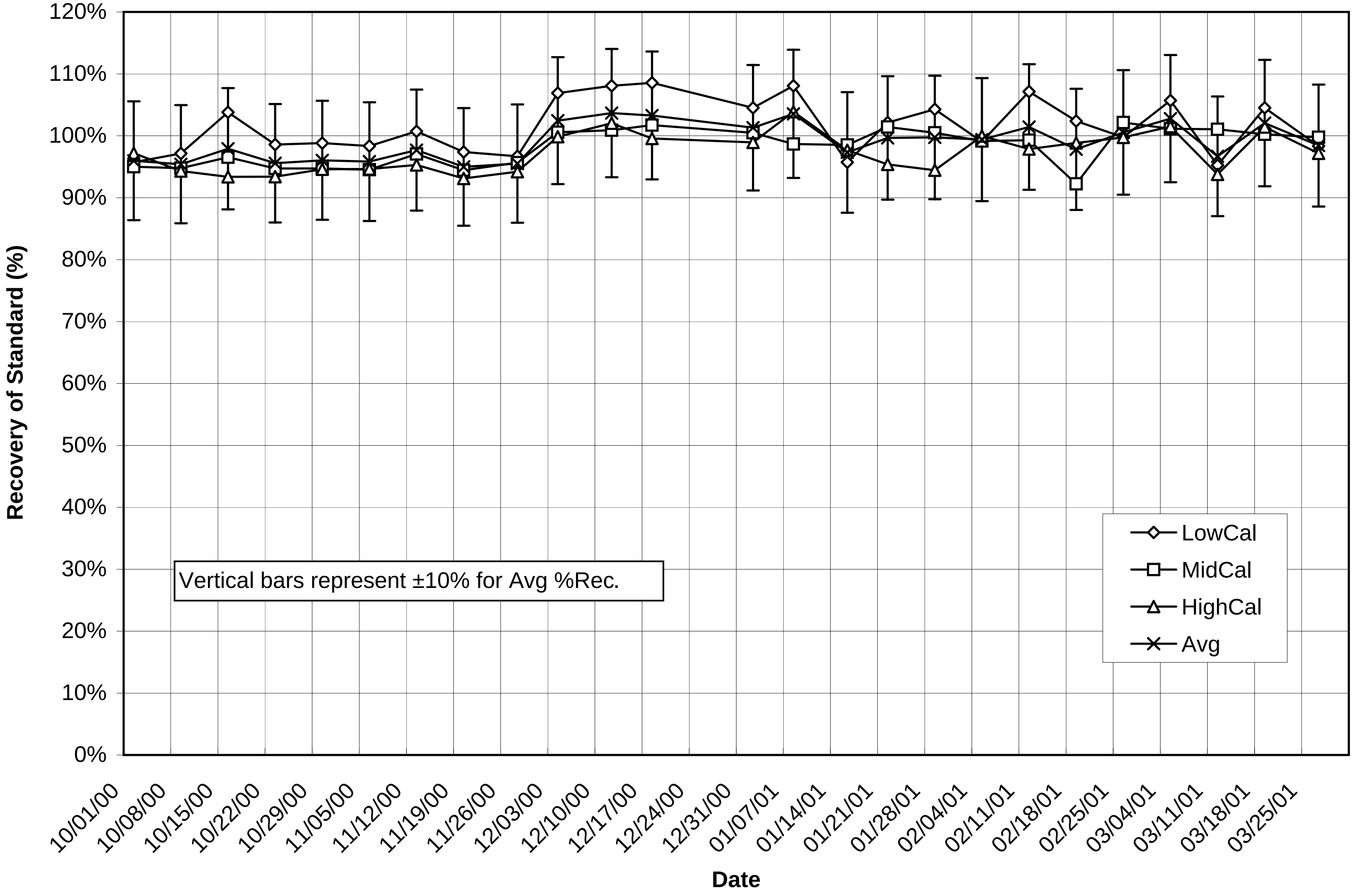

Vertical bars represent ±10% for Avg %Rec.

Figure 4. Percent Recoveries for Three-Point Calibration Standards on the Retrofit OC/EC Analyzer

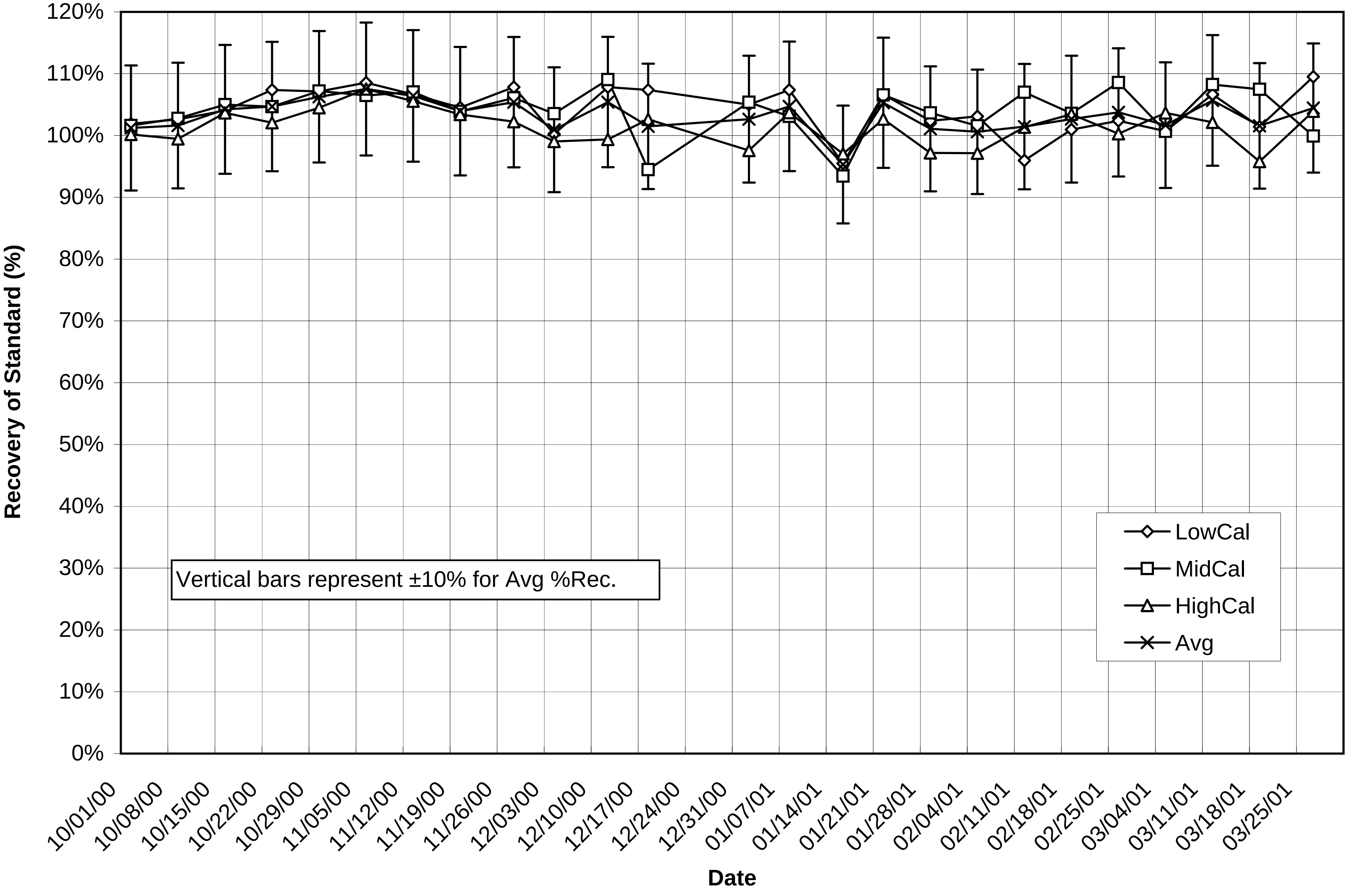


Figure 5. FID Response Factors for Three-Point Calibration Standards on the New OC/EC Analyzer

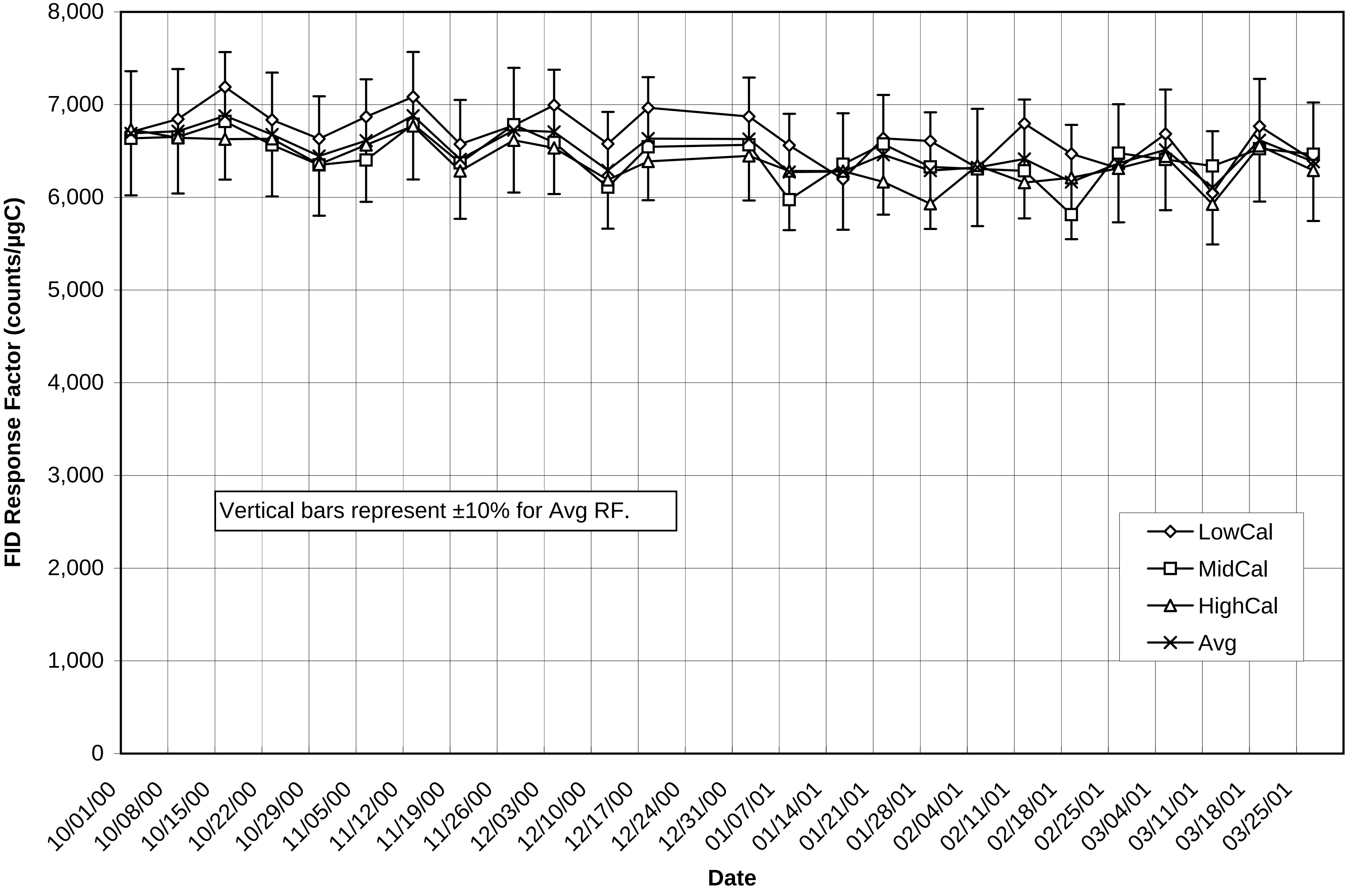


Figure 6. FID Response Factors for Three-Point Calibration Standards on the Retrofit OC/EC Analyzer

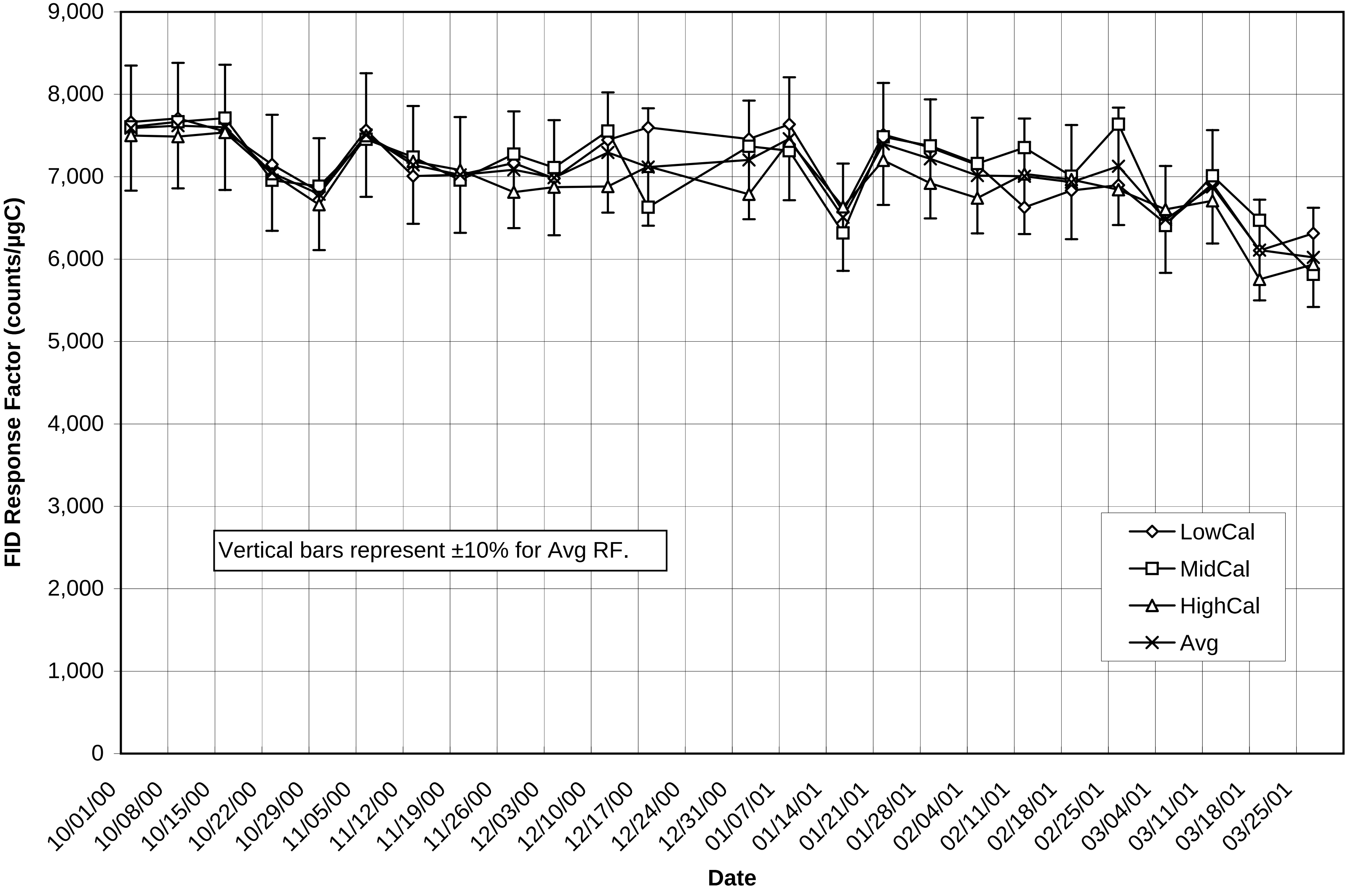


Figure 7: Relative Percent Difference of Duplicates vs. Average Value for TC on New OC/EC Analyzer - October 1, 2000, through March 31, 2001

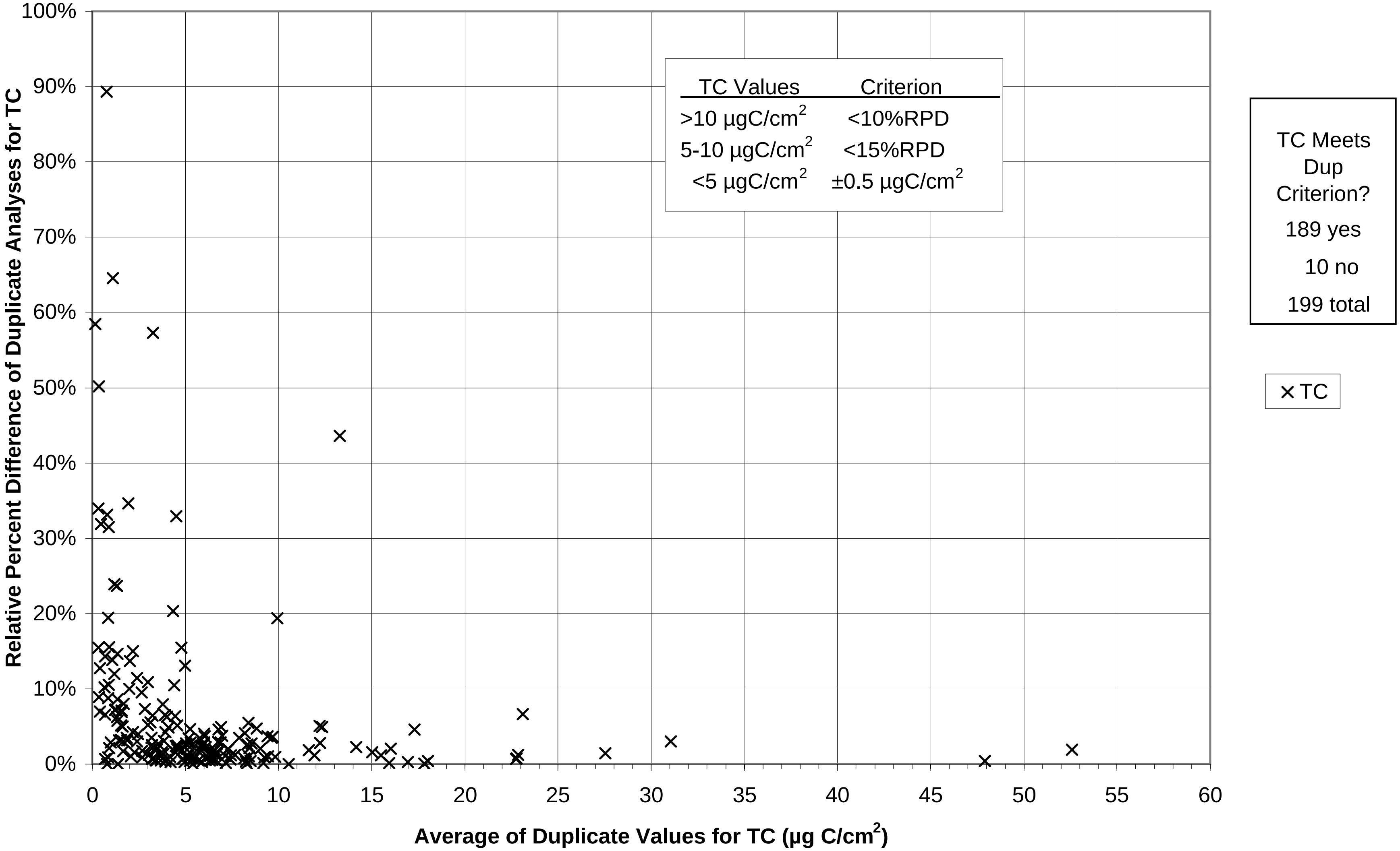
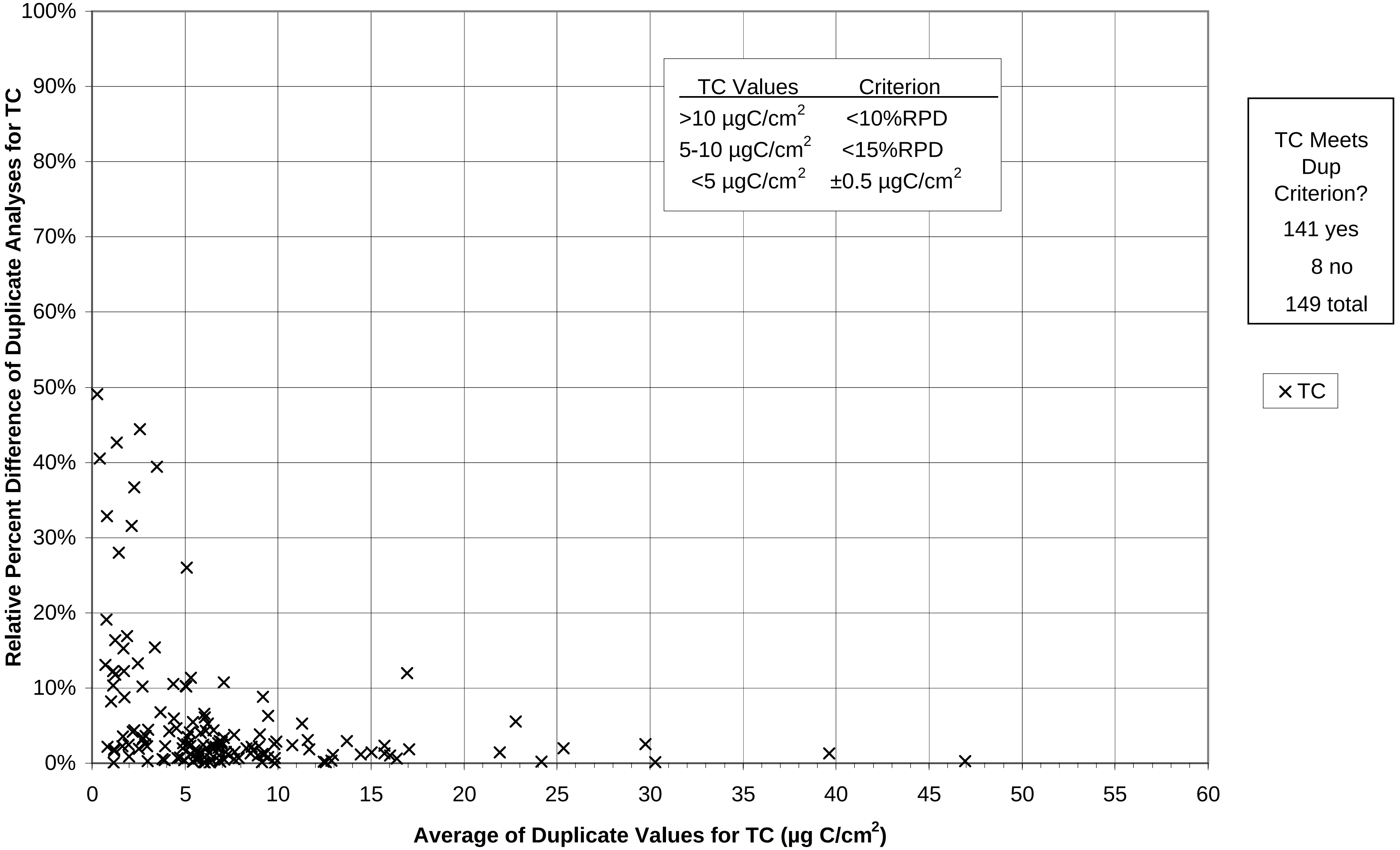


Figure 8: Relative Percent Difference of Duplicates vs. Average Value for TC on Retrofit OC/EC Analyzer - October 1, 2000, through March 31, 2001



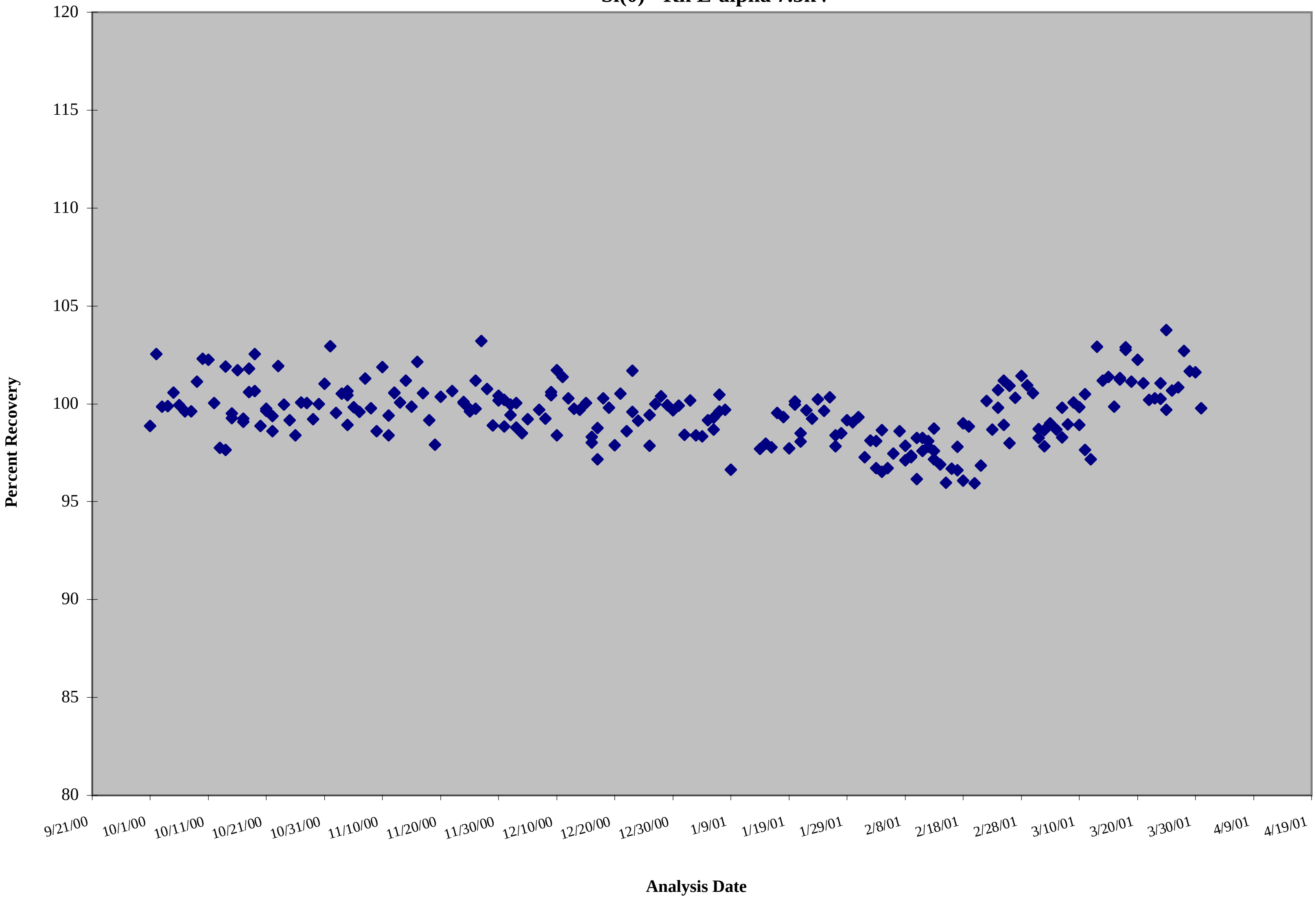


Figure 9. Recovery Precision for Si(0) - Rh L-alpha 7.5kV

Figure 10. Recovery Precision for Si(1) - Ti target 25kV

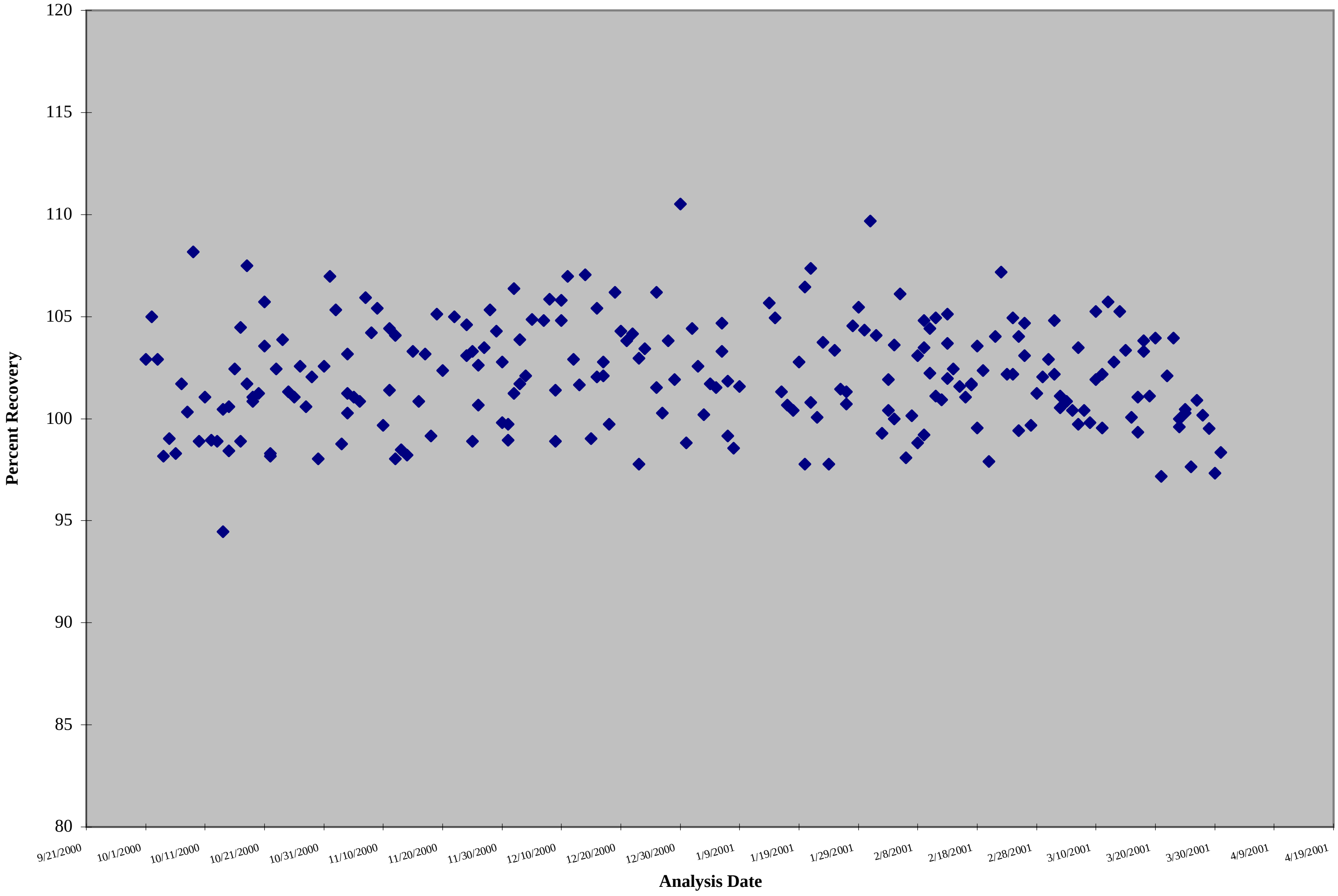


Figure 11. Recovery Precision for Ti(2) - Fe target 35mA

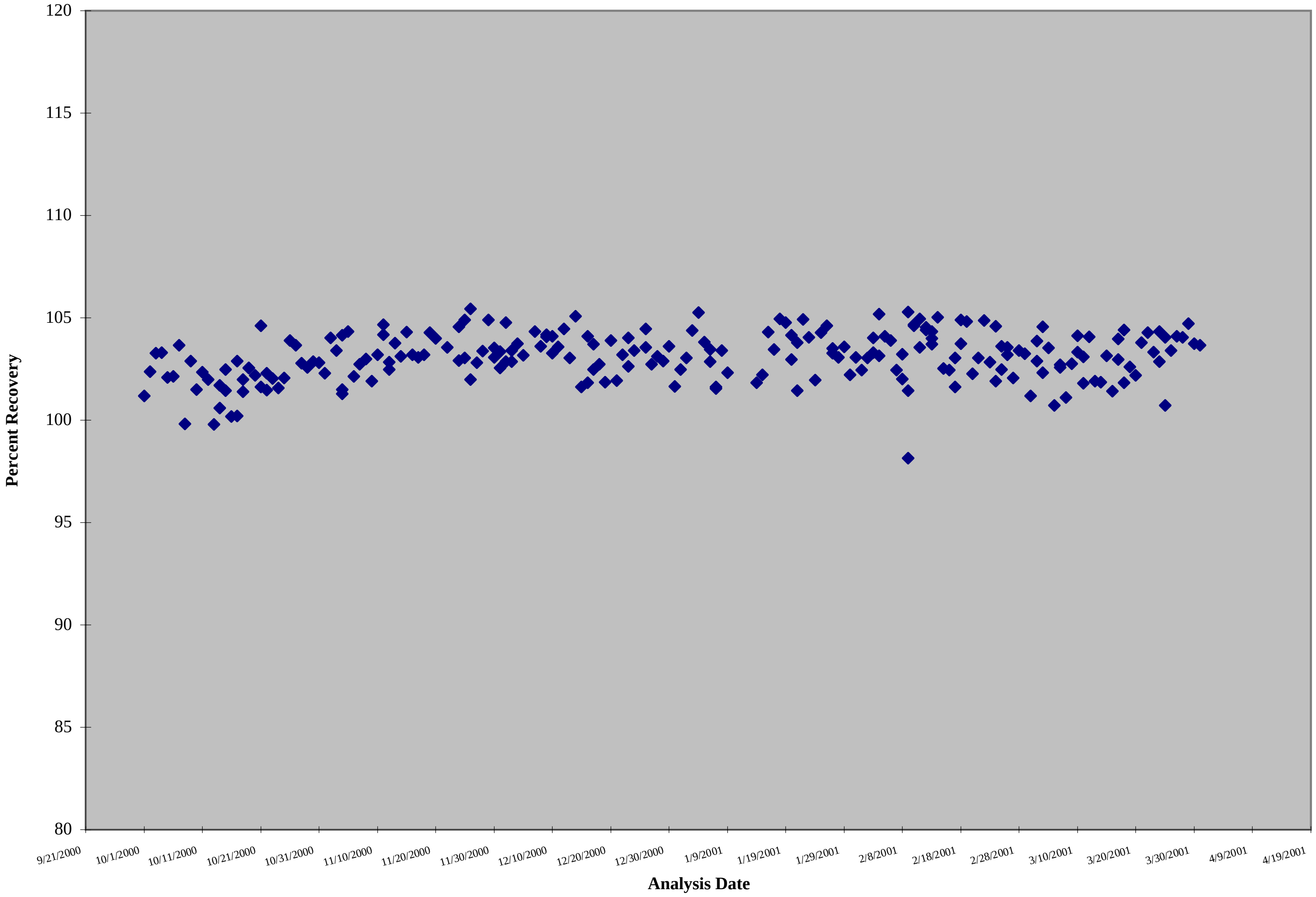


Figure 12. Recovery Precision for Fe(3) - Ge target 35mA

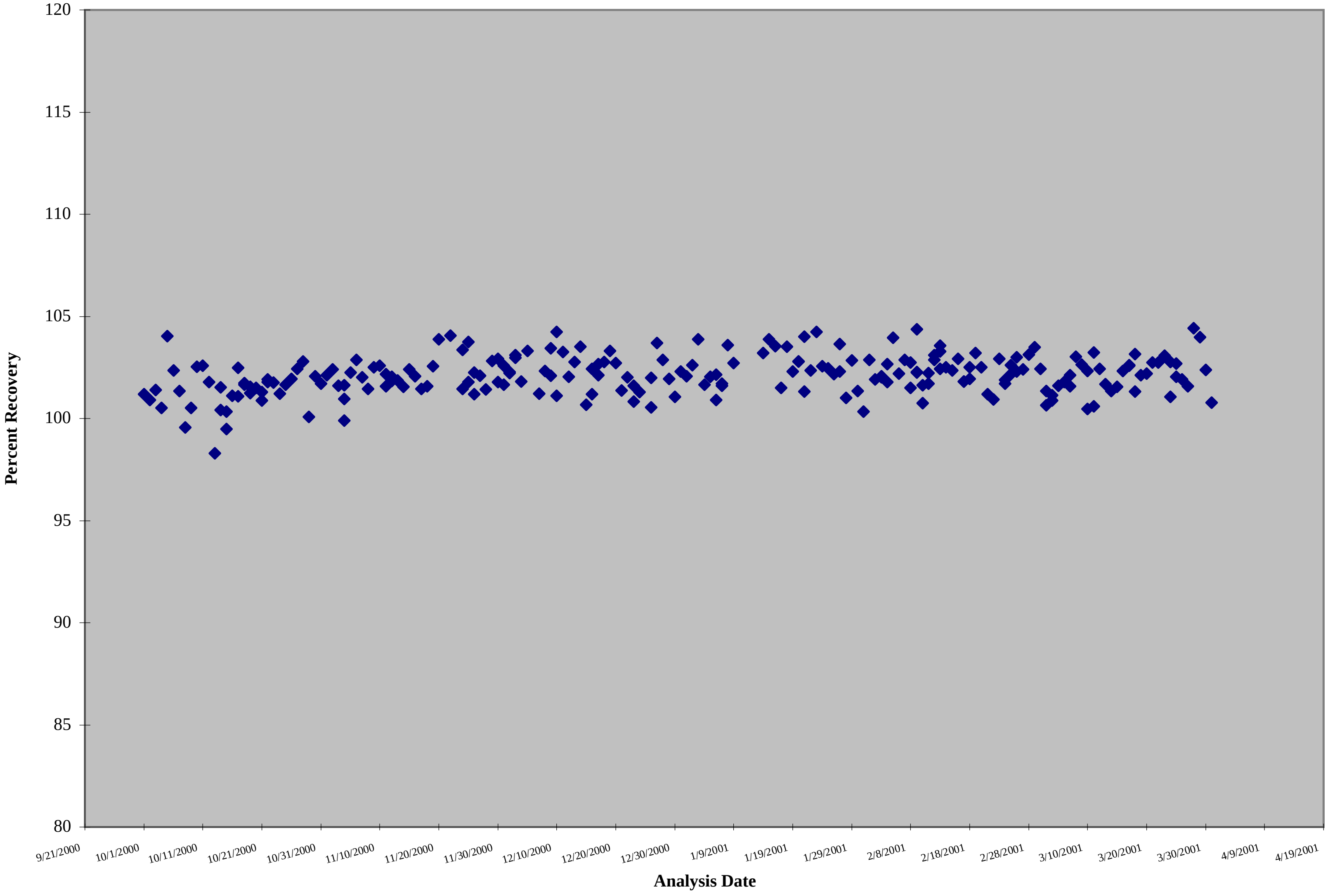


Figure 13. Recovery Precision for Se(4) - Rh K-alpha 35kV

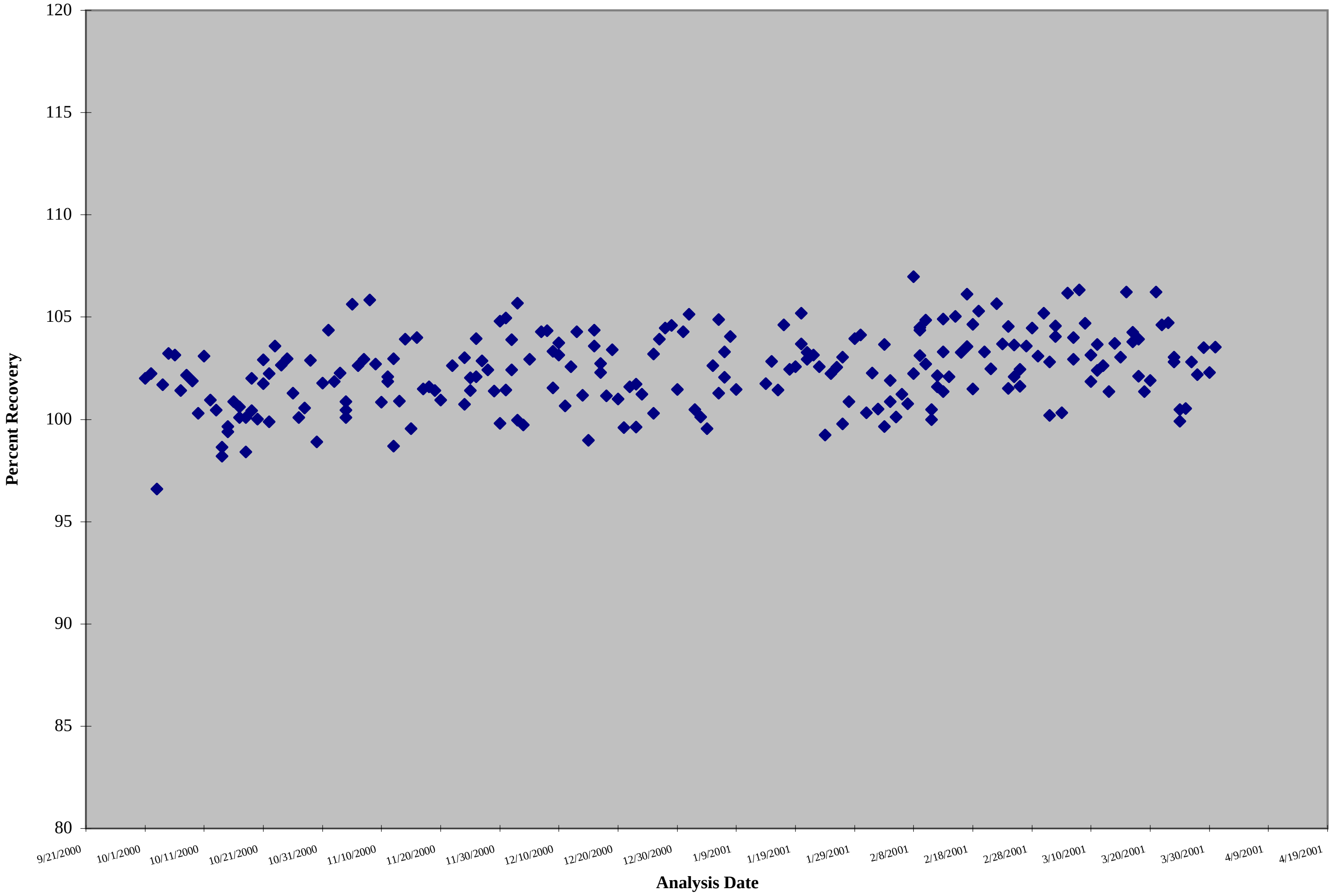


Figure 14. Recovery Precision for Pb(4) Rh K-alpha 35kV

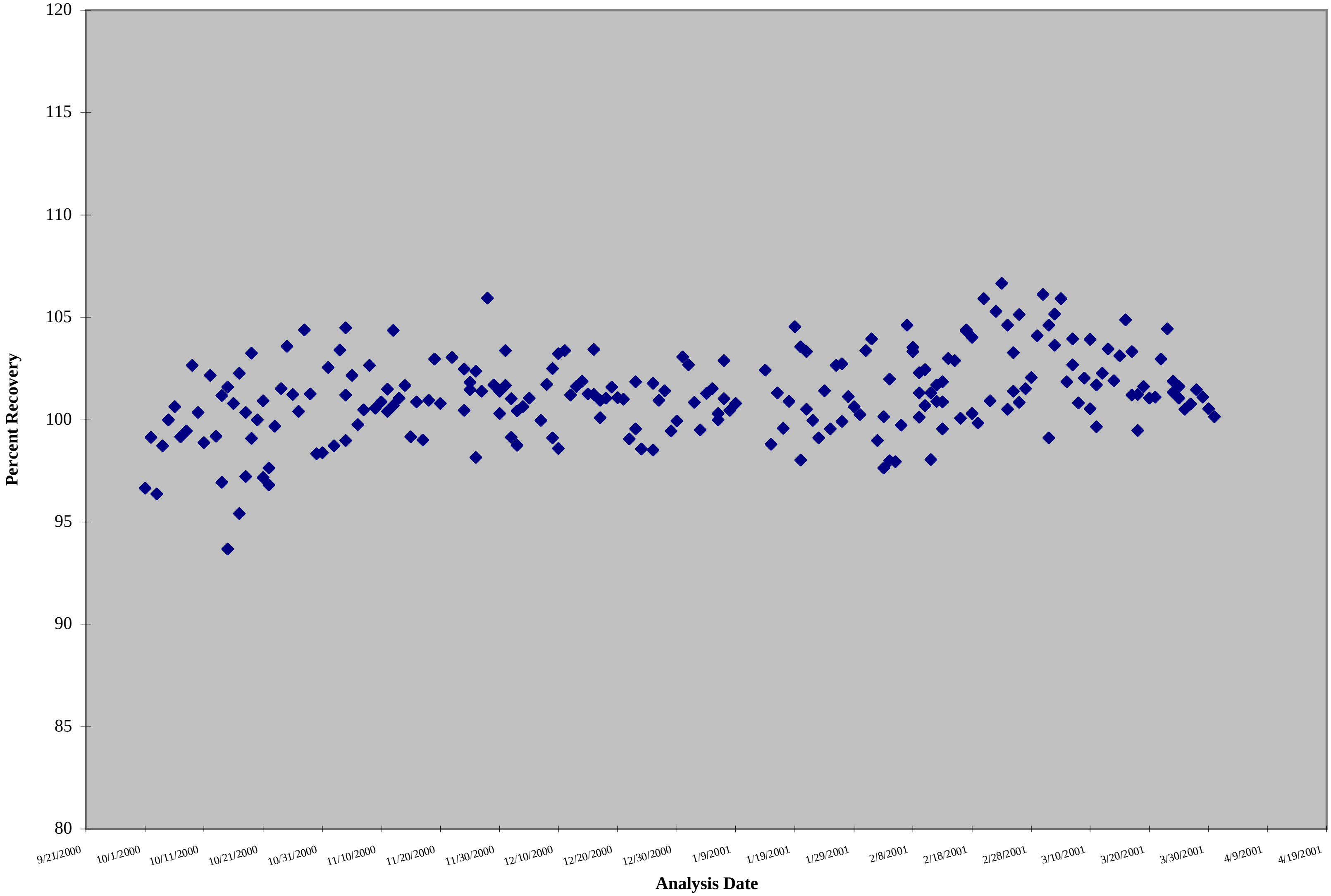


Figure 15. Recovery Precision for
Cd(5) W filter 55kV

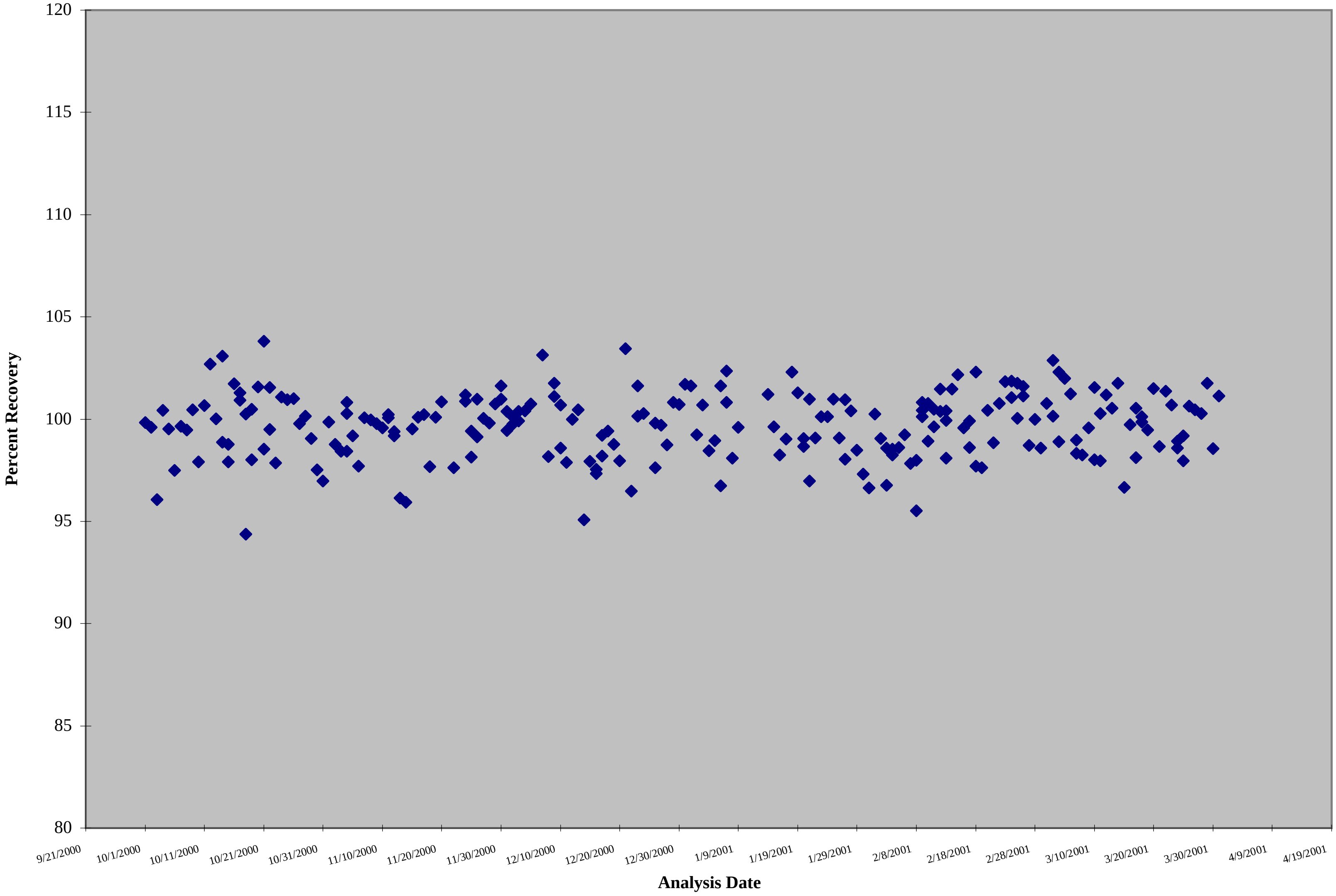


Figure 16. Recovery for Aluminum (Al) in NIST SRM 1832

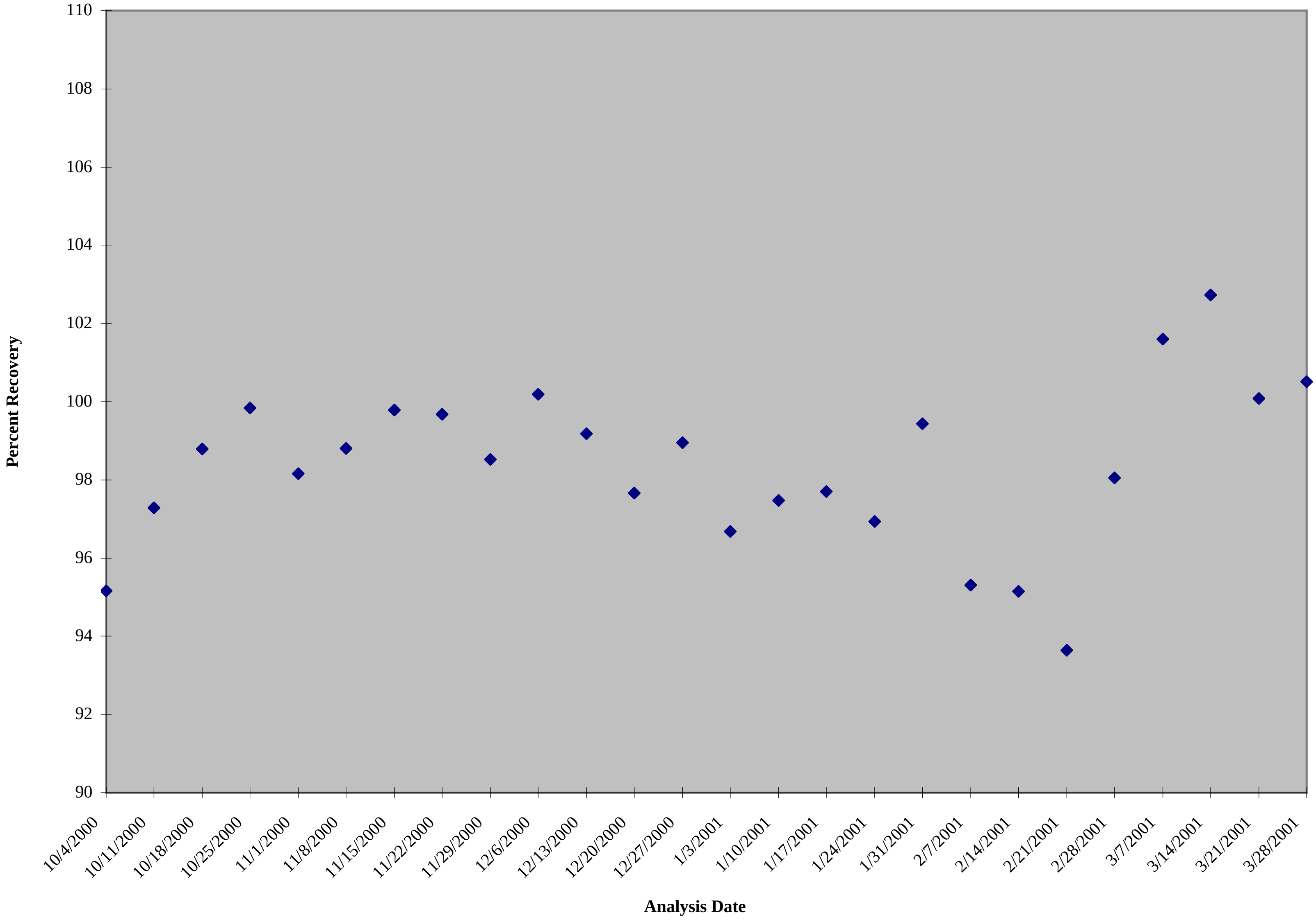


Figure 17. Recovery of Silicon (Si) in NIST SRM 1832

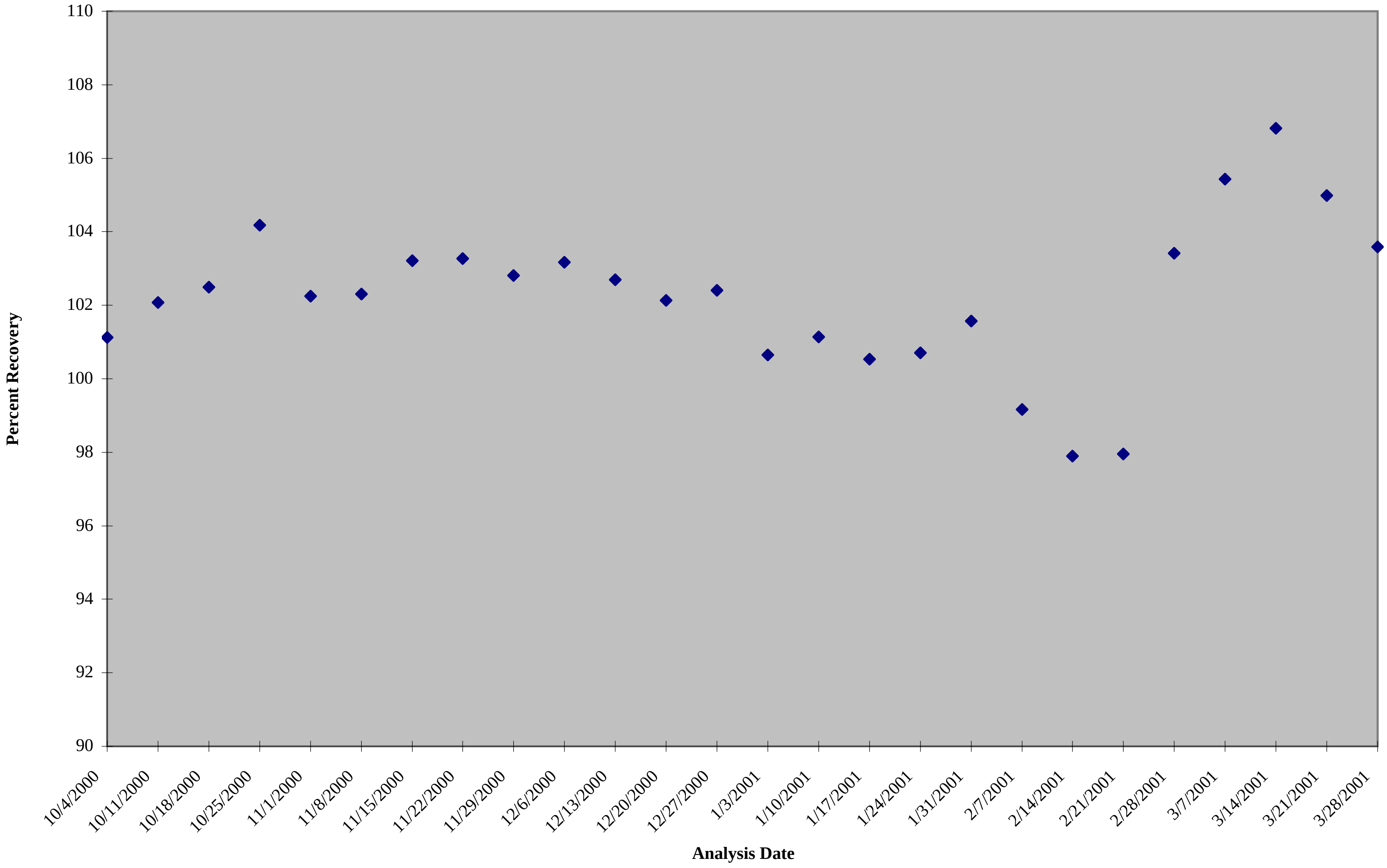


Figure 18. Recovery for Silicon (Si) in NIST SRM 1833

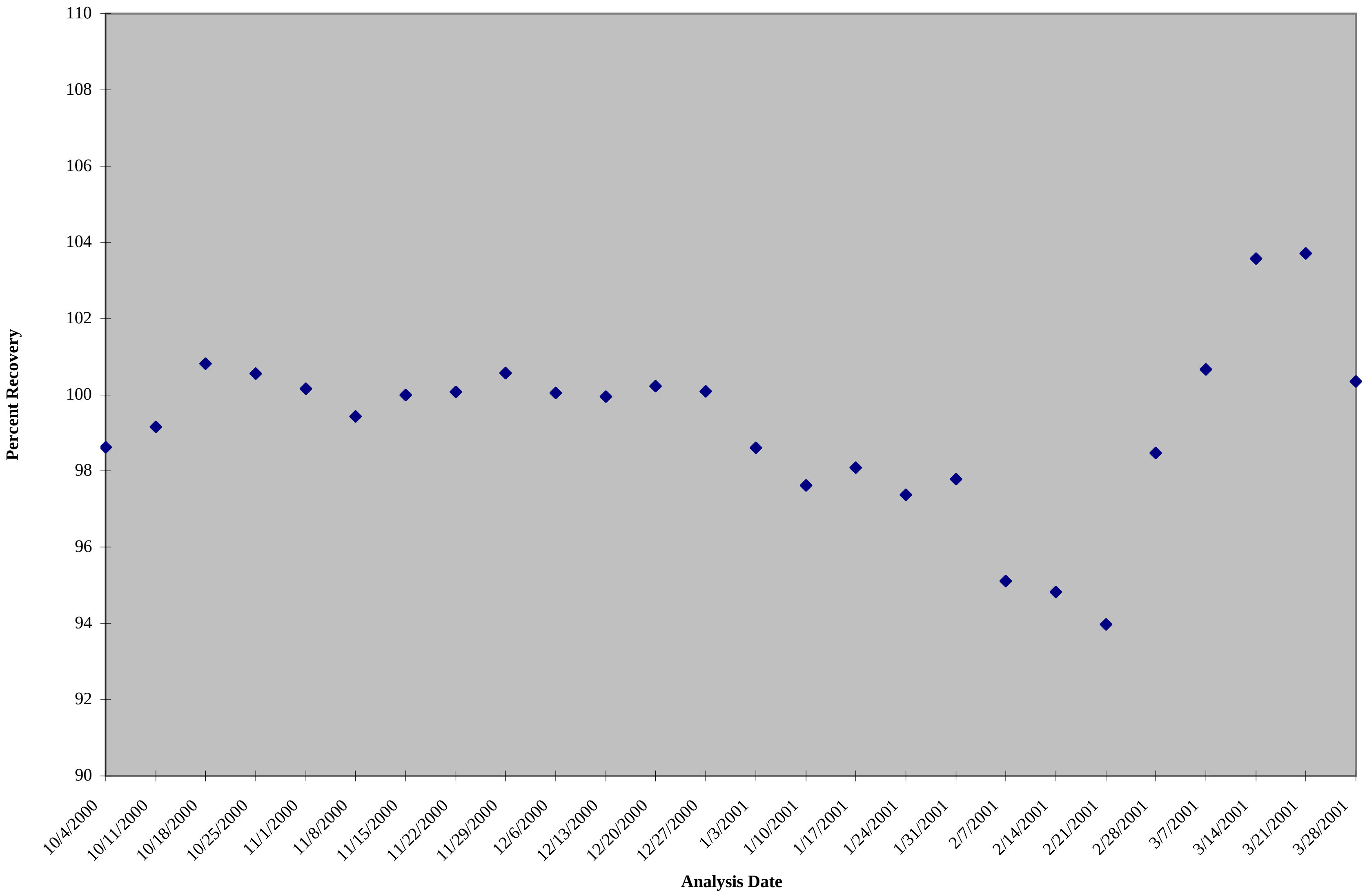


Figure 19. Recovery for Sulfur (S) in NIST SRM 2708

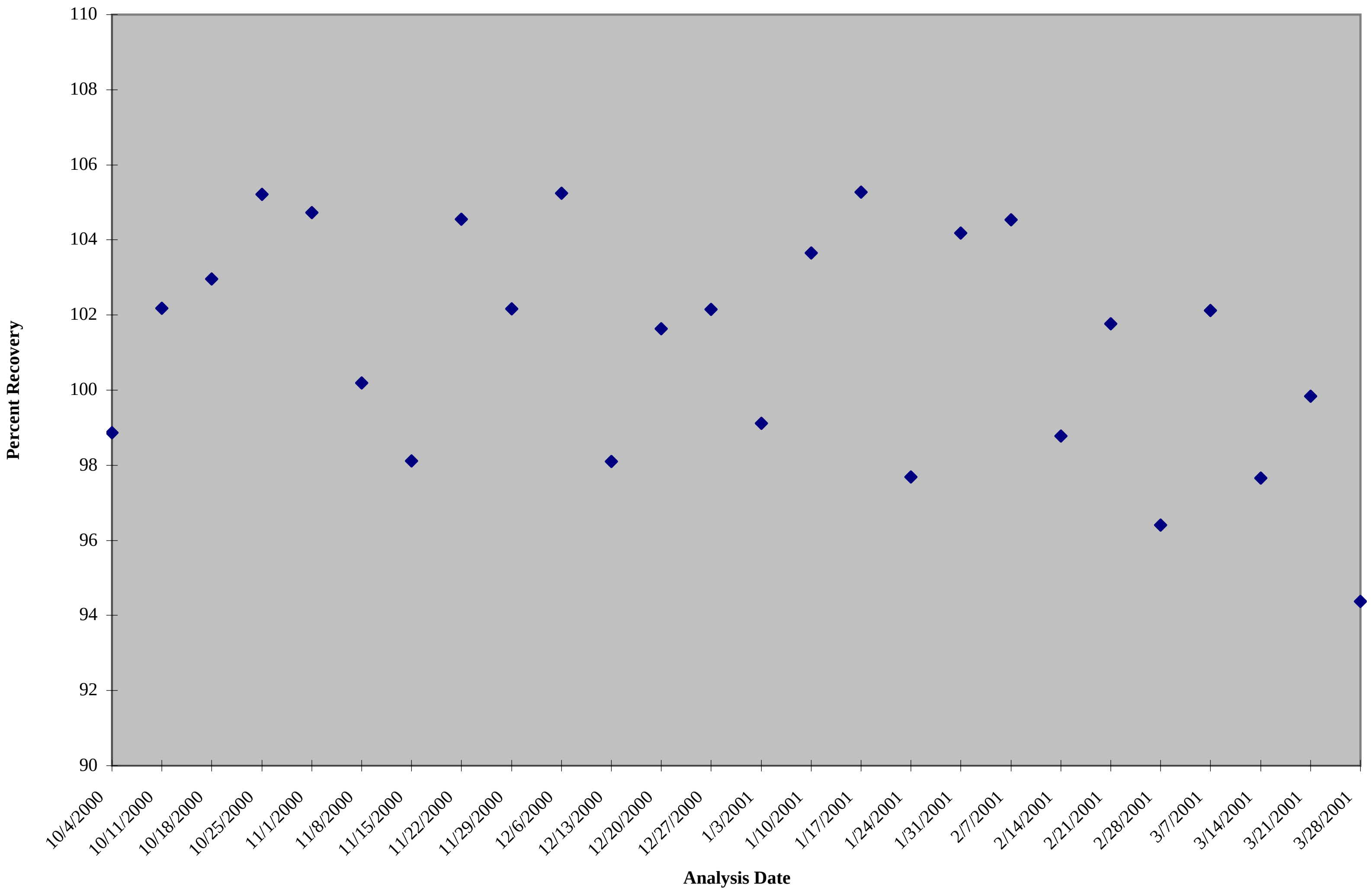


Figure 20. Recovery for Potassium (K) in NIST SRM 1833

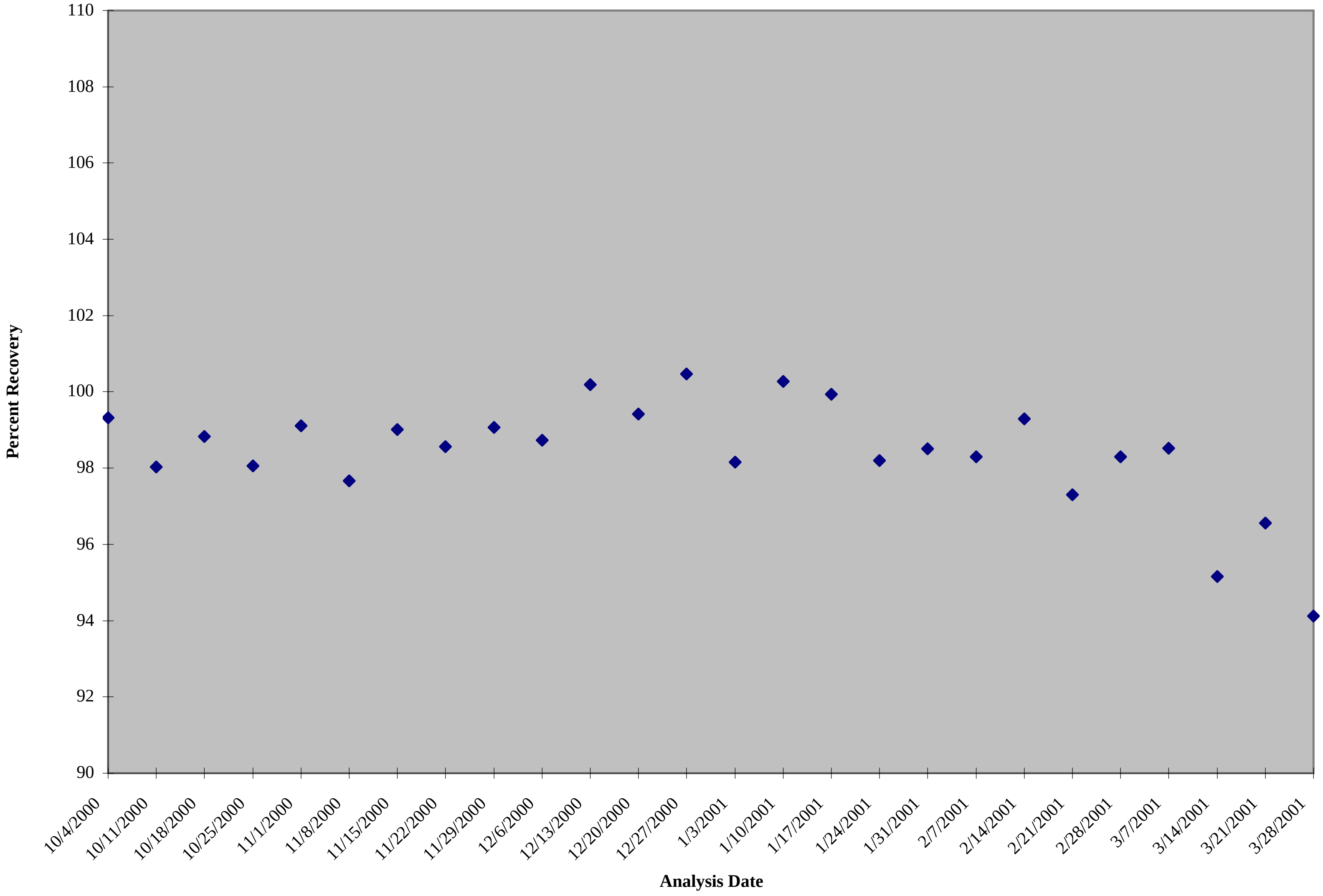


Figure 21. Recovery for Calcium (Ca) in NIST SRM 1832

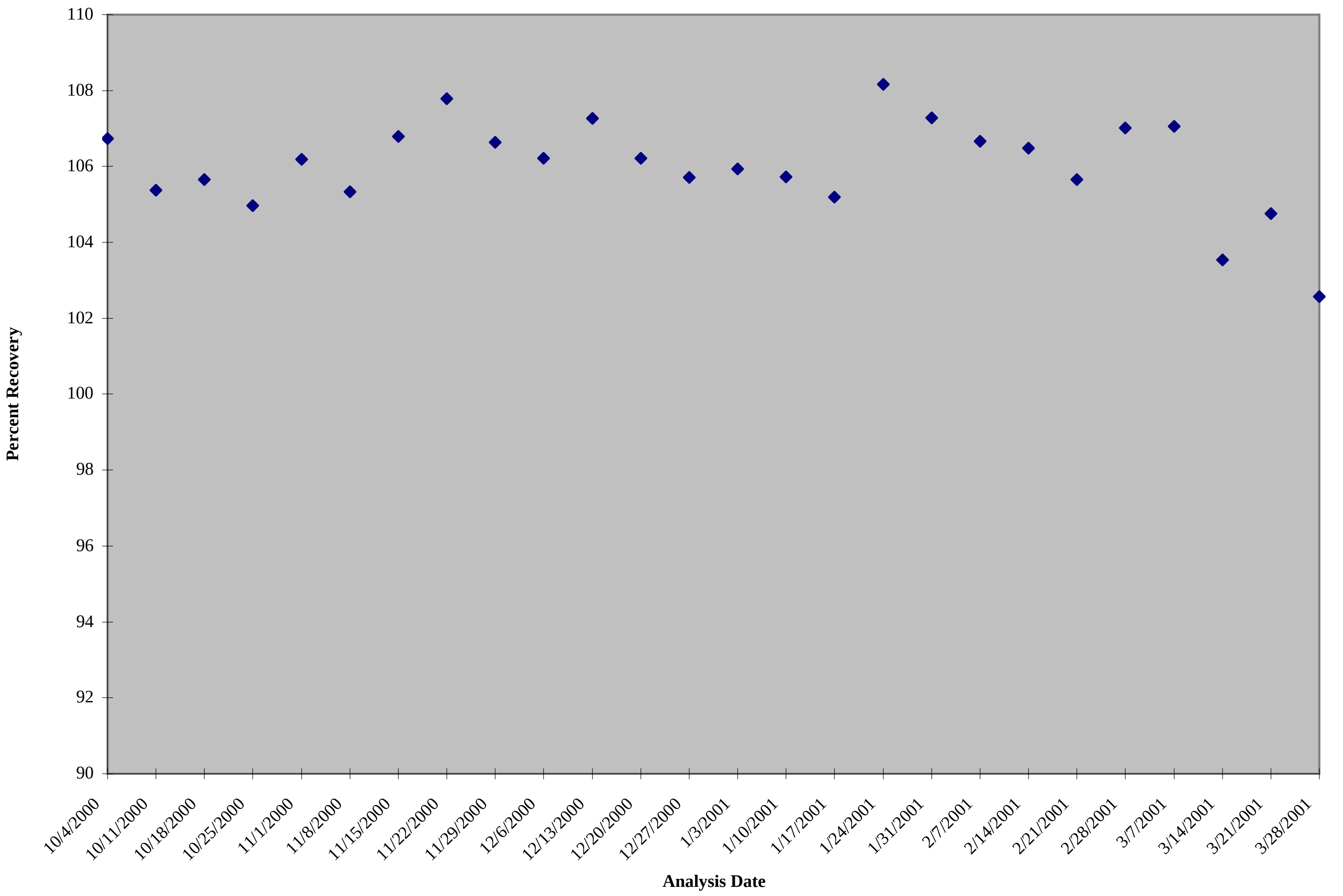


Figure 22. Recovery for Titanium (Ti) in NIST SRM 1833

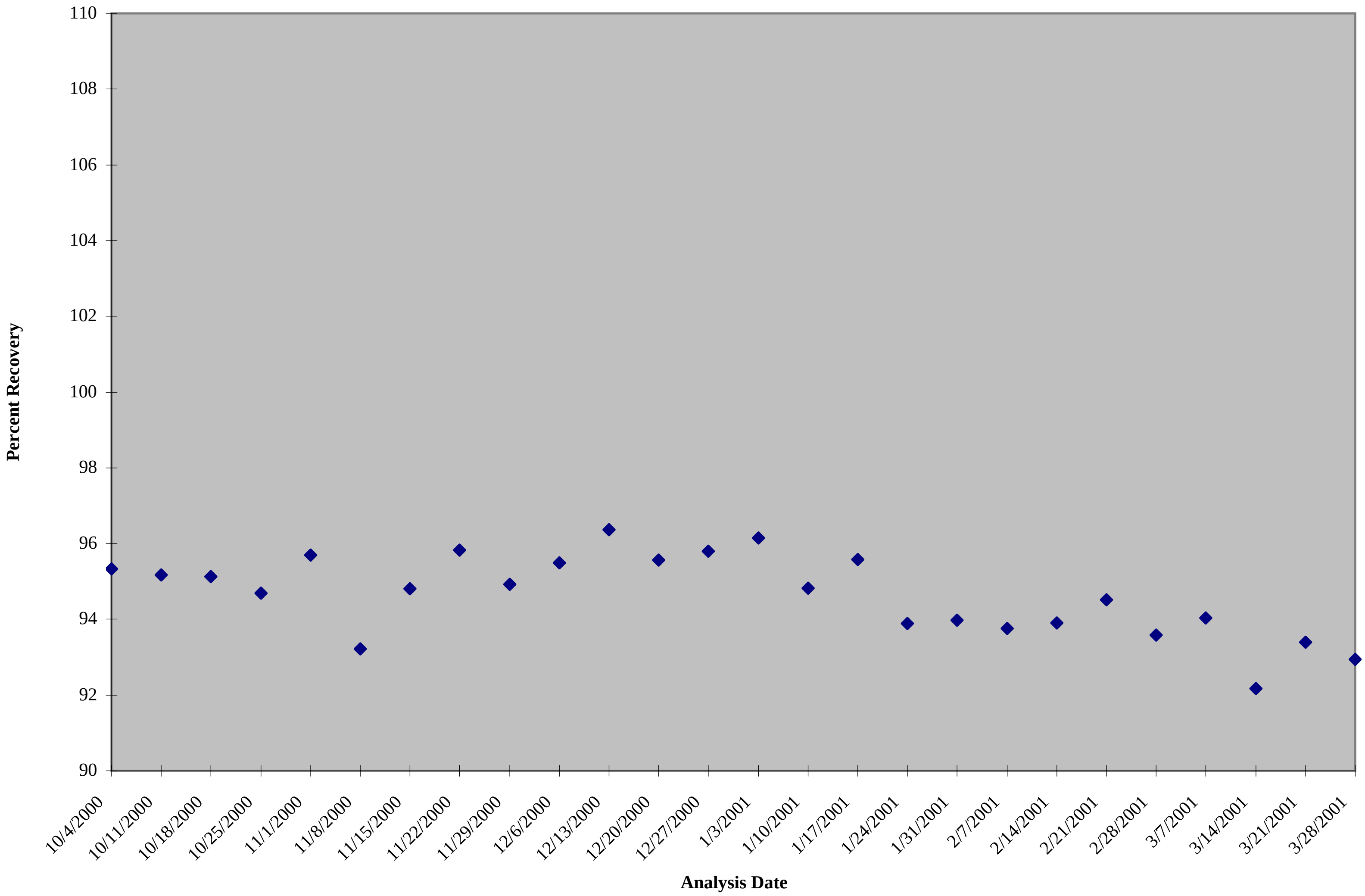


Figure 23. Recovery of Vanadium (V) in NIST SRM 1832

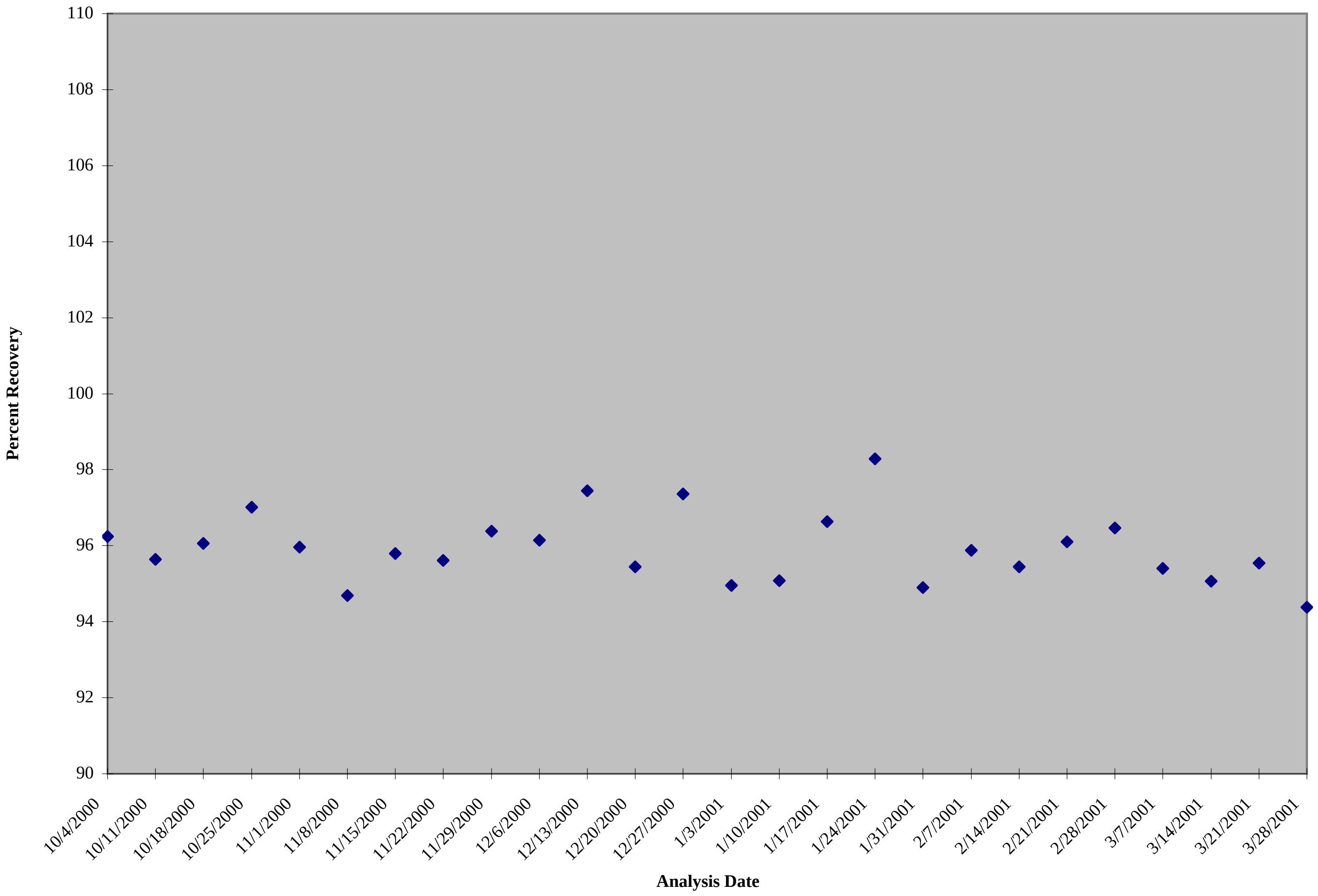


Figure 24. Recovery of Manganese (Mn) in NIST SRM 1832

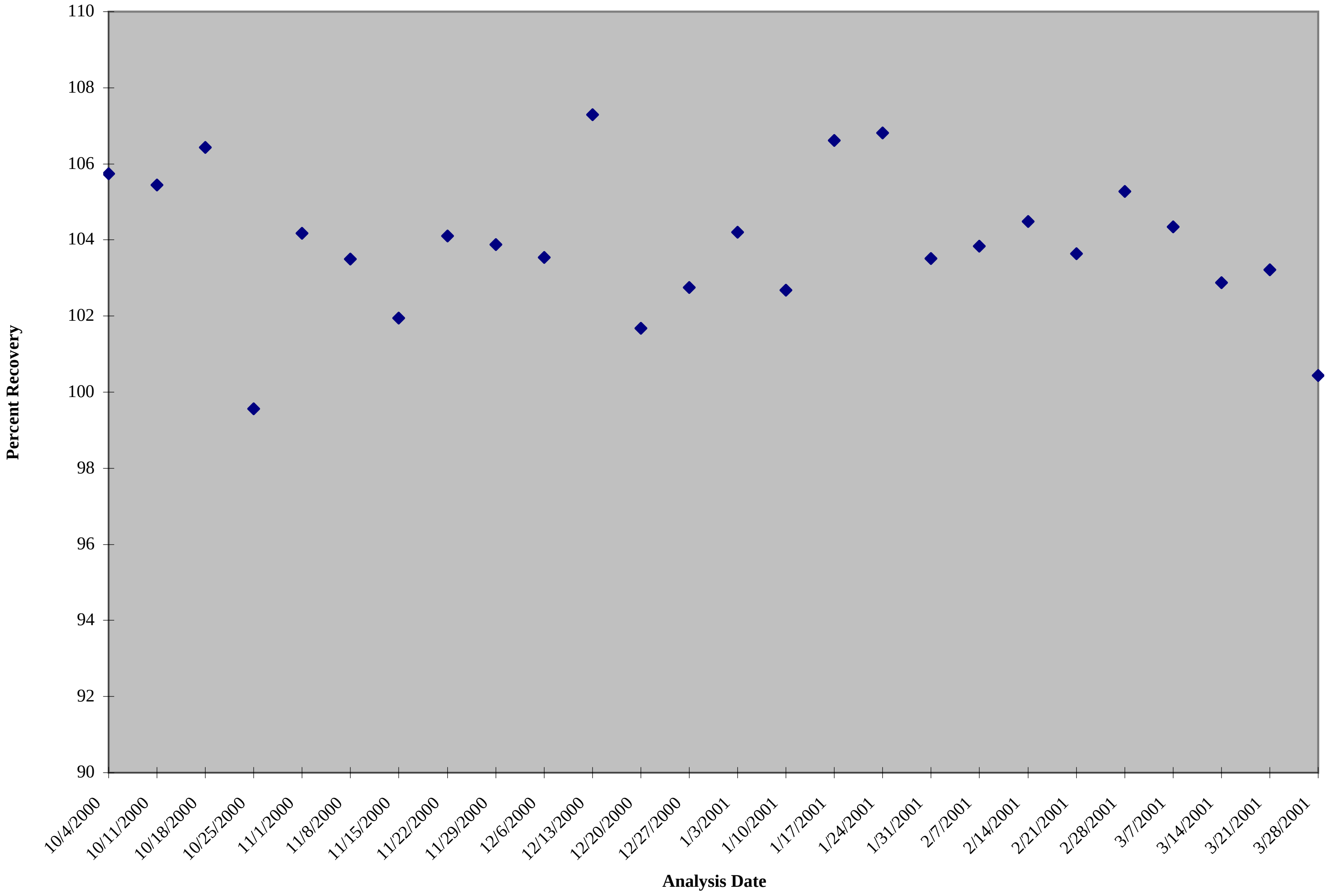


Figure 25. Recovery of Iron (Fe) in NIST SRM 1833

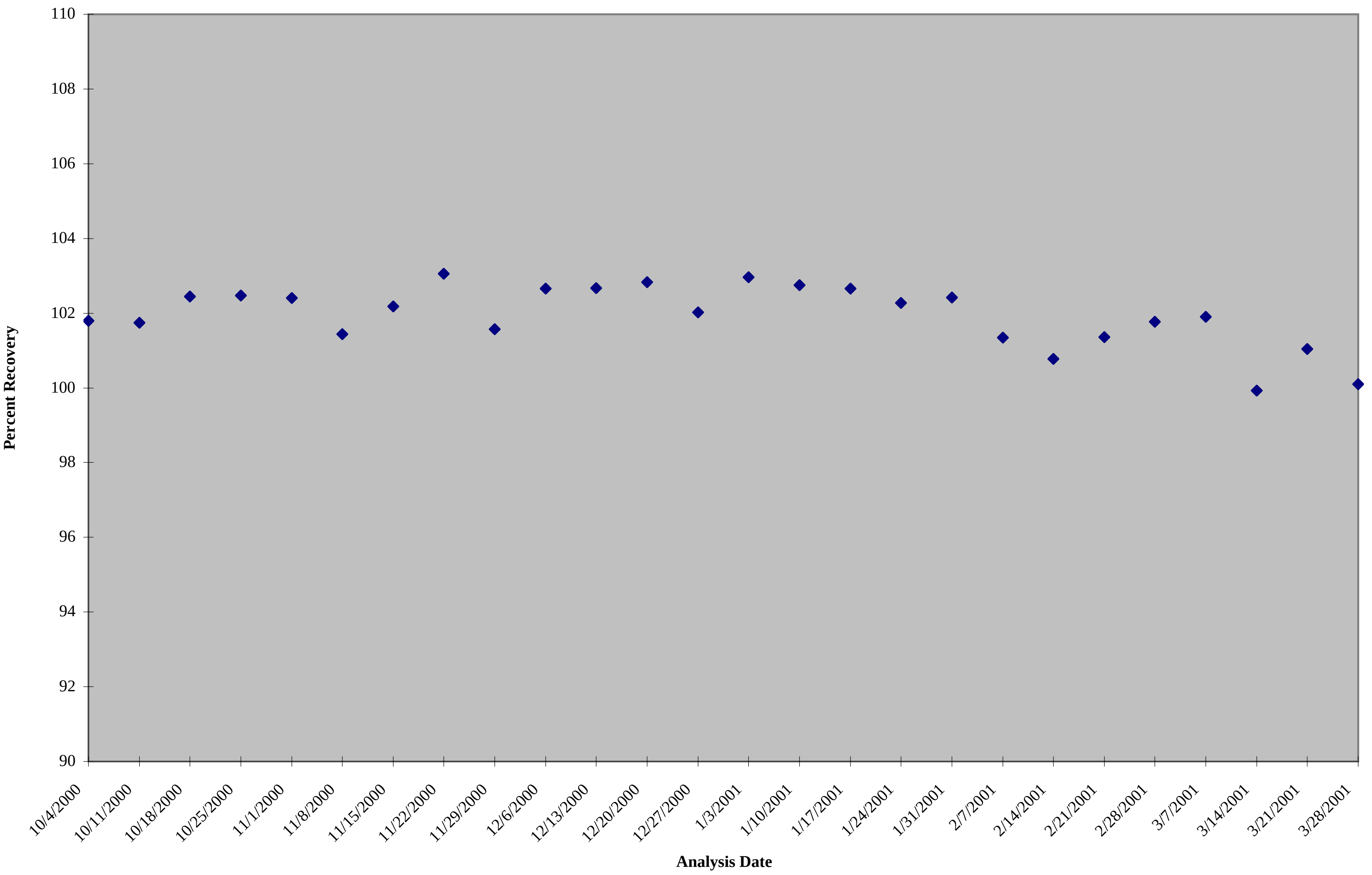


Figure 26. Recovery of Copper (Cu) in NIST SRM 1832

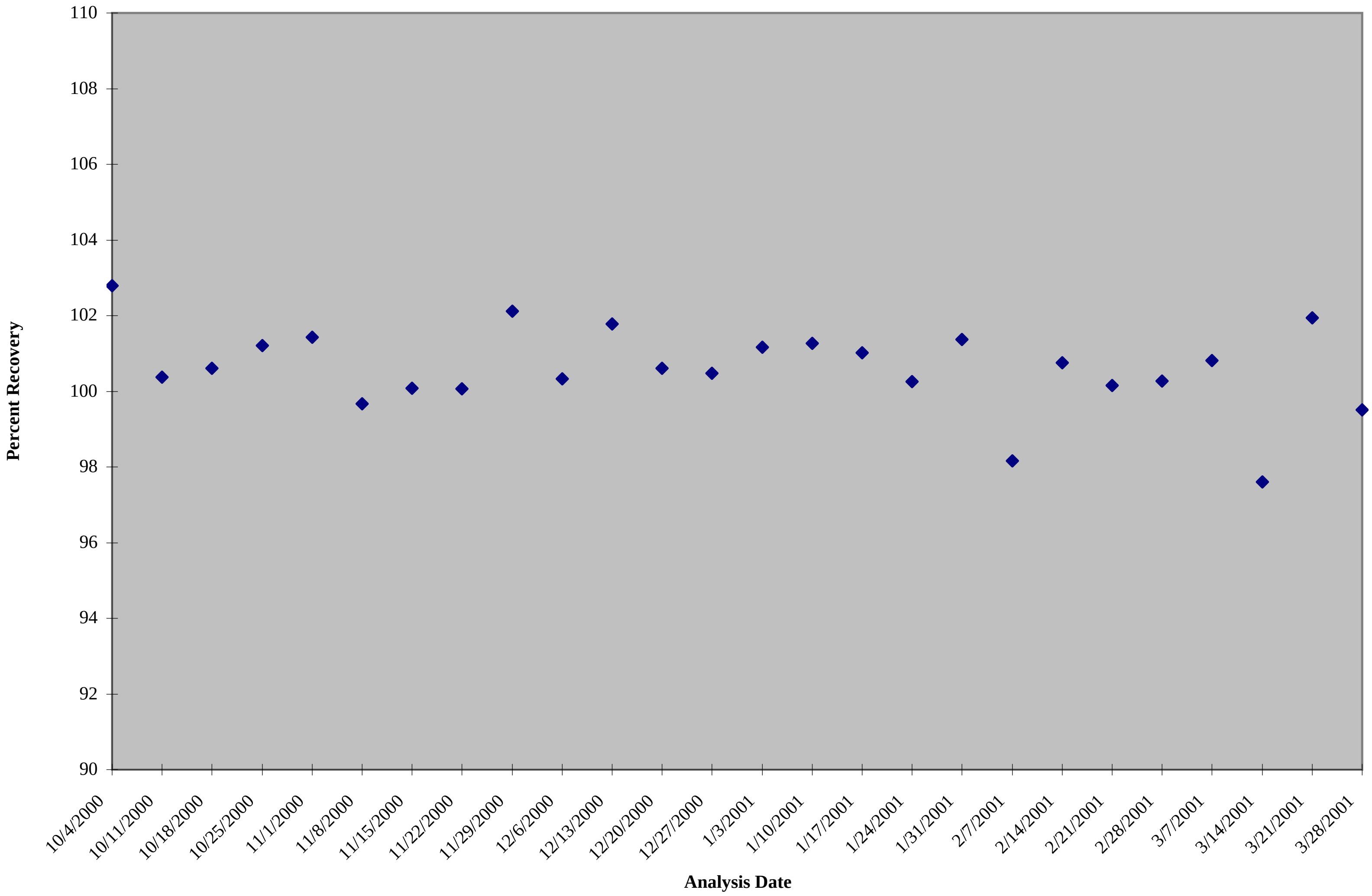


Figure 27. Recovery of Zinc (Zn) in NIST SRM 1833

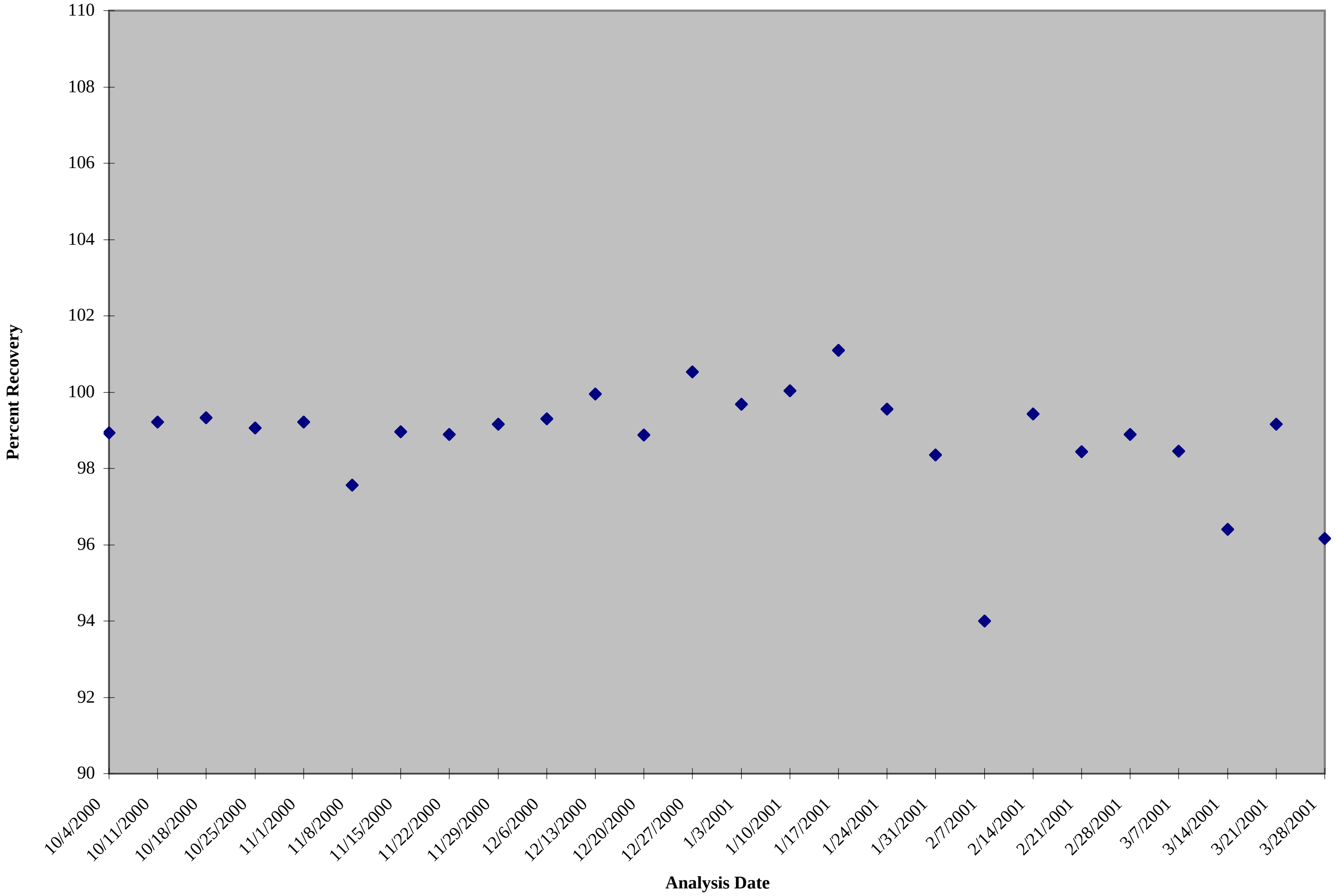


Figure 28. Recovery of Lead (Pb) in NIST SRM 1833

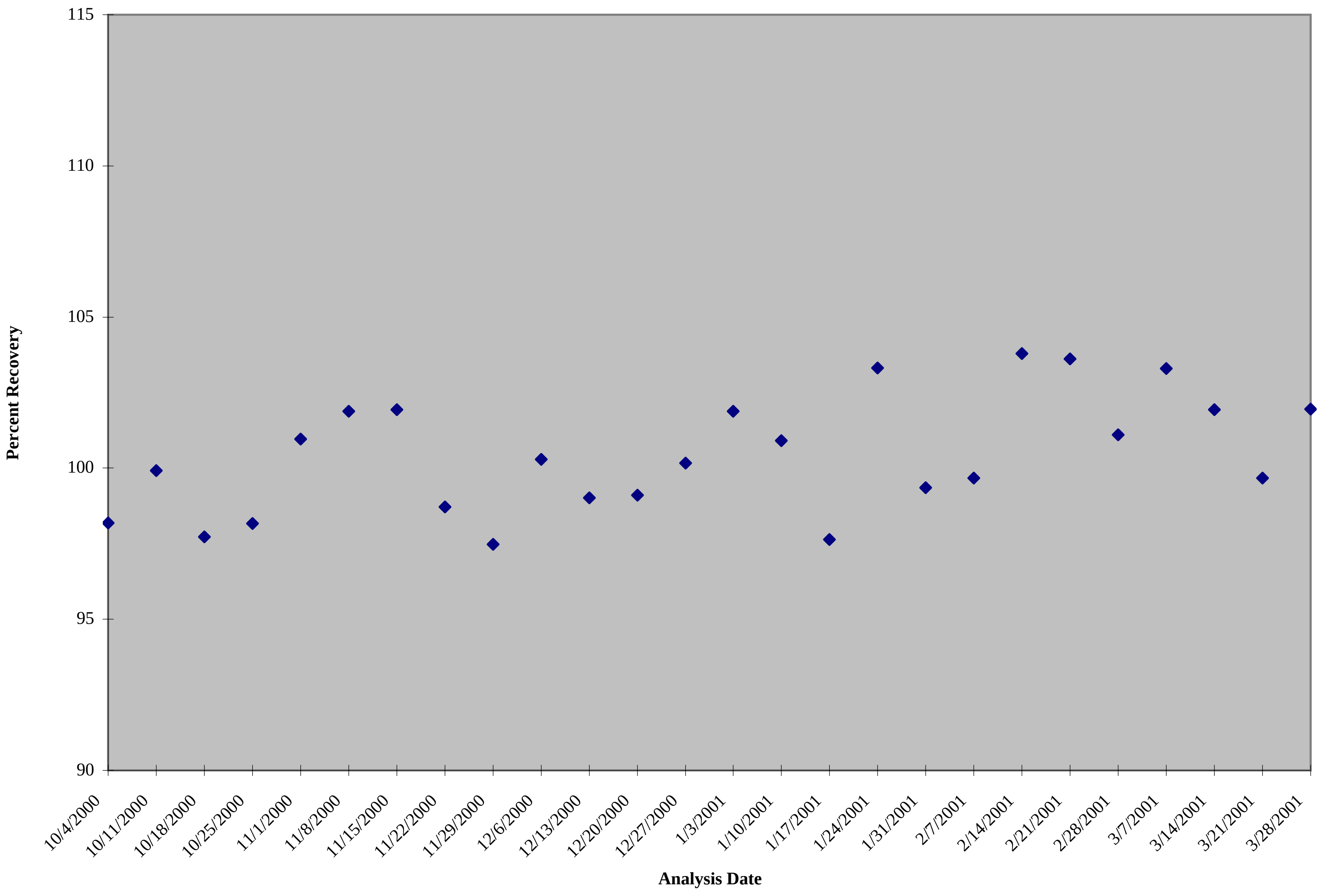


Figure 29. Results of Replicate Silicon (Si) Analysis
October 1, 2000 through March 31, 2001
$m = 1.001$, $r^2 = 0.9988$

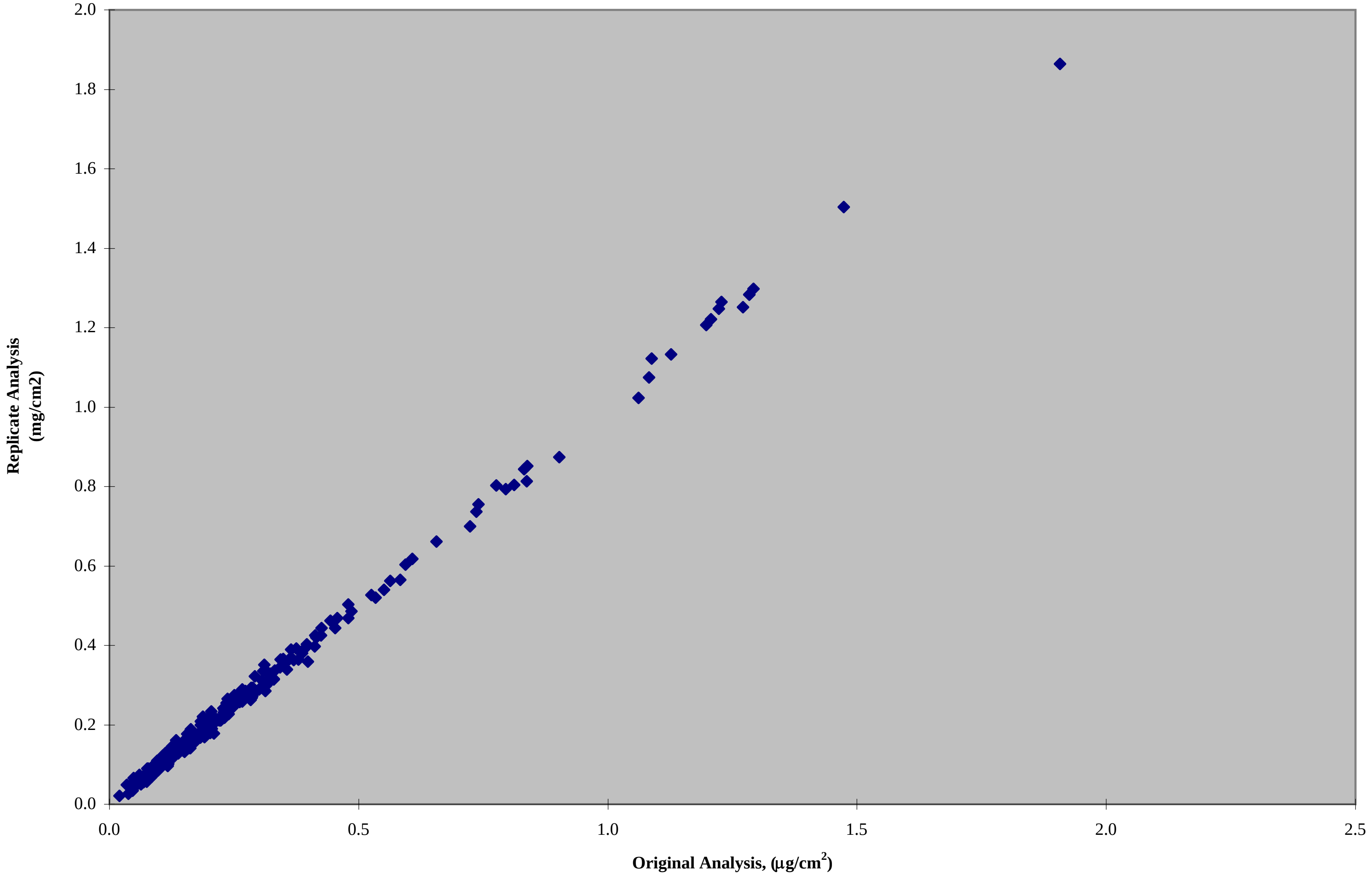


Figure 30 Results of Replicate Sulfur (S) Analysis
October 1, 2000 through March 31, 2001
m = 1.001, r2 = 0.9988

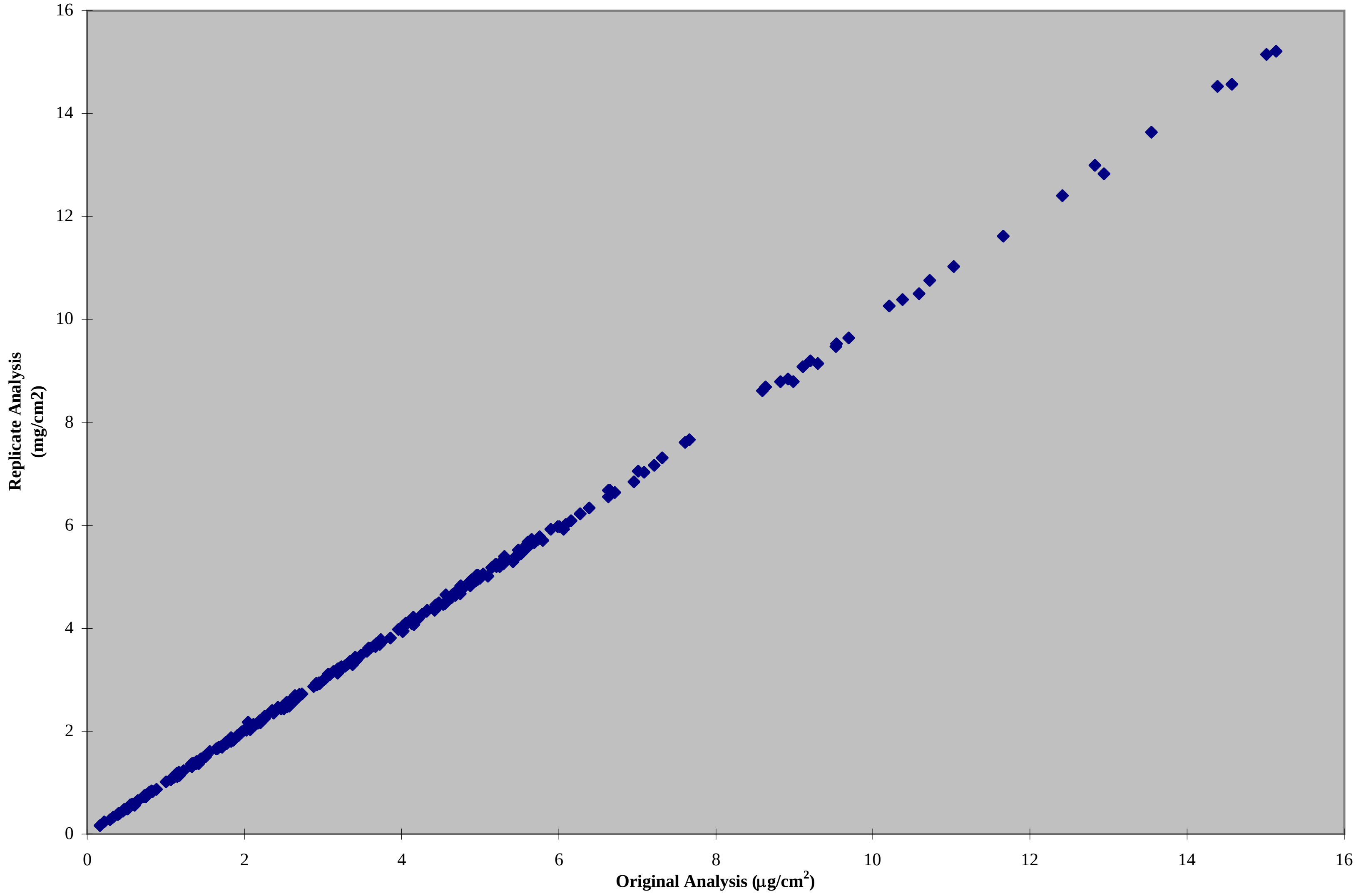


Figure 31. Results of Replicate Potassium (K) Analysis
October 1, 2000 through March 31, 2001
m = 1.001, r2 = 0.9988

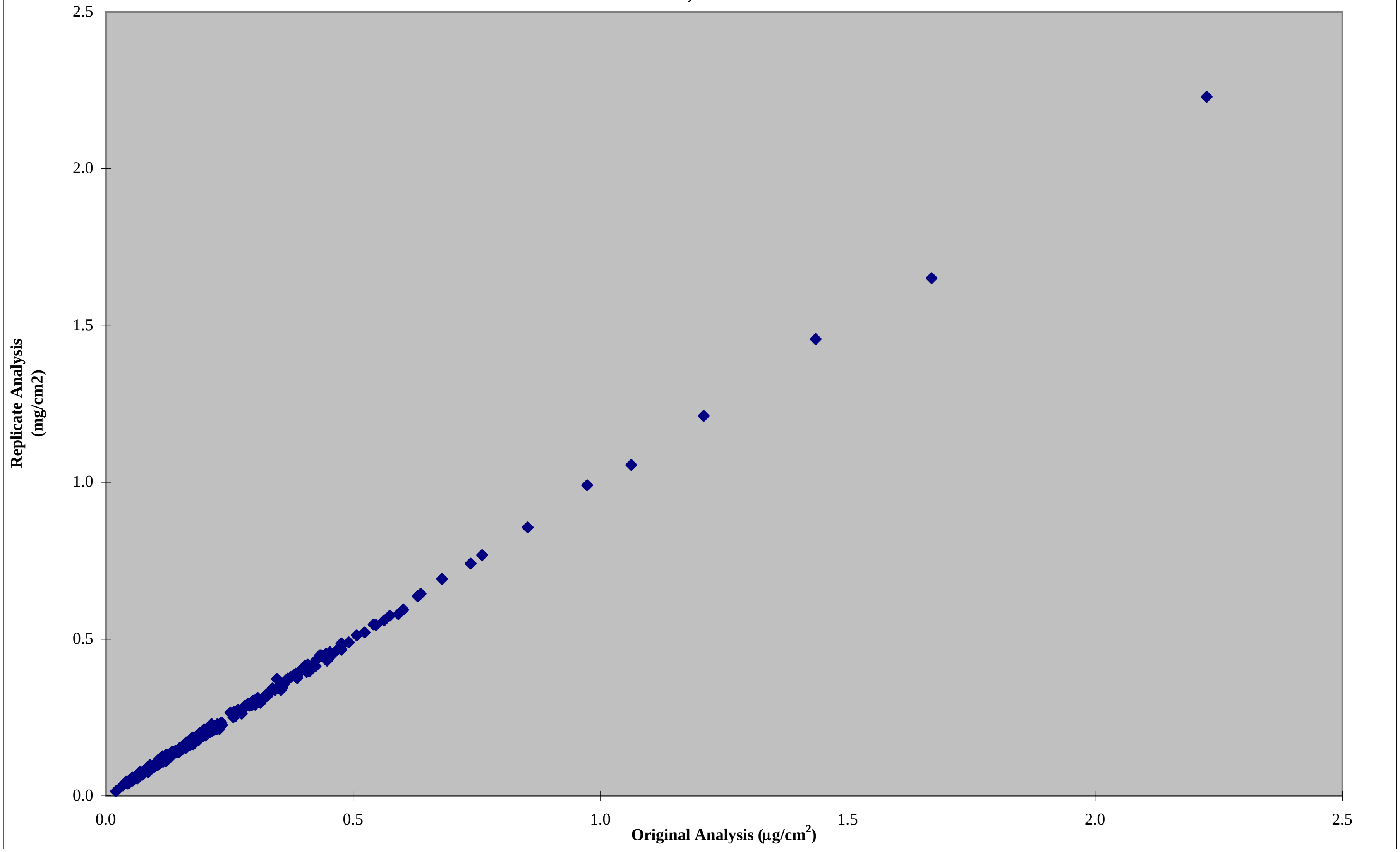
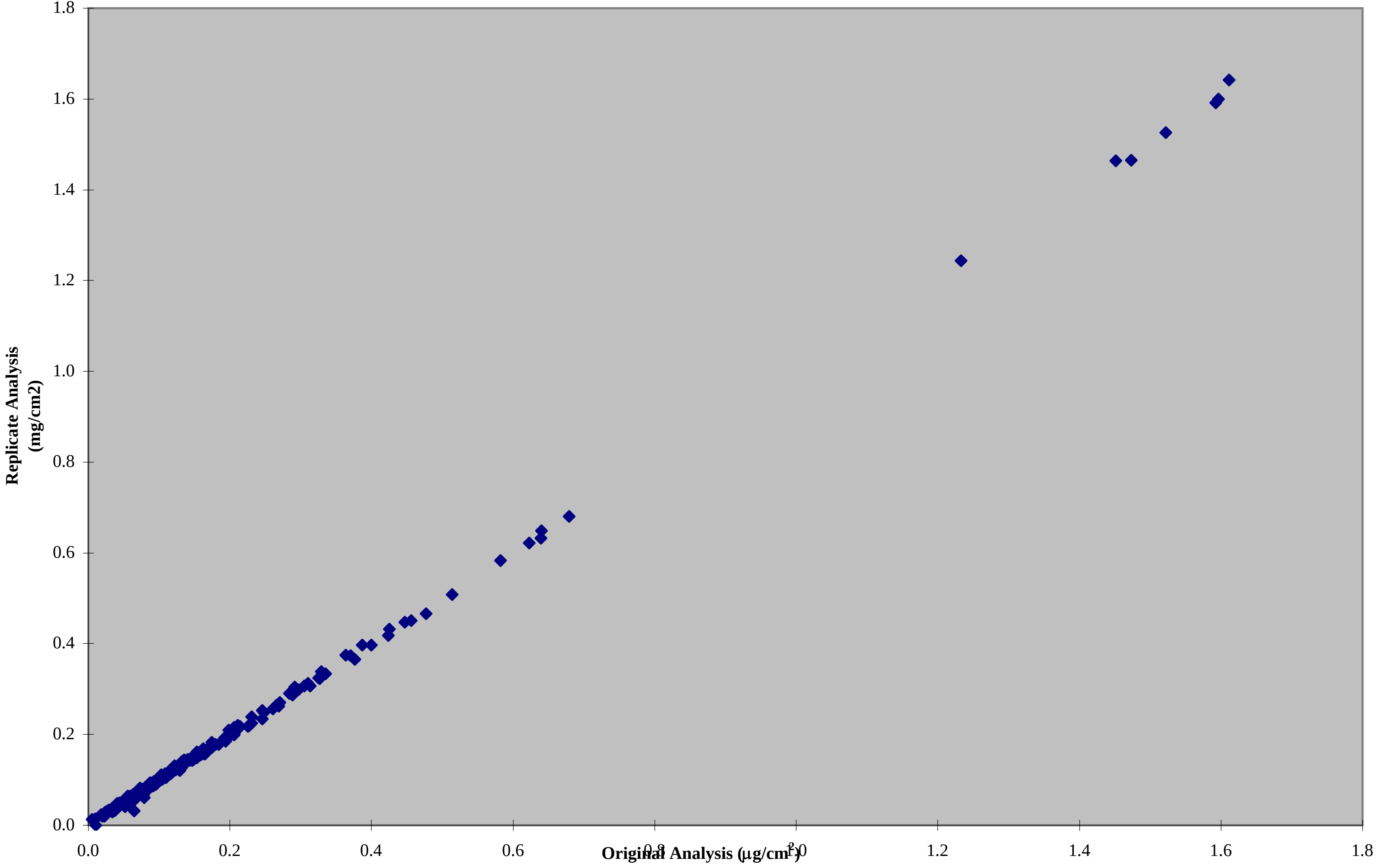


Figure 32. Results of Replicate Calcium (CA) Analysis
October 1, 2000 through March 31, 2001
m = 1.001, r2 = 0.9988



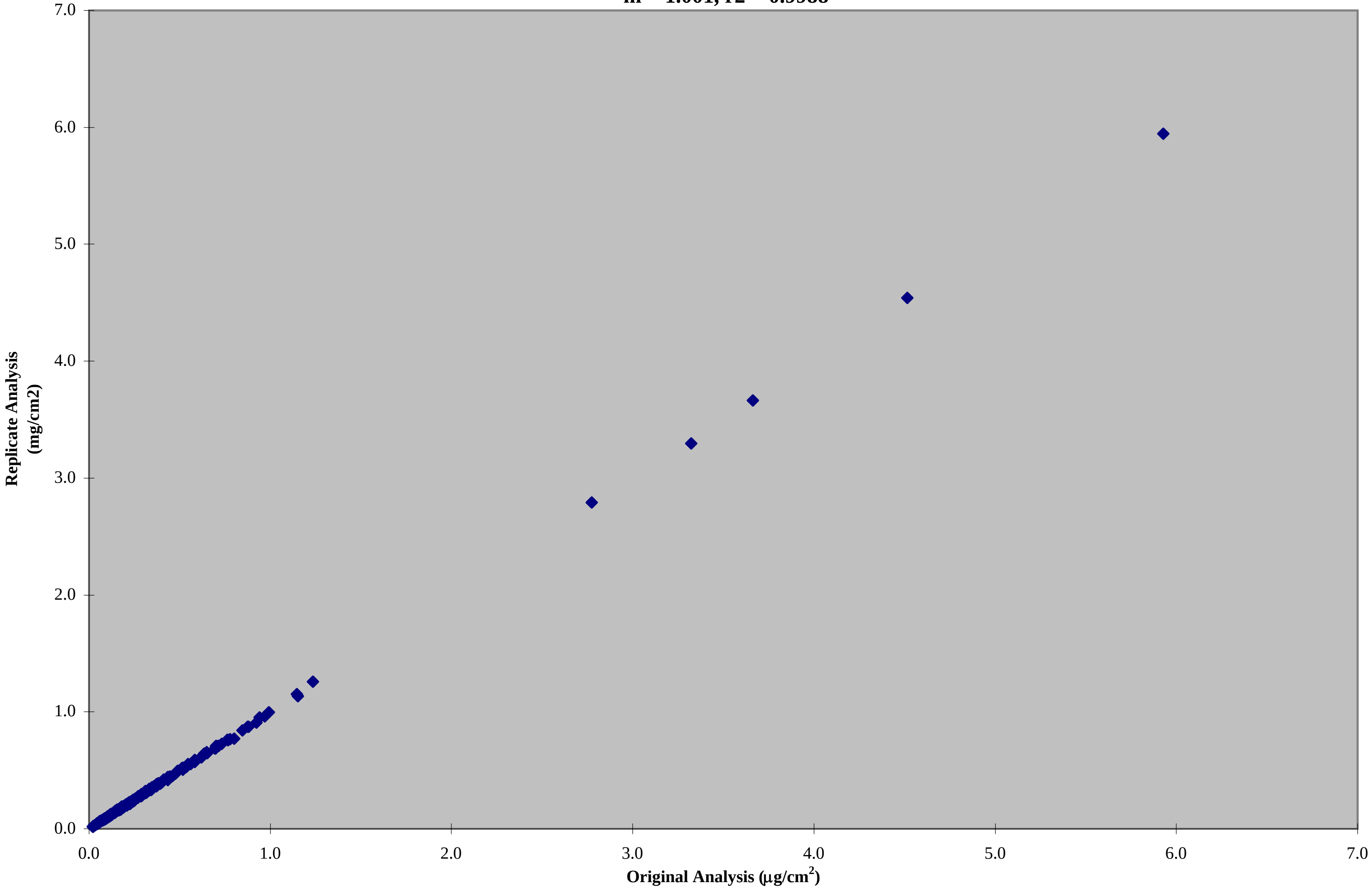
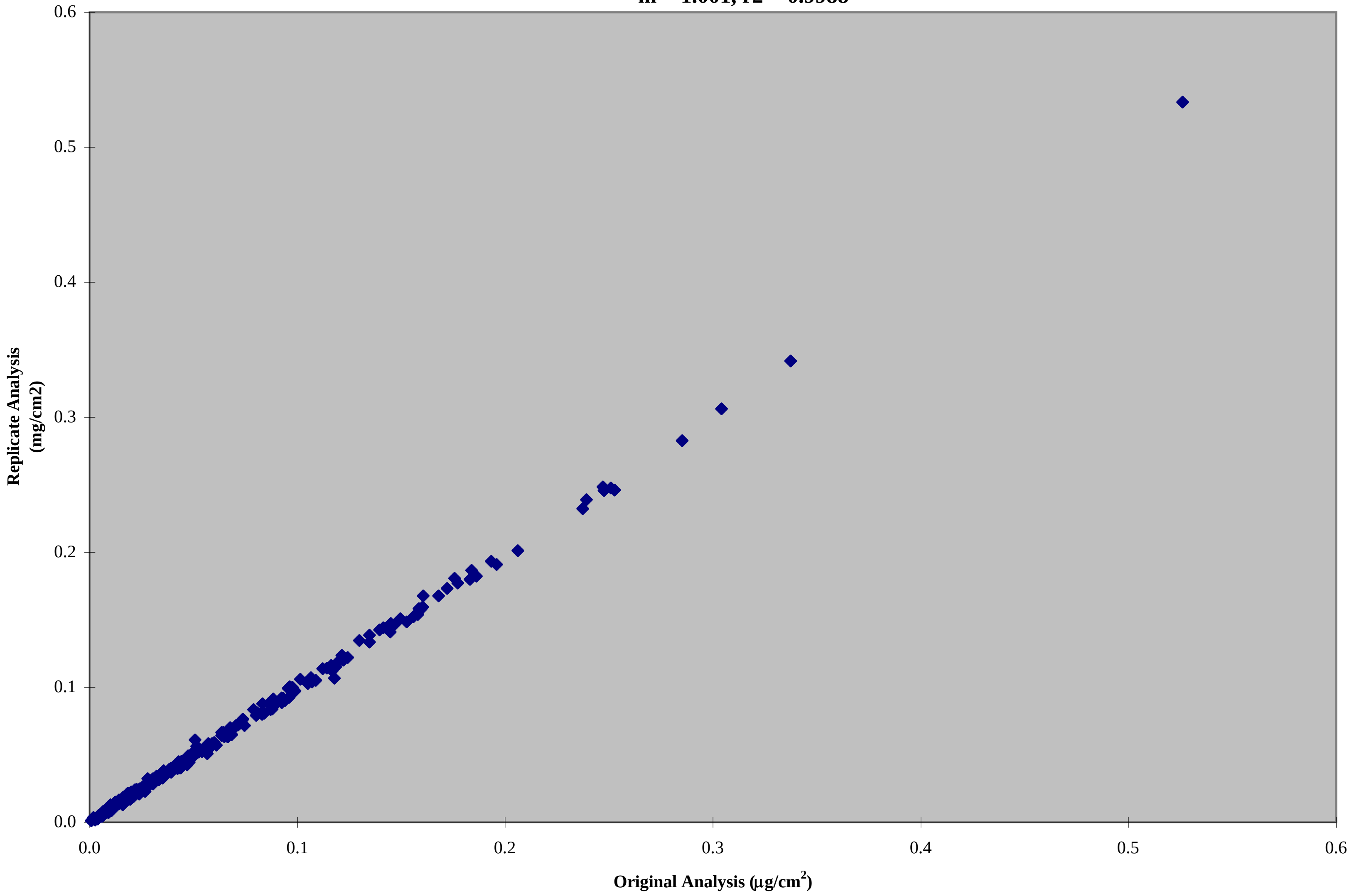


Figure 33. Results of Replicate Iron (Fe) Analysis
October 1, 2000 through March 31, 2001
m = 1.001, r2 = 0.9988

Figure 34. Results of Replicate Zinc (Zn) Analysis

October 1, 2000 through March 31, 2001

$m = 1.001$, $r2 = 0.9988$



Appendix A
EPA PE Audit Findings

TO: Jim Homolya/OAQPS
FROM: Mary Wisdom / NAREL
COPY: Dr. R.K.M. Jayanty, RTI
Dennis Mikel / OAQPS
Robert Maxfield / NERL
Dick Siscanaw / NERL
Michael S. Clark/NAREL
Dr. John Griggs / NAREL
DATE: January 25, 2001
SUBJECT: Performance Evaluation - RTI Laboratories

Introduction

A study has been conducted as part of the QA oversight for the $PM_{2.5}$ Speciation Trends Network. The purpose of this study was to evaluate performance of the gravimetric and the Ion Chromatography (IC) laboratories located at Research Triangle Institute (RTI). RTI is the prime contractor performing gravimetric analysis and IC analysis of air samples collected by the $PM_{2.5}$ Speciation Trends Network. A gravimetric analysis of the sample is needed to determine the mass of very fine Particulate Matter (PM) captured from the sampled air. The IC analysis is needed to determine selected ionic species potentially present in the PM capture.

Mass determination typically proceeds by weighing the Teflon® collection filter before and after the sampling event. The amount of PM captured onto the surface of the filter can be calculated by a simple subtraction of the tare weight from the loaded filter weight. RTI routinely provides clean pre-weighed air filters to the various field sites within the network. At the field site, an approved sampling device must be used to sample the air and deposit the very fine PM onto the collection filter. A field technician must ship the filter back to RTI where the gravimetric analysis may be completed.

RTI also provides clean Nylon® air filters to the various field sites. The Nylon® filters are used to capture PM for subsequent IC analysis. After the loaded filters are returned to the laboratory, the IC analysis typically proceeds by first extracting the filter using an appropriate solvent. The extract must be analyzed using an IC instrument that is optimized to determine the ions of interest. Target anions and target cations must be analyzed on separate IC instruments.

Gravimetric Analysis

For this study, ten new filters were pre-weighed at RTI in the usual manner but were not shipped directly to a field site. These ten filters were shipped to the National Air and Radiation Environmental Laboratory (NAREL) in Montgomery, AL. All ten filters were immediately placed into the weighing chamber at NAREL for equilibration and determination of a NAREL tare weight. After the NAREL tare weights were determined, seven of the ten filters were loaded with very fine PM captured from the outside air near NAREL. An Andersen air sampler was used to load seven of the filters, and the remaining three filters were utilized as field blanks. Following sample collection, filters were returned to the weighing chamber at NAREL to equilibrate and to determine the loaded mass. Finally, the ten filters were shipped back to RTI for their routine determination of the final filter weights.

Gravimetric Results

The results of this study are summarized in Figure 1. The critical information needed by the program is the mass of PM deposited onto the surface of a collection filter, and therefore, PM capture is plotted in Figure 1 for the seven loaded filters, three travel blanks, and one laboratory chamber blank. Figure 2 presents the inter-laboratory differences. Inter-laboratory differences were calculated by subtracting the PM capture value determined at RTI from the capture value determined at NAREL. Notice that a negative bar on the Figure 2 graph represents a smaller PM capture value determined at NAREL.

The raw data reported from both laboratories have been tabulated for easy viewing. At the end of this report, Table 1 includes the results of ten shared filters and one independent chamber blank weighed at each laboratory. Table 1 contains the filter tare weight, the final loaded weight, and the calculated PM capture for each filter. Table 1 also contains the calculated inter-laboratory difference for measuring the PM capture which is graphed in Figure 2.

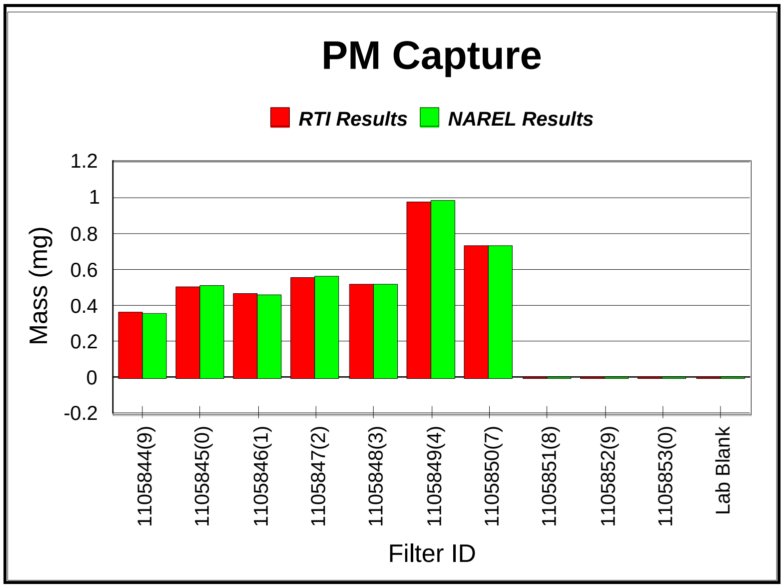


Figure 1

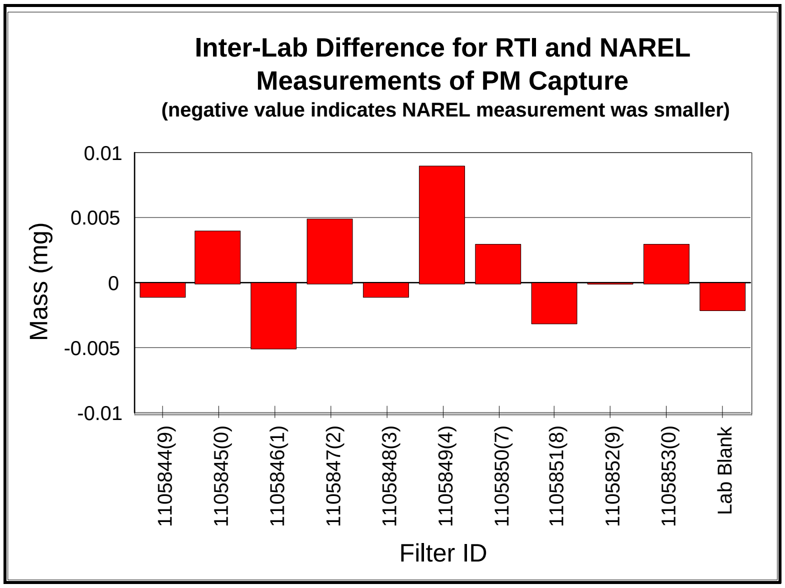


Figure 2

IC Analysis

For this study, six IC spike solutions were carefully prepared at the National Air and Radiation Environmental Laboratory (NAREL) in Montgomery, AL, and shipped to RTI for analysis. Each solution was designed for dilution by a factor of ten using reagent water available at the receiving laboratory. After dilution to full volume, each spike solution was utilized as the solvent to extract a clean blank collection filter available at the receiving laboratory. The filter extracts were analyzed using an appropriate IC instrument available at the receiving laboratory. Results were reported for each sample based upon the concentration of analyte present in the final extract.

Three solutions were prepared at NAREL for determination of selected anions, and three solutions were prepared for the determination of selected cations. These solutions were designed to offer a mid-level concentration, a low-level concentration, and a blank for each analyte. RTI was told to expect a concentration range of 0-10 mg/L for each analyte in all of the samples. All samples were analyzed at NAREL before they were shipped to RTI.

IC Results

Results for the mid-level spikes are presented as a bar graph in Figure 3. For each analyte, the mid-level concentration of the fully diluted spike solution was 2 mg/L. Figure 3 presents the expected result, the RTI result, and the NAREL result for each analyte.

Results for the low-level spikes are presented as a bar graph in Figure 4. For sulfate the low-level spike level was 0.2 mg/L. For all other analytes, the low-level spike level was 0.15 mg/L. Since the concentrations presented in Figure 4 are low, an extra bar was added to this graph showing the Method Detection Limit (MDL) reported by RTI. The IC results are summarized in Table 2 at the end of this report.

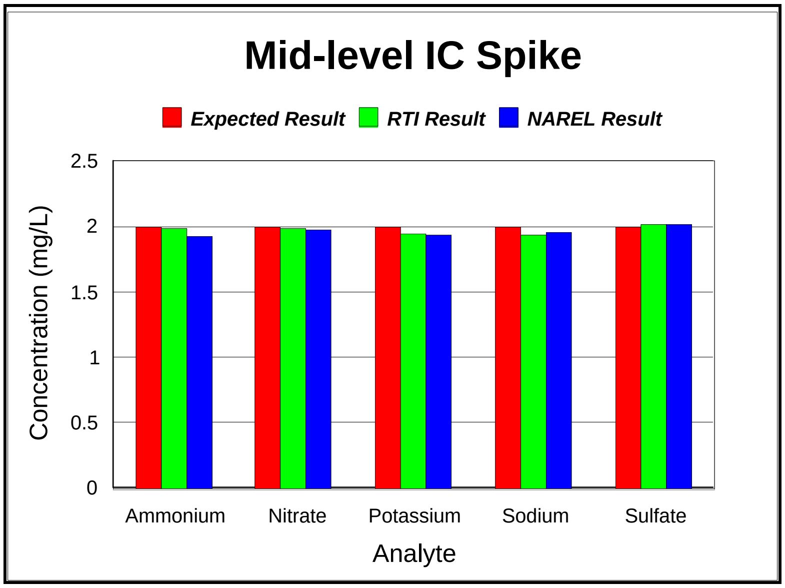


Figure 3

Conclusions

Good agreement was observed for all mass measurements performed at RTI and at NAREL. All three field blanks showed PM capture well below the 0.030-mg failure threshold. The independent chamber blank at both laboratories also showed PM capture well below the program limit of 0.015 mg. The largest inter-laboratory difference for captured PM was 0.009 mg which is smaller than a reasonable warning limit of 0.015 mg and significantly below a reasonable failure limit of 0.030 mg. This study indicates overall good performance by the gravimetric laboratory at RTI. Excellent recoveries (96-101%) were obtained at both laboratories for the mid-level IC spikes. As expected, a slightly wider range of recoveries (87-109%) was observed for the low-level spikes, but in no case did the difference between the expected value and the reported value exceed the MDL expressed by RTI.

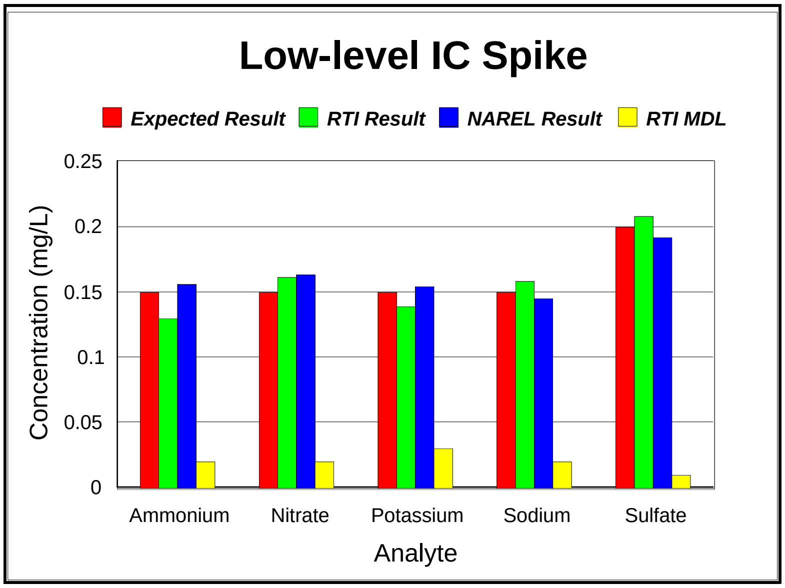


Figure 4

Sample spike solutions identified as A-3 and C-3 were actually blank water. These blanks provided a mechanism to measure laboratory contamination from a variety of sources such as (1) the reagent water used to dilute every sample, (2) the “clean” filter extracted by the test solution which is normally provided to the field for PM capture, and (3) containers used to hold and transfer the sample during the extraction and analysis process. No contamination was reported for the cation blank (C-3), but very low levels of nitrate and sulfate were reported for the anion blank (A-3). Nitrate was reported at 0.023 mg/L which is slightly above the 0.02 mg/L MDL, and sulfate was reported at 0.009 mg/L which is slightly below the 0.01 mg/L MDL. If the MDL is defined as the smallest concentration that can be distinguished from a blank, it seems that RTI has done a good job estimating the MDL for nitrate and sulfate.

This study indicates overall good performance by the IC laboratory as well as the gravimetric laboratory at RTI.

Table 1

Filter ID	**RTI Tare Mass (mg)**	**NAREL Tare Mass (mg)**	**RTI Final Mass (mg)**	**NAREL Final Mass (mg)**	**RTI Captured PM (mg)**	**NAREL Captured PM (mg)**	**Inter-Lab Difference* for Measurement of Captured PM (mg)**
1105844(9)	139.985	139.984	140.346	140.344	0.361	0.360	-0.001
1105845(0)	140.955	140.955	141.459	141.463	0.504	0.508	0.004
1105846(1)	141.473	141.475	141.939	141.936	0.466	0.461	-0.005
1105847(2)	143.565	143.567	144.122	144.129	0.557	0.562	0.005
1105848(3)	141.667	141.668	142.183	142.183	0.516	0.515	-0.001
1105849(4)	142.431	142.431	143.408	143.417	0.977	0.986	0.009
1105850(7)	140.568	140.564	141.297	141.296	0.729	0.732	0.003
1105851(8)	142.138	142.138	142.143	142.140	0.005	0.002	-0.003
1105852(9)	142.869	142.867	142.873	142.871	0.004	0.004	0.000
1105853(0)	142.833	142.828	142.832	142.830	-0.001	0.002	0.003
Lab Blank	141.275	140.466	141.280	140.469	0.005	0.003	-0.002

**** Negative values indicate a larger capture determined by RTI.***

Table 2

Sample ID	Analyte	Expected Result (mg/L)	RTI Result (mg/L)	NAREL Result (mg/L)	RTI Recovery	NAREL Recovery	RTI MDL (mg/L)
A-1	Nitrate	0.150	0.161	0.163	107%	109%	0.02
A-1	Sulfate	2.000	2.022	2.017	101%	101%	0.01
A-2	Nitrate	2.000	1.986	1.979	99%	99%	0.02
A-2	Sulfate	0.200	0.208	0.192	104%	96%	0.01
A-3	Nitrate	0.000	0.023	0.000	N/A	N/A	0.02
A-3	Sulfate	0.000	0.009	0.000	N/A	N/A	0.01
C-1	Ammonium	2.000	1.990	1.927	100%	96%	0.02
C-1	Potassium	0.150	0.139	0.154	93%	103%	0.03
C-1	Sodium	0.150	0.158	0.144	105%	96%	0.02
C-2	Ammonium	0.150	0.130	0.156	87%	104%	0.02
C-2	Potassium	2.000	1.944	1.931	97%	97%	0.03
C-2	Sodium	2.000	1.939	1.952	97%	98%	0.02
C-3	Ammonium	0.000	0.000	0.000	N/A	N/A	0.02
C-3	Potassium	0.000	0.000	0.000	N/A	N/A	0.03
C-3	Sodium	0.000	0.000	0.000	N/A	N/A	0.02

Appendix B
EPA Laboratory Audit Findings

TO: Jim Homolya/OAQPS
FROM: Michael S. Clark/NAREL
COPY: Dr. R.K.M. Jayanty, RTI
Dennis Mikel / OAQPS
Robert Maxfield / NERL
Dick Siscanaw / NERL
Mary Wisdom / NAREL
Dr. John Griggs / NAREL
DATE: January 25, 2001
SUBJECT: RTI Laboratory Audit

Introduction

On December 5, 2000, a laboratory audit was conducted at the Research Triangle Institute (RTI) as part of the QA oversight for the $PM_{2.5}$ Speciation Trends Network (STN). RTI is the prime contractor responsible for the analysis of air samples collected for the $PM_{2.5}$ STN. The USEPA audit team consisted of Michael Clark, Steve Taylor, and Jewell Smiley from the National Air and Radiation Environmental Laboratory (NAREL), Dennis Mikel from the Office of Air Quality Planning and Standards (OAQPS), and Dick Siscanaw from the New England Regional Laboratory (NERL). Scott Faller was present for the audit as an observer from the Radiation and Indoor Environments National Laboratory (R&IE) located in Las Vegas. This audit was a routine annual inspection of the laboratory systems and operations required for acceptable contract performance.

Summary of Audit Proceedings

After a brief meeting with the RTI senior staff and supervisors, the audit team separated as necessary to complete specific assignments for the audit process. At least one member of the RTI staff was always available to escort and assist each auditor. The following specific areas on the RTI campus were visited and inspected.

Sample Handling and Archiving Laboratory (SHAL) - Jim O'Rourke
Gravimetric Laboratory - Dr. Bob Perkins, Lisa Greene
Ion Chromatography (IC) Laboratory - Dr. Eva Hardison
Organic Carbon/Elemental Carbon (OC/EC) Laboratory - Dr. Max Peterson

Besides the areas mentioned above, interviews were conducted with the following RTI staff.

Dr. R.K.M. Jayanty - RTI Services Program Manager
Dr. Jim Flanagan - Quality Assurance Manager
Ed Rickman - Data Management Technical Supervisor
X-Ray Fluorescence Analysis (subcontracted) - Dr. Bill Gutknecht

Members of the audit team were familiar with RTI's Quality Assurance Project Plan (QAPP) and pertinent SOPs. A report from the previous year's on-site audit was available. RTI has analyzed many samples from the $PM_{2.5}$ STN since the network became operational in February of this year. The most recent set of Performance Evaluation (PE) samples prepared at NAREL were submitted to RTI in October, and those PE results were discussed with RTI staff during the audit (see reference 1). Furthermore, a special study was initiated in October which required the re-analysis of old samples stored at RTI (see reference 2). Selected samples older than six months were removed from cold storage at RTI and shipped to NAREL and NERL for re-analysis. The results from this special study were also discussed with RTI staff during the audit. Check lists were available to assist the auditors with the numerous questions directed to RTI staff.

Sample Handling and Archiving Laboratory (SHAL)

The first laboratory to be visited was the SHAL currently located in building 3 and 6. Most members of the audit team visited this area at least once during the audit. The SHAL is organized to be a central point for all laboratory operations. Every sample passes through the SHAL three times. Clean air filters are delivered to the SHAL from the analytical laboratories ready to be packaged and delivered to the field sites. Critical bookkeeping is required to insure sample integrity and to make sure that the proper equipment and information is sent to the field in a timely manner. Loaded filters returning from the field are received at the SHAL, removed from the sampler module, logged into the electronic database, and physically delivered back to the analytical laboratories where the final analysis is completed. After the final analysis is completed, the sample is returned to the SHAL where it is placed into refrigerated storage for at least six months.

The air filter is protected from the time it leaves the SHAL until it is returned. Each air filter must be mounted into an appropriate sampler module to protect it from accidental contamination. Three different types of filters are required for all of the analytical fractions, and four different types of air samplers are currently operated in the field. Different samplers require different filter modules which are expensive and must be cleaned for reuse. It can be readily seen that the SHAL has a critical role for the overall operations. The SHAL maintains direct interaction with the field sites and was of special interest to Scott Faller. Scott will be auditing field sites, and he was able to observe the intricate details of the laboratory operations as they relate to field activities.

Gravimetric Laboratory

The gravimetric laboratory is located in building 11. Dr. Bob Perkins is the technical area supervisor and Lisa Greene is the supervisor of the gravimetric laboratory. This part of the audit was conducted by Steve Taylor. The interviews and inspections were performed to determine compliance with good laboratory practices, the QAPP, and the following SOPs and documents.

Standard Operating Procedure for PM2.5 Gravimetric analysis
Standard Operating Procedures for Procurement and Acceptance Testing of Teflon, Nylon, and Quartz Filters
Reference method for the determination of fine particulate matter as $PM_{2.5}$ *in the atmosphere.* U.S. Environmental Protection Agency 40 CFR Part 50, Appendix L. 1997.
Monitoring $PM_{2.5}$ *in Ambient Air Using Designated Reference or Class I Equivalent Methods.* Quality Assurance Guidance Document 2.12. U.S. Environmental Protection Agency. Office of Research and Development, Research Triangle Park, NC. 1998.

Building 11 is equipped with two weighing chambers, but thus far only one chamber has been used for all of the $PM_{2.5}$ STN samples. The weighing chamber was configured to satisfy conditions of cleanliness, constant temperature, and constant humidity required by the program. The chamber was equipped with two microbalances although only one balance has been used to weigh all of the $PM_{2.5}$ STN samples so far. Mass determination typically proceeds by weighing the Teflon® collection filter before and after the sampling event. The amount of Particulate Matter (PM) captured onto the surface of the filter can be calculated by a simple subtraction of the tare weight from the loaded filter weight.

Documentation was available for recent and historical chamber conditions, balance calibration checks, and chamber blanks. Result were also available from a recent Technical Systems Audit (TSA) audit conducted in October by EPA Region II. This TSA assessed the accuracy of temperature, humidity, and mass measurements performed at the gravimetric laboratory. The audit showed acceptable comparison to all three NIST traceable standards.

The only specific samples discussed were those from the recent PE study and those from the special study of archived extracts. Results from both of these studies are described with detail in separate reports (see reference 1 and 2), but the results from both studies indicate good performance from the gravimetric laboratory.

Ion Chromatography (IC) Laboratory

The IC laboratory is located in building 6 where Dr. Eva Hardison is the technical supervisor, and David Hardison is an analyst. Both of them were interviewed by Jewell Smiley for compliance to good laboratory practices, the QAPP, and the following SOPs.

Standard Operating Procedures for PM2.5 Anion Analysis
Standard Operating Procedures for PM2.5 Cation Analysis
Standard Operating Procedures for Cleaning Nylon Filters Used for Collection of PM2.5 Material

The laboratory is equipped with four automated Dionex IC instruments and also has access to equipment for cleaning and extracting Nylon® filters. At the instrument, multilevel calibration curves are established daily and the calibration is checked by a second source standard. Duplicate injections have been used to evaluate precision, and post spikes have been used to evaluate accuracy. Control charts were available for recent spikes, duplicates, and laboratory blanks.

The only specific samples discussed were those from the recent PE study and those from the special study of archived extracts. Results from both of these studies are described with detail in separate reports (see reference 1 and 2), but the results from both studies indicate good performance from the IC laboratory.

Carbon Analysis Laboratory

The carbon analysis laboratory is located in building 3 where Dr. Max Peterson is the technical supervisor and Melville Richards is an analyst. This part of the audit was conducted by Dick Siscanaw. The interviews and inspections were performed to determine compliance to good laboratory practices, the QAPP, and the following SOP.

> *Standard Operating Procedure for the Determination of Organic, Elemental, Carbonate, Total Carbon and OCX in Particulate Matter Using a Thermal/Optical Carbon Analyzer.*

The carbon analysis is based upon NIOSH method 5040 (see reference 3) which includes the determination of organic carbon (OC), elemental carbon (EC), and carbonate carbon (CC) all of which are components of the total carbon (TC).

New quartz filters must be thermally cleaned before they are delivered to the SHAL, mounted into the appropriate sampler module, and shipped to the field for sample collection. Upon return to the laboratory, a loaded filter may be analyzed for captured carbon by using a punch device to remove a representative 1.5-cm^2 subsample from the filter. The subsample may be analyzed using one of the two thermal/optical transmittance (TOT) analyzers available in the laboratory. The following specific equipment was available to support the carbon analysis.

Two Sunset TOT Instruments
Mettler AT 400 analytical balance (certified on 7/28/2000)
Lindberg/Blue M box furnace
Kenmore Freezer, F42978 (daily temperatures recorded)

Various laboratory documents were examined during the audit as well as instrument data files. The laboratory has routinely analyzed a weekly three point calibration with a linear regression coefficient (r^2) better than 0.99, a daily instrument blank less than 0.3 µg/cm^2, 10% duplicates, and a daily standard within 90-110% recovery with no problems observed. The quality control data were being collected and plotted for trend analysis. There were no critical findings, and generally the laboratory operations were excellent. The personnel were qualified, highly competent, and conscientious about doing a fine job. This auditor enjoyed spending the time and sharing information with them.

X-Ray Fluorescence Analysis (subcontracted)

The PM captured onto the surface of the Teflon® filter is not only weighed to determine its mass but is also analyzed to determine its elemental composition using the energy dispersive X-Ray Fluorescence (XRF) technique. The XRF analysis may not proceed before the gravimetric analysis has been completed and the filter is shipped to the remote subcontractor laboratory.

Since the XRF analysis is not performed locally, Dr. Bill Gutknecht was interviewed by Jewell Smiley and Steve Taylor for his role as the elemental analysis technical supervisor. Bill is responsible for more than a completeness review of the XRF results received from the subcontractor. He is sufficiently familiar with the technique to review the data for reasonableness of the values reported.

NAREL has planned an on-site audit of the remote subcontractor laboratory for early 2001.

Other Staff Interviews

Dr. R.K.M. Jayanty, Dr. Jim Flanagan, and Ed Rickman were interviewed by Michael Clark and Dennis Mikel. The following topics were discussed.

Facility and Equipment
Facility, Equipment, and Support Services
Security
Health and Safety
Waste Management
Organizational Structure and Management Policies
Personnel
Job Descriptions and Qualifications
Training Program and Training Records
Quality Assurance
Standard Operating Procedures
Performance Evaluation Results and Corrective Action Responses
Previous Audit Reports and Responses
Quality Reports to Management
Quality Control Records and Oversight
Review Process for QAPP’s
Review Process for Client Data Packages
Procurement
Materials and Equipment
Services
Document Control
Controlled Document Production
Document Distribution and Tracking
Revisions to Control Documents
Retrieval and Disposal of Outdated Documents
Computer Management and Software Control
Personnel and Training
Facilities and Equipment
Procedures
Security
Data Entry
Records and Archives

Conclusions

Observations have been made by the audit team to determine RTI's compliance with good laboratory practices, the QAPP, and SOPs. This audit has produced the following comments and recommendations.

According to the current SOP for gravimetric measurements, the acceptance criteria for temperature and humidity control is based upon the average and standard deviation of measured values, and variations such as those presented in Figure 1 are within the acceptance limits. The 24-hour period presented in Figure 1 has an average relative humidity of 36% with a standard deviation of 4%. We realize that this is an extreme example, and RTI personnel would not allow weighing to proceed under these conditions.

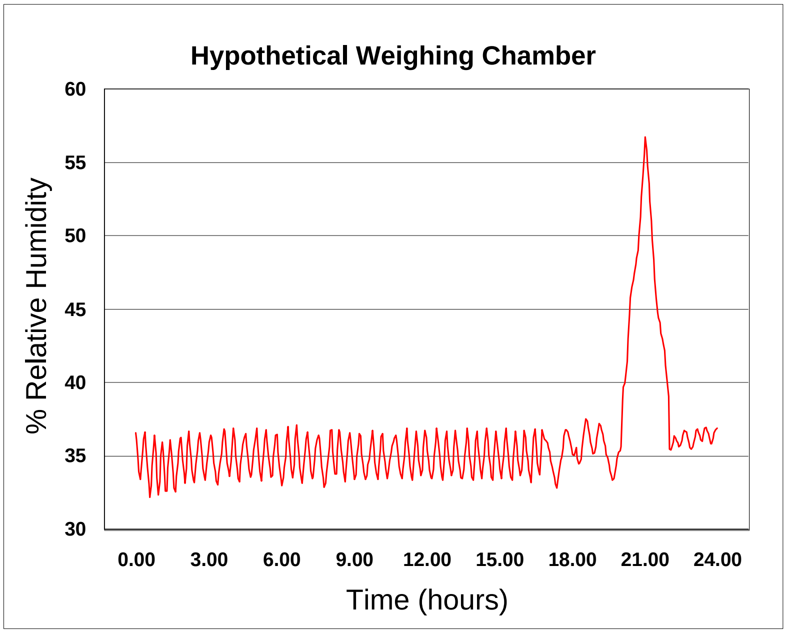


Figure 1

Recommendation. Criteria should be written which is reasonable to achieve and appropriate for good data quality. For example at NAREL the following criteria are used for chamber conditions.

> *For the previous 24-hour period, the mean temperature must be 20-23 °C (68.0-73.4 °F) and the mean relative humidity must be 30-40 %. Furthermore during the previous 24-hour period, there must be no temperature excursions outside 20-23 °C (68.0-73.4 °F), and there must be no excursion of relative humidity outside 30-40 %. Failure to meet these criteria for chamber conditions prevents a valid weighing session and corrective actions must be taken to bring the chamber back into control. If all chamber criteria are satisfied, the weighing session may proceed.*

Only one Dickson device is currently available to monitor the official temperature and humidity inside the weighing chamber.

Recommendation. Since this device must be re-certified periodically, it may be useful to purchase a second device to serve as backup. A second device is also useful for experiments to discover the effects which chamber activities have on the local temperature and humidity.

The current SOP for pre-cleaning nylon filters requires the analysis of two filters from each batch, and the residual concentration of each analyte must be less than 1.0 µg/filter.

Recommendation. Since each analyte is reported to RTI's Minimum Detection Limit

(MDL), it seems appropriate that each filter should be pre-cleaned to a contaminant level at least as low as the MDL. If it is not possible to pre-clean and certify the nylon filters to the MDL level, then report limits should be adjusted to the certification level.

No SOPs are currently in place covering computer system security, training, hardware and software change control, data change procedures, procedures for manual operations during system downtime, disaster recovery, backup and restore procedures, and general system safety.

Recommendation. One or more SOPs should be written and implemented to address these activities.

The operating parameters for the carbon analysis need to be standardized. Both TOT instruments have different parameter tables, and the OCX peak is set for 615-900 °C.

Recommendation. This was the primary focus for meetings on 9/21/2000 and 12/5/2000 at RTP, EPA. The most recent operational file is called SPEC.PAR and is listed below. The OCX peak should be set for 550-900 °C.

SPEC.PAR (Operating Parameters)

Operating Step	**Comment**
Helium, 10, 1	purge for 10 sec
Helium, 65, 250	OC temperature ramp, 65 sec, 250°C
Helium, 45, 400	OC temperature ramp, 45 sec, 400°C
Helium, 70, 550	OC temperature ramp, 70 sec, 550°C
Helium, 100, 900	OC temperature ramp, 100 sec, 900°C (OCX)
Helium, 55, 0	Cool the oven to approximately 550°C
Oxygen, 35, 550	EC temperature ramp, 35 sec, 550°C
Oxygen, 35, 650	EC temperature ramp, 35 sec, 650°C
Oxygen, 35, 750	EC temperature ramp, 35 sec, 750°C
Oxygen, 35, 850	EC temperature ramp, 35 sec, 850°C
Oxygen, 110, 900	EC temperature ramp, 110 sec, 900°C
CalibrationOx, 30, 1	Methane Calibration
CalibrationOx, 80, 0	Methane Calibration
Offline, 1, 0	End of sample analysis

During the audit four carbon filters were measured with a Craftsman® caliper, and sample A111046R had a sample deposit measuring 4.08 cm in diameter. The diameter of sample deposit is theoretically 3.87 cm for a 4.7-cm quartz filter. Measurements for the other three filters were 3.87, 3.88, and 3.91 cm.

> Recommendation. Investigate why this sample had an 11% error in the filter deposit area. RTI should purchase a caliper to spot check the filter diameter.

A recent qualitative analysis of calcium carbonate could not be found to check for CC in the field samples. Two thermograms examined during the audit had suspicious peaks in the CC region. A calcium carbonate standard was analyzed during the audit, and the CC time in the thermogram was slightly off the expected value.

> Recommendation. Run a calcium carbonate once per month on each instrument to determine the location of the peak on the thermogram.

According to the current SOP for carbon analysis (section 9.5), the FID response to the internal standard for any analysis run on a given day may not be outside the range of 90-100% of the daily mean.

> Recommendation. At the meeting on 9/21/2000 at RTP, NC with Dr. Max Peterson, Dr. Gary Norris, and Dick Siscanaw, it was agreed to decrease the acceptance range of the methane calibration counts to 95-105% of the daily mean. Some of RTI's data were reviewed, and the variation was less than 2% of the daily mean. The SOP should be revised to reflect this change in the acceptance range.

The current SOP for carbon analysis (section 9.2.2) requires a regression coefficient (r^2) of 0.99 for the weekly calibration, but does not include instructions to force the calibration curve through the origin.

> Recommendation. The SOP needs to include the fact that this linear regression is a force fit through the origin (0,0). RTI is already doing the correct calculations. This needs to be added to the SOP.

A discussion of the method parameter file is not included in the current SOP for carbon analysis.

> Recommendation. Since the analytical results are dependent on the operational conditions used to run the TOT instrument, it is important to include these temperature and times in the SOP.

The current SOP for carbon analysis does not contain a discussion of when and how to update the calibration factor.

> Recommendation. The calibration factor in the OCECPAR.TXT file must be updated when the initial calibration or daily standards are outside of the 90-110% acceptance range. The procedure should be included in the SOP. The information was provided to RTI during the audit. In Region 1, the calibration factor is updated routinely with each weekly initial calibration, but this practice is not necessary because the calibration factor is relatively constant.

RTI is using the pinch clamp that is supplied by Sunset Laboratory to seal the ball and socket joint for the sample helium line.

> Recommendation. This pinch clamp is susceptible to small leaks because the support screw is on one side. This problem is noted in RTI's SOP (section 9.5). Another type that uses two screws for more even support is a horseshoe type (part number CG-151-03) from Chemglass (800-843-1794) and costs $8.90.

One of the Sunset instruments (the retrofit instrument) has Teflon® lines in the helium supply. This was to be corrected on August 7, 2000. The NO-OX tubing is more opaque than Teflon tubing.

> Recommendation. Teflon® is permeable to oxygen, and these lines need to be changed to copper or NO-OX tubing from Altech. Any oxygen in the helium will enhance an early split phenomenon.

Sample A107403B duplicate in the sample log book for carbon analysis was crossed out, and the correction was not initialed and dated.

> Recommendation. All amendments to an official laboratory record should be initialed (or signed) and dated.

There is no acceptance range in the SOP for carbon analysis, the QAPP, or the daily log for the temperature that is being recorded for the Kenmore freezer.

> Recommendation. The common acceptance range for a freezer is -10 to -20 °C. The SOP should be revised to include an acceptance range for the freezer temperature.

The MDL study for one of the Sunset Instruments did not match the raw data done on 3/23/2000.

> Recommendation. Both sets of data were excellent and below the NIOSH 0.15 $\mu g/cm^2$, but they must agree. RTI needs to use the raw data on the csv file or repeat the MDL study.

According to the auditor's records, the transit time for carbon analysis was 6 seconds on December 14, 1999, but the transit time was changed to 10 seconds. This is a large change, and a record of this change could not be found in the maintenance log book. There was some maintenance done on 11/1/2000, but the transit time change was not recorded.

> Recommendation. Significant instrument maintenance should be recorded in the log book..

Response to the comments and recommendations presented in this audit report should be submitted to Michael Clark at NAREL within two weeks of receiving this report. It is clear that the staff at RTI are experienced and knowledgeable, and the facilities are excellent for $PM_{2.5}$ work. The audit team appreciates the cooperation of the RTI staff during this audit.

References

EPA. 2000. Performance evaluation study of $PM_{2.5}$ contractor laboratory. U.S. Environmental Protection Agency. Document reference number #.

EPA. 2000. Special study of archived samples from the $PM_{2.5}$ Speciation Trends Network. U.S. Environmental Protection Agency. Document reference number #.

NIOSH. 1999. Method 5040, Issue 3, Elemental Carbon (Diesel Particulate), NIOSH Manual of Analytical Methods, Fourth Edition. National Institute for Occupational Safety & Health, Cincinnati, OH.

Appendix C
RTI Response to EPA OC/EC Audit Findings

RTI’s Responses to the OC/EC Comments and Recommendations

1. The operating parameters for the carbon analysis need to be standardized. Both TOT instruments have different parameter tables, and the OCX peak is set for 615-900 °C. Recommendation. This was the primary focus for meetings on 9/21/2000 and 12/5/2000 at RTP, EPA. The most recent operational file is called SPEC.PAR and is listed below. The OCX peak should be set for 550-900 °C.

SPEC.PAR (Operating Parameters)

Operating Step	Comment
Helium, 10, 1	purge for 10 sec
Helium, 65, 250	OC temperature ramp, 65 sec, 250°C
Helium, 45, 400	OC temperature ramp, 45 sec, 400°C
Helium, 70, 550	OC temperature ramp, 70 sec, 550°C
Helium, 100, 900	OC temperature ramp, 100 sec, 900°C (OCX)
Helium, 55, 0	Cool the oven to approximately 550°C
Oxygen, 35, 550	EC temperature ramp, 35 sec, 550°C
Oxygen, 35, 650	EC temperature ramp, 35 sec, 650°C
Oxygen, 35, 750	EC temperature ramp, 35 sec, 750°C
Oxygen, 35, 850	EC temperature ramp, 35 sec, 850°C
Oxygen, 110, 900	EC temperature ramp, 110 sec, 900°C
CalibrationOx, 30, 1	Methane Calibration
CalibrationOx, 80, 0	Methane Calibration
Offline, 1, 0	End of sample analysis

RTI Response: *RTI fully supports a uniform set of operating parameters for all carbon analyzers used in the Chemical Speciation of $PM_{2.5}$ program. At the September 21, 2000, meeting at EPA/RTP, operating parameters for all four (2 at RTI, 1 at EPA Region 1, and 1 at EPA/RTP) of the OC/EC instruments operated by attendees were slightly different although interlaboratory and split sample-studies had indicated acceptable agreement in results among the instruments. EPA/RTP personnel are evaluating several candidate sets of parameters, including the one proposed above, and will decide on a standard for the program. Assuming any cost issues that might arise due to a longer analysis time (if required by the chosen standard operating parameters) can be resolved, RTI will use the set of parameters EPA deems best for the program.*

2. During the audit four carbon filters were measured with a Craftsman® caliper, and sample A111046R had a sample deposit measuring 4.08 cm in diameter. The diameter of

sample deposit is theoretically 3.87 cm for a 4.7-cm quartz filter. Measurements for the other three filters were 3.87, 3.88, and 3.91 cm.
Recommendation. Investigate why this sample had an 11% error in the filter deposit area. RTI should purchase a caliper to spot check the filter diameter.

> ***RTI Response:*** *RTI uses the theoretical 3.87 cm as the effective diameter of the deposit area, which is presumed to be a circle with an area of 11.76 cm^2. Sample A111046R was traced to a sampling event using module I12648 in a URG MASS speciation sampler. Six quartz filter samples (including A111046R) collected in URG Mass sampler modules were tracked down and inspected. The outer 1-2 mm of all six URG filter deposits (including the deposit on A111046R) have a feather-edged non-uniform appearance that defies an accurate measurement of the deposit diameter. The poorly defined deposit edge appears to result from the dimensions of the module components that hold the quartz filter. The inside diameter of the upstream part of the filter holder (the part that is in contact with the top of the quartz filter) is 4.13 cm while the circular pattern of holes in the URG filter-support screen has a diameter of just 3.8 cm. This means that 13.4 cm^2 of the filter surface is exposed to sampled air, but all air is pulled through air holes in a circular pattern with an area of only 11.3 cm^2 in the filter support screen.*
>
> *Given that the deposit area is used as a multiplier to convert μgC/cm^2 of filter to μgC/filter, the area that gives the most accurate value for μgC/filter is the more desirable one. The multiplier should be the effective uniform deposit area rather than simply the area over which the deposit is spread. Visual inspection suggests that the theoretical deposit area of 11.76 cm^2 (3.87 cm in diameter) would give a more accurate value for μgC/filter than would 13.07 cm^2 (4.08 cm in diameter). RTI can easily change to a different multiplier (or effective uniform deposit area) for carbon analysis calculations for URG quartz filters, if a more accurate value can be determined by EPA and approved for use in RTI's calculations. Until such a value is determined and approved by EPA, RTI will continue to use 11.76 cm^2 as the effective uniform deposit area of $PM_{2.5}$ collected on quartz filters using the URG speciation samplers.*
>
> *Deposit areas of several quartz filter samples from Andersen, MetOne, and R&P FRM samplers (being used as $PM_{2.5}$ speciation samplers) were also examined and measured. Deposits on filters from these three samplers all appeared uniform and had well-defined deposit edges. Measured deposit diameters gave calculated deposit areas within 2% of the expected theoretical deposit area of 11.76 cm^2.*

3. A recent qualitative analysis of calcium carbonate could not be found to check for CC in the field samples. Two thermograms examined during the audit had suspicious peaks in the CC region. A calcium carbonate standard was analyzed during the audit, and the CC time in the thermogram was slightly off the expected value.
   Recommendation. Run a calcium carbonate once per month on each instrument to determine the location of the peak on the thermogram.

> ***RTI Response:*** *RTI performed qualitative analyses of calcium carbonate at the beginning of the* $PM_{2.5}$ *chemical speciation program to determine the time in the thermogram that calcium carbonate. None of the thermograms to date have had a significant characteristic peak (that is, a peak corresponding to a filter loading of carbonate carbon at or above the minimum detection limit of 0.2* $\mu g/cm^2$*) in the calcium carbonate region. The suspicious peaks (which were smaller than the criterion given in the previous sentence) described in the finding were not calcium carbonate because the time they appeared in the thermogram was not the same as the time the calcium carbonate standard (run during the audit) appeared. As recommended, RTI will run a qualitative calcium carbonate standard on each instrument once per month to confirm the location of the peak in the thermogram.*

4. According to the current SOP for carbon analysis (section 9.5), the FID response to the internal standard for any analysis run on a given day may not be outside the range of 90-100% of the daily mean.
   Recommendation. At the meeting on 9/21/2000 at RTP, NC with Dr. Max Peterson, Dr. Gary Norris, and Dick Siscanaw, it was agreed to decrease the acceptance range of the methane calibration counts to 95-105% of the daily mean. Some of RTI's data were reviewed, and the variation was less than 2% of the daily mean. The SOP should be revised to reflect this change in the acceptance range.

> ***RTI Response:*** *At the 9/21/2000 meeting, RTI agreed to try the 95-105% range and see if it was feasible in a production-type environment. Trying the new acceptance range was reasonable because both of RTI's analyzers typically have a relative percent standard deviation in the methane calibration counts of less than 2%. With the old-style pinch, or ball-and-socket, clamps (mentioned below), RTI could not switch permanently to the 95-105% acceptance range because of the increase in number of repeat analyses required. The change was not affordable from a labor/cost standpoint. RTI will again try to meet the tighter acceptance range with the new horseshoe-type clamps (mentioned below) now in use.*

5. The current SOP for carbon analysis (section 9.2.2) requires a regression coefficient (r^2) of 0.99 for the weekly calibration, but does not include instructions to force the calibration curve through the origin.
   Recommendation. The SOP needs to include the fact that this linear regression is a force fit through the origin (0,0). RTI is already doing the correct calculations. This needs to be added to the SOP.

> ***RTI Response:*** *RTI agrees and will add the force-fit to its SOP.*

6. A discussion of the method parameter file is not included in the current SOP for carbon analysis.
   Recommendation. Since the analytical results are dependent on the operational conditions used to run the TOT instrument, it is important to include these temperature and times in the SOP.

> *RTI Response: The method parameter file was not included in the current SOP because a standard EPA-approved method parameter file was not available. When a standard method parameter file has been approved by EPA and put in use by RTI, it will be included in the SOP.*

7. The current SOP for carbon analysis does not contain a discussion of when and how to update the calibration factor.
   Recommendation. The calibration factor in the OCECPAR.TXT file must be updated when the initial calibration or daily standards are outside of the 90-110% acceptance range. The procedure should be included in the SOP. The information was provided to RTI during the audit. In Region 1, the calibration factor is updated routinely with each weekly initial calibration, but this practice is not necessary because the calibration factor is relatively constant.

   > ***RTI Response:*** *A discussion of when the calibration factor must be updated and how to update it will be added to the SOP.*

8. RTI is using the pinch clamp that is supplied by Sunset Laboratory to seal the ball and socket joint for the sample helium line.
   Recommendation. This pinch clamp is susceptible to small leaks because the support screw is on one side. This problem is noted in RTI's SOP (section 9.5). Another type that uses two screws for more even support is a horseshoe type (part number CG-151-03) from Chemglass (800-843-1794) and costs $8.90.

   > ***RTI Response:*** *RTI is now using horseshoe-type clamps on both of its instruments, and the number of analyses that must be repeated because of leaks has decreased.*

9. One of the Sunset instruments (the retrofit instrument) has Teflon® lines in the helium supply. This was to be corrected on August 7, 2000. The NO-OX tubing is more opaque than Teflon tubing.
   Recommendation. Teflon® is permeable to oxygen, and these lines need to be changed to copper or NO-OX tubing from Altech. Any oxygen in the helium will enhance an early split phenomenon.

   > ***RTI Response:*** *RTI has had the Teflon® helium supply lines in the retrofit instrument replaced with NO-OX® tubing.*

10. Sample A107403B duplicate in the sample log book for carbon analysis was crossed out, and the correction was not initialed and dated.
    Recommendation. All amendments to an official laboratory record should be initialed (or signed) and dated.

    > ***RTI Response:*** *All amendments to the laboratory record, including analyses planned for a given day but not performed that day, will be initialed and dated in the future.*

11. There is no acceptance range in the SOP for carbon analysis, the QAPP, or the daily log for the temperature that is being recorded for the Kenmore freezer.
Recommendation. The common acceptance range for a freezer is -10 to -20 °C. The SOP should be revised to include an acceptance range for the freezer temperature.

> ***RTI Response:*** *The acceptance range for archival storage of quartz filters in RTI's SHAL is ≤15°C. That acceptance range, which has also been used in the OC-EC Laboratory for many months, will be added to the carbon analysis SOP.*

12. The MDL study for one of the Sunset Instruments did not match the raw data done on 3/23/2000.
Recommendation. Both sets of data were excellent and below the NIOSH 0.15 $\mu g/cm^2$, but they must agree. RTI needs to use the raw data on the csv file or repeat the MDL study.

> ***RTI Response:*** *The MDL study will be repeated on both instruments.*

13. According to the auditor’s records, the transit time for carbon analysis was 6 seconds on December 14, 1999, but the transit time was changed to 10 seconds. This is a large change, and a record of this change could not be found in the maintenance log book. There was some maintenance done on 11/1/2000, but the transit time change was not recorded.
Recommendation. Significant instrument maintenance should be recorded in the log book..

> ***RTI Response:*** *RTI depends upon Sunset Laboratory (the manufacturer and marketer of the carbon analyzers) for essentially all instrument maintenance. More details will be obtained from the Sunset Laboratory technician in the future and will be placed in the instrument maintenance log book.*