

DRAFT
Semi-Annual
Data Summary Report for
the Chemical Speciation
of PM_{2.5} Filter Samples Project

April 1, 2000 through September 31, 2001

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1.0 Introduction

1.1 Program Overview

In 1997, the U.S. Environmental Protection Agency (EPA) promulgated the new National Ambient Air Quality Standards (NAAQS) for particulate matter. The regulations (given in 40 CFR Parts 50, 53, and 58) apply to the mass concentrations ($\mu\text{g}/\text{cubic meter of air}$) of particles with aerodynamic diameters less than 10 micrometers (the PM₁₀ standard) and less than 2.5 micrometers (the PM_{2.5} standard). Establishment of a 1500-site mass measurements network and a 200-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 200 other sites. Chemically speciated data will be used to serve the needs associated with development of emission mitigation approaches to reduce ambient PM_{2.5} 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 PM_{2.5} and its components, and evaluating potential linkages to health effects.

RTI is assisting in the PM_{2.5} 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 PM_{2.5} chemical speciation monitors to enable various sampler intercomparisons. The mini-trends network ran from February 2000 to July 31, 2000. As of September 30, 2001, RTI is providing support for 108 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 data reports for EPA management and the states, and entering data to the Aerometric Information Retrieval System (AIRS) data bank 60 days after initial data reports are first submitted to the DOPO and the states.
4. Establishing and applying a comprehensive quality assurance/quality control (QA/QC) system. RTI's Quality Management Plan, QAPP, and associated Standard Operating Procedures (SOPs) provide the documentation for RTI's quality system.

1.3 Schedule

The initial portion of the STN program was a six-month pilot project at 13 different sites. This "mini-trends" project was conducted from February 2000 to July 2000. This period gave all participants an opportunity to work out technical and logistical problems. Additional sites are now coming on line. As of September 2001, we were providing support to 108 sites which include the 54 STN sites. This QA report covers the collection and analysis of samples from April 1, 2001 through September 30, 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 or Teflon filters 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

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

- Gravimetric Mass – No significant correction actions have been taken.
- Elemental Analysis – No significant correction actions have been taken.

- Ion Analysis – Beginning in September 2001, it was observed that the relative percent difference for replicate analyses were higher than usual for sodium and sulfate. A contamination problem was suspected and subsequently corrected by replacing all tubing in the ion chromatographs and established a more rigorous cleaning procedure for auto sampler vials and injection vials.

During the same time period, it was observed during the nylon filter extraction procedure, that material (apparently nylon) was being removed from some of the filters, leaving bare (transparent) areas on filter substrate. It was concluded after several experiments in the laboratory that the nylon filters in that particular lot were defective and subsequently the manufacturer (Whatman) replaced these filters with a new batch.

- OE/EC Analysis – No significant corrective actions have been taken.
- Sample Handling and Archiving Laboratory (SHAL) – There were many anomalous data points for R&P samplers. The staff were retrained in the processing of the R&P modules. Similarly RTI has identified the major cause of the higher masses for Teflon filters as the white Delrin rings in the Met One samplers. RTI has subsequently replaced all the white Delrin rings with the blue poly rings for the cassettes holding the Teflon filters in the Met One modules.
- Data Processing – No significant correction actions have been taken.

1.6 Delrin Ring Study

In June 2001, the RTI QA Manager for this contract screened the trends for high field blank levels. The screening revealed that the MetOne SASS samplers were associated with most of the high field blanks. RTI staff looked into the sources for high blank levels and finally concluded that the contamination could be coming from the cassette filter holder rings. RTI also learned from the sampler manufacturer that these rings are made of Delrin, a plastic based on polyformaldehyde, which may be out-gassing from the rings. In an effort to find a solution to this significant problem, a series of experiments was performed to determine the extent of transfer of material from the Delrin cassettes to the Teflon filter and at the same time, to devise a method (based on either heating and/or washing the cassette) to minimize such transfer. A report summarizing the experiments performed and the results obtained was presented to EPA (see **Appendix A** of this report).

The heating experiments performed indicated that the Delrin rings sets lose more than 15,000 µg of weight with heating. They also showed that heating filters in new, untreated rings for 20 hours at about 40°C resulted in a mass contamination of the filters of 10 to 25 µg.

This work continued at EPA/Montgomery laboratories and confirmed RTI's preliminary findings. The Delrin rings were subsequently replaced with blue poly rings in all the Teflon filter holders in the MetOne Samplers for this project.

2.0 Laboratory Quality Control Summaries

2.1 Gravimetric Laboratory

2.1.1 Personnel and Facilities

The Earth and Mineral Science Department's responsibility for the Chemical Speciation project since the Gravimetry Laboratory's previous QA report has not changed. Staff changes have occurred since the previous QA report. In April 2001, Stacy Doorn assumed the primary responsibility for review and submittal of gravimetry data to the personnel responsible for Chemical Speciation database management. Emily Holton, who returned to the Gravimetry Laboratory in May 2001, performs data review and submittal when Stacy Doorn is unavailable. Since May 2001, three full-time experienced analysts have performed the bulk of the PM_{2.5} gravimetric analyses. Their experience and dependability allows analyses to be completed successfully in a timely manner.

Table 1 details facility problems and corrective actions taken since the previous QA report. A recently installed alarm system allows RTI HVAC personnel to respond to any malfunctions expediently. Weigh chamber malfunctions since the previous QA report have not resulted in any damage to filters or analytical equipment; however, excessive laboratory holding times can result.

2.1.2 Description of Quality Control Checks Applied

Quality Control checks applied to the gravimetric analysis of Teflon® filters for the PM_{2.5} 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 PM_{2.5} network.

2.1.3 Statistical Summary of Quality Control Results

The types and frequency of QC checks applied to the gravimetric analysis of filters for the PM_{2.5} Chemical Speciation Trends Network have not changed since the previous QA report. QC data for the laboratory are summarized in **Tables 2 and 3**.

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

Duration of Problem	Nature of Problem	Corrective Action
03/16/01-03/17/01	Vibrational "humming" noise originating in air plenum	03/19/01, early a.m. - RTI HVAC personnel opened air plenum access door to check fans; found no problem with fans, but did find loose bolts on access door; tightening bolts eliminated noise. No impact on filters.
05/22/01	High RH; High temperature	RTI Building 11 water pump servicing both Bay 6 weigh chambers malfunctioned overnight; RTI HVAC personnel repaired the pump early a.m. 05/22/01. No filters were weighed on 05/22/01 to allow chamber to stabilize after repairs.
07/14/01-07/25/01	Low temperature	<p>07/23/01 - RTI HVAC personnel determined that actuator on chill water valve had once again malfunctioned (actuator had been replaced on 01/25/01); RTI HVAC personnel determined that a more suitable actuator model was available and ordered it for overnight delivery.</p> <p>07/24/01 - RTI HVAC installed new actuator, but found output signal from chamber control board to be incompatible with new actuator.</p> <p>07/25/01 - RTI HVAC remained in close communication with both chamber installation contractor and manufacturer of actuator; RTI HVAC personnel added signal conditioner to actuator circuit and ordered small enclosure for signal conditioner to protect it from possible leaks.</p> <p>Problems was corrected on 7/25/01. Dates following 7/25/01 refer to measures taken to maintain chamber HVAC system.</p> <p>08/16/01 - RTI HVAC personnel installed enclosure for signal conditioner.</p> <p>08/21/01 - RTI HVAC completed most of wiring changes necessary to accommodate new actuator.</p> <p>08/21/01 - RTI HVAC personnel installed system alarm, tying chamber temperature, humidity, and alarm contacts into RTI HVAC's dial-out system. Anytime chamber temperature or humidity alarm contacts close for more than 15 minutes, a dial-out will be initiated - first to RTI HVAC supervisor's office, then to RTI HVAC control room, then to RTI HVAC on-call cell phone, and finally to RTI HVAC on-call pager. This will continue for up to 12 hours until the alarm is acknowledged. The system also allows the Laboratory Supervisor to check chamber temperature and humidity over the telephone.</p>
08/13/01	RH spikes over the weekend	RTI HVAC personnel confirmed that Building 11 Bay 6 air handler had been shut down over the weekend for repairs.
08/13/01	Laboratory staff reported gasoline-like odor in chamber	Determined that RTI Maintenance personnel had sprayed a hornet's nest near the fresh air intake; odor dissipated within an hour.
09/26/01	High temperature	RTI HVAC personnel confirmed that they had received an alarm from the system and had already responded before laboratory staff noticed temperature increase. Temperature increase was due to failure of the smaller of the two chillers that provide chilled water to Building 11; time delay in larger chiller coming online designed into unit by manufacturer; HVAC contacted manufacturer's service rep - trying to determine whether this can be adjusted .

Table 2. 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 \pm 3 μ g (Verified by North Carolina Department of Agriculture (NCDA) Standards Laboratory)	100-mg Verified Value = 99.957 mg (NCDA 8/01) 200-mg (A) Verified Value = 199.977 mg (NCDA 8/01) 20-mg Verified Value = 20.008 mg (NCDA 3/00) 200-mg (B) Verified Value = 200.004 mg (NCDA 11/99)	99.960 mg \pm .002 for 759 weighings 199.980 mg \pm .005 for 680 weighings 19.991mg \pm .002 for 275 weighings 199.996 mg \pm .001 for 262 weighings	Laboratory mean falls within range. Laboratory mean falls within range. Laboratory mean falls outside of range for both 20-mg and 200-mg (B) standard reference weights. Weights were used while other weights were certified. Replicate weighings of the 20-mg and the 200-mg (B) weights fell within \pm 3 μ g of the mean of the replicate weighings during the period of their use.
Laboratory (Filter) Blanks	Initial weight \pm 15 μ g	238 total replicate weighings of 26 lab blank filters	Mean difference between final and initial weight: 3 μ g \pm 6.4 μ g	5 (2.1%) of the 238 replicate weighings exceeded the 15 μ g criterion, as follows: -0.031 μ g, -0.030 μ g, -0.033 μ g, -0.034 μ g, and -0.032 μ g. Affected filters were flagged in the database spreadsheet.
Lot Blanks (Lot Stability Filters)	24-hour weight change $<$ \pm 5 μ g	Whatman Lot 1045025 - 6 filters weighed (6 randomly selected from 1 randomly selected box) Whatman Lot 1045023 - 9 filters weighed (3 randomly selected filters from 3 randomly selected boxes) Whatman Lot 1169018 - 9 filters weighed (3 randomly selected filters from 3 randomly selected boxes)	24 hours = -3 μ g 48 hours = 0 μ g 72 hours = 3 μ g 96 hours = 0 μ g 24 hours = -1 μ g 48 hours = -2 μ g 72 hours = 2 μ g 96 hours = 0 μ g 24 hours = -1 μ g 48 hours = 0 μ g 72 hours = -1 μ g	Fall well within required range.
Replicates	Initial weight \pm 15 μ g	496 Presampled Replicates (2/23/01 - 8/10/01) 499 Postsampled Replicates (3/29/01 - 10/2/01)	-1 μ g -1 μ g	Max = -13 μ g; within required range Max = -14 μ g; within required range

Table 2 (continued).

QC Check	Requirements	QC Checks Applied to RTI Laboratory	Laboratory Mean	Comments
Calibrations				
• Working Mass Reference Standards	Annually	Last calibrated by NCDA August 6, 2001	N/A	
• Balance	Auto (internal) calibration daily	Daily	N/A	
	External calibration annually or as needed	Last inspected and calibrated by Mettler Toledo on July 18, 2001 using NIST-traceable weights	N/A	
• 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 May 10, 2001 using Class S-1 NIST-traceable weights	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)		James Davies, Louisiana Dept. of Environmental Quality, Louisiana Environmental Laboratory Accreditation Program, May 14, 2001	N/A	Minor deficiencies listed in Table 4

Table 3. Sample Throughput for the Gravimetric Laboratory

Number of Filters	Previous QA Report	This QA Report
Tared	2626 (9/1/01 - 2/23/01)	5502 (2/23/01 - 8/10/01)
Retained by Grav Lab for use as Lab Blanks	27 (1.0%)	26 (0.47%)
Initially Transferred to SHAL to be Loaded into Sampler Modules	2599	5476
Returned to Grav Lab for Retaring - Exceeded 30-day Sampling Window in SHAL	205	0
Reconditioned and Retared	169	0
Tared Filters Used for Background Monitoring of New SHAL Facilities and Bldg 3. Refrigerator	0	6
Tared Filters Used for Met One Cassette Experiment	0	20
Total Transferred to and Retained by SHAL for Sampler Modules (Incl . Retared)	2563	5450
Returned to Grav Lab by SHAL for Final Weighing	2235 (87.2% return rate) 9/18/00 - 3/29/01	5223 (95.8% return rate) 3/29/01 - 10/2/01
Voided	3 (0.1%)	4 (0.08%)
Flagged by Grav Lab for Exceeding 10-day Holding Time in Lab	129 (5.8%)	63 (1.2%)
Filters Reweighed after XRF Analysis	25 (1.1%)	2 (0.04%)

2.1.4 Data Validity Discussion

Filters were assigned the appropriate Chemical Speciation Data Flags due to problems arising in the Gravimetry Laboratory. Problems consisted of excessive laboratory holding times, laboratory blank replicate weighings exceeding the 15- μg criterion, and standard reference weights weighing outside the $\pm 3 \mu\text{g}$ range of the verified value. Each of the problems are discussed below.

Laboratory holding times exceeding 10 days: The analyses of 63 (1.2%) of the filters were flagged due to laboratory holding times exceeding the 10-day limit. The analyses of these filters occurred after a period of weigh chamber repair and subsequent downtime which resulted in excessive holding times.

Laboratory blank replicate weighings: One of the 26 laboratory blanks exhibited replicate weight differences exceeding the 15- μg criterion. The anomalous differences between the final and initial weights of the laboratory blank may have resulted from analytical error during the initial weighing of the laboratory blank because the weight differences have a large negative value, as seen in **Table 2**. The laboratory blank from a previous batch of filters was then erroneously substituted for the original laboratory blank. A corrective action memorandum was then issued which describes the problem and the corrective actions taken. A copy of this memorandum is included in **Appendix B**. The original laboratory blank was then used for the remaining analyses of this batch of filters, and the analyses were flagged to indicate that the laboratory blank duplicate weight differences were outside the accepted limit.

Standard reference weights: Due to a scheduling error by the NCDA Standards Laboratory, the March 2001, appointment for recertification of the 100-mg and 200-mg (A) standard reference weights was missed. The weights were then recertified in August 2001, and the schedule for recertification is now on an August/November basis. While the 100-mg and 200-mg (A) weights were at the standards laboratory, a set of 20-mg and 200-mg (B) standard reference weights were used in the Gravimetry Laboratory for approximately one month. The mean weights of each of the standard reference weights fell outside of the $\pm 3\mu\text{g}$ range of the verified weights which had been determined by the NCDA Standards Laboratory one to two years ago. However, the 20-mg and 200-mg (B) standard reference weights exhibited replicate weights which were within $\pm 3\mu\text{g}$ of their mean weights for that one-month period of use.

2.1.4.1 Invalidated Data - Four (0.07%) of the filters analyzed were invalidated by the Gravimetry Laboratory due to analyst error which resulted in anomalous net mass loadings. These filters were flagged appropriately.

2.1.5 Audits, Performance Evaluations, and Accreditations

Since March 2001, the Gravimetry Laboratory has had one formal audit and has maintained its accreditation by the Louisiana Department of Environmental Quality's Louisiana Environmental Laboratory Accreditation Program (LELAP). The LELAP accreditation requires the laboratory's quality system to fulfill the requirements of both Louisiana administrative code and the National Environmental Laboratory Accreditation Conference (NELAC) standards. Audit findings are summarized in **Table 4**.

Table 4. LELAP/NELAC Audit

Responsible Agency	Date/Activity	Recommendation	RTI Response
Louisiana Department of Environmental Quality	May 14, 2001 - Quality Systems assessment for Louisiana Environmental Laboratory Accreditation Program (LELAP)	<ul style="list-style-type: none"> • Have a signed and dated title page to show evidence of annual review. • Have a Chain of Custody Procedure • Reference procedures for the control and maintenance of documents • Reference the laboratory's procedures for achieving traceability of measurements to NIST reference materials or other traceable commercial vendors • Reference to major equipment in the laboratory • Reference to procedures for calibration, verification, and maintenance of equipment • Reference to verification practices including inter-laboratory comparisons, proficiency testing programs, use of reference materials, and internal quality control schemes • Reference to policy and procedures for the resolution of complaints from clients or other parties; maintain records of the complaint and subsequent action • Reference to procedures for protecting confidentiality and proprietary rights • Identification of the laboratory's approved signatories • Reference procedures for reporting analytical results • Give SOPs forceful language 	<p>RTI has completed a corrective action plan (CAP) with proposed corrective actions for each deficiency noted.</p> <p>RTI has submitted a draft revised Quality Assurance Project Plan (QAPP) addressing each finding for LDEQ/LELAP review and approval.</p>

2.2 Ion Analysis Laboratory

2.2.1 Facilities

Ion chromatographic analyses are performed by personnel from RTI's Environmental Industrial Chemistry Department (EICD). Two ion chromatographic systems were used for performance of the measurements. These are described in **Table 5**. The use of these two systems was determined by the workload.

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

System No.	Dionex IC Model	Ions Measured
1	Model 500 (S3A)	SO ₄ , NO ₃
2	DX-600 (D6C)	Na, NH ₄ , K

2.2.2 Description of QC Checks Applied

QC checks for ion analyses are summarized in **Table 6**. 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⁺, NH₄⁺, and K⁺ for cation analyses; NO₃⁻ and SO₄²⁻ 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 6. 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 7 shows recoveries for NO₃⁻ with low, medium, and high concentration QC samples (prepared by RTI) and with low and medium-high QA samples (commercially prepared and NIST-traceable) for the instrument used for anion analysis. Average recoveries for the three QC samples ranged from 98.0% to 101.5% over the six month period; average recoveries for the two QA samples ranged from 98.2% to 101.4%.

Table 8 shows recoveries for SO₄²⁻ with low, medium, and high QC samples and with low and medium-high QA samples for the instrument used for anion analysis. Average recoveries for the three QC samples ranged from 98.7% to 102.0% over the six month period; average recoveries for the two QA samples ranged from 97.8% to 101.8%.

Table 9 shows relative percent different (RPD) values for replicate measurements of nitrate and sulfate at concentrations <0.050 ppm (approximately the limit of quantitation) and at concentrations >0.050 ppm. For measured concentrations <0.050 ppm, the average RPD value for the instrument used over the six month period ranged from -2.4% to 1.2 % for nitrate and from -1.7% to 4.3% for sulfate. For measured concentrations >0.050 ppm, the average RPD value ranged from 0.0% to 0.13 % for nitrate and from -2.0% to 0.19% for sulfate. Higher than normal RPDs for sulfate were observed beginning in mid-September, concurrent with the observation of higher RPDs for sodium ion (Section 2.2.3.2). At this time, it was also observed that the nylon filters eroded during the filter washing and sample extraction procedures. The laboratory experiments performed in an attempt to identify and eliminate these problems are discussed in Section 2.2.5.

Table 10 shows percent recovery for nitrate and sulfate spikes by filter type for the six month period. There was no significant difference in the spike recoveries of nitrate or sulfate for the three different filter types. The average recoveries of nitrate for all types of filters ranged from 99.2% to 100.6%, while the average recoveries for sulfate ranged from 99.8% to 100.9%.

Table 11 presents filter blank (N BLANK) and reagent blank values for nitrate and sulfate over the six month period. The highest average value for filter blanks was 0.0139 ppm (25 mL extract) for nitrate and 0.0125 ppm for sulfate; the highest average reagent blank deionized water was 0.0099 ppm for nitrate and 0.0156 for sulfate, and the highest average reagent blank eluent was 0.0071 ppm for nitrate and 0.0365 ppm for sulfate.

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

Analyte:		NO3		Units:		Percent Recovery	
Type:		QA-LOW		Standard Conc:		0.6 ppm	
Inst:		S3A					
Date:	Apr-01	May-01	Jun-01	Jul-01	Aug-01	Sep-01	Total
Average	98.38%	98.76%	98.70%	98.36%	98.23%	98.59%	98.51%
Std Dev	0.85%	0.58%	0.51%	0.67%	0.90%	0.56%	0.70%
N	16	18	20	17	18	17	106
Min	97.15%	97.27%	97.95%	96.96%	96.87%	97.53%	96.87%
Max	100.54%	99.76%	99.83%	99.16%	100.22%	99.38%	100.54%

Analyte:		NO3		Units:		Percent Recovery	
Type:		QA-MED-HI		Standard Conc:		3 ppm	
Inst:		S3A					
Date:	Apr-01	May-01	Jun-01	Jul-01	Aug-01	Sep-01	Total
Average	101.41%	101.14%	101.33%	101.11%	101.04%	100.50%	101.11%
Std Dev	0.51%	0.83%	0.91%	0.33%	0.95%	1.01%	0.81%
N	11	13	14	13	15	9	75
Min	100.55%	100.06%	100.14%	100.68%	99.92%	99.37%	99.37%
Max	102.18%	103.31%	103.01%	101.56%	102.88%	102.63%	103.31%

Analyte:		NO3		Units:		Percent Recovery	
Type:		QC-LOW		Standard Conc:		0.6 ppm	
Inst:		S3A					
Date:	Apr-01	May-01	Jun-01	Jul-01	Aug-01	Sep-01	Total
Average	98.00%	98.58%	98.66%	98.51%	98.37%	99.61%	98.60%
Std Dev	1.11%	0.56%	0.87%	1.03%	0.80%	1.32%	1.05%
N	23	25	28	25	27	21	149
Min	96.24%	97.14%	97.56%	96.87%	96.64%	97.50%	96.24%
Max	99.42%	99.63%	101.62%	101.71%	100.41%	102.99%	102.99%

Analyte:		NO3		Units:		Percent Recovery	
Type:		QC-MED		Standard Conc:		1.5 ppm	
Inst:		S3A					
Date:	Apr-01	May-01	Jun-01	Jul-01	Aug-01	Sep-01	Total
Average	98.27%	98.97%	98.80%	98.54%	98.49%	99.40%	98.74%
Std Dev	0.84%	0.55%	0.99%	0.63%	1.01%	0.69%	0.86%
N	20	24	25	21	21	18	129
Min	97.05%	97.89%	96.86%	97.18%	96.98%	98.23%	96.86%
Max	100.74%	100.26%	100.48%	99.54%	100.63%	100.46%	100.74%

Analyte:		NO3		Units:		Percent Recovery	
Type:		QC-HIGH		Standard Conc:		6 ppm	
Inst:		S3A					
Date:	Apr-01	May-01	Jun-01	Jul-01	Aug-01	Sep-01	Total
Average	101.31%	101.43%	101.35%	101.23%	101.27%	101.48%	101.34%
Std Dev	0.21%	0.24%	0.44%	0.41%	0.87%	1.05%	0.62%
N	13	13	15	16	20	13	90
Min	100.90%	101.04%	100.67%	100.81%	99.97%	100.22%	99.97%
Max	101.72%	101.72%	102.08%	102.52%	103.02%	103.02%	103.02%

Table 8. Average Percent Recovery for Sulfate QA and QC Samples

Analyte:		SO4		Units:		Percent Recovery	
Type:		QA-LOW		Standard Conc:		1.2 ppm	
Inst:		S3A					
Date:	Apr-01	May-01	Jun-01	Jul-01	Aug-01	Sep-01	Total
Average	98.54%	98.89%	98.70%	98.14%	97.83%	98.41%	98.42%
Std Dev	0.62%	0.76%	0.64%	0.72%	0.88%	1.34%	0.91%
N	16	18	20	17	18	17	106
Min	97.24%	97.60%	97.55%	96.88%	96.52%	95.54%	95.54%
Max	100.03%	100.90%	100.02%	99.38%	99.64%	100.23%	100.90%

Analyte:		SO4		Units:		Percent Recovery	
Type:		QA-MED-HI		Standard Conc:		6 ppm	
Inst:		S3A					
Date:	Apr-01	May-01	Jun-01	Jul-01	Aug-01	Sep-01	Total
Average	101.73%	101.64%	101.79%	101.26%	101.23%	101.19%	101.48%
Std Dev	0.49%	0.91%	0.80%	0.43%	0.68%	0.87%	0.74%
N	11	13	14	13	15	9	75
Min	101.04%	100.48%	100.72%	100.67%	100.03%	100.13%	100.03%
Max	102.36%	104.09%	103.65%	101.97%	102.46%	102.79%	104.09%

Analyte:		SO4		Units:		Percent Recovery	
Type:		QC-LOW		Standard Conc:		1.2 ppm	
Inst:		S3A					
Date:	Apr-01	May-01	Jun-01	Jul-01	Aug-01	Sep-01	Total
Average	98.71%	99.17%	99.04%	99.10%	99.10%	99.48%	99.09%
Std Dev	0.88%	0.63%	0.70%	0.82%	0.85%	1.27%	0.88%
N	23	25	28	25	27	21	149
Min	96.88%	97.54%	97.83%	97.53%	97.45%	96.77%	96.77%
Max	99.86%	100.28%	100.64%	101.10%	101.06%	101.92%	101.92%

Analyte:		SO4		Units:		Percent Recovery	
Type:		QC-MED		Standard Conc:		3 ppm	
Inst:		S3A					
Date:	Apr-01	May-01	Jun-01	Jul-01	Aug-01	Sep-01	Total
Average	99.57%	100.34%	100.10%	99.95%	100.29%	100.20%	100.08%
Std Dev	0.56%	0.55%	0.88%	0.57%	1.15%	0.75%	0.80%
N	20	24	25	21	21	18	129
Min	98.47%	99.25%	98.11%	98.78%	98.59%	99.02%	98.11%
Max	100.52%	101.36%	101.52%	101.17%	103.23%	101.43%	103.23%

Analyte:		SO4		Units:		Percent Recovery	
Type:		QC-HIGH		Standard Conc:		12 ppm	
Inst:		S3A					
Date:	Apr-01	May-01	Jun-01	Jul-01	Aug-01	Sep-01	Total
Average	101.73%	101.88%	101.74%	101.52%	101.96%	101.66%	101.76%
Std Dev	0.24%	0.28%	0.93%	1.13%	0.73%	0.95%	0.79%
N	13	13	15	16	20	13	90
Min	101.29%	101.33%	98.74%	98.85%	100.37%	100.36%	98.74%
Max	102.12%	102.32%	102.74%	103.26%	103.09%	103.14%	103.26%

Table 9. Relative Percent Difference for Replicate Nitrate and Sulfate Measurements at Concentrations >0.050 ppm and < 0.050 ppm.

Analyte: RPD NO3		Units: Relative Percent Difference					
Type: NO3, Conc < 0.05 ppm							
Inst: S3A							
Date:	Apr-01	May-01	Jun-01	Jul-01	Aug-01	Sep-01	Total
Average	-2.35%	1.22%	-1.05%	0.83%	-0.06%	-0.74%	-0.08%
Std Dev	3.05%	3.88%	3.75%	3.93%	4.07%	2.81%	3.58%
N	4	9	6	9	4	8	40
Most Neg.	-6.38%	-3.83%	-5.46%	-7.99%	-5.88%	-4.29%	-7.99%
Most Pos.	0.81%	8.81%	5.82%	4.82%	3.56%	4.65%	8.81%

Analyte: RPD SO4		Units: Relative Percent Difference					
Type: SO4, Conc < 0.05 ppm							
Inst: S3A							
Date:	Apr-01	May-01	Jun-01	Jul-01	Aug-01	Sep-01	Total
Average	1.35%	2.51%	3.56%	4.34%	2.33%	-1.71%	1.88%
Std Dev	6.34%	5.46%	11.71%	6.25%	3.25%	17.10%	10.14%
N	9	10	7	14	6	14	60
Most Neg.	-10.48%	-4.32%	-4.63%	-3.80%	-2.18%	-49.11%	-49.11%
Most Pos.	9.41%	15.30%	29.20%	18.75%	6.65%	28.82%	29.20%

Analyte: RPD NO3		Units: Relative Percent Difference					
Type: NO3, Conc>0.05 ppm							
Inst: S3A							
Date:	Apr-01	May-01	Jun-01	Jul-01	Aug-01	Sep-01	Total
Average	-0.13%	0.13%	0.00%	-0.11%	0.11%	-0.15%	-0.01%
Std Dev	0.71%	0.86%	0.65%	0.95%	0.45%	1.34%	0.82%
N	32	29	37	29	42	25	194
Most Neg.	-1.49%	-0.88%	-1.46%	-3.96%	-0.80%	-3.27%	-3.96%
Most Pos.	1.62%	3.83%	1.90%	1.39%	1.30%	3.50%	3.83%

Analyte: RPD SO4		Units: Relative Percent Difference					
Type: SO4, Conc>0.05 ppm							
Inst: S3A							
Date:	Apr-01	May-01	Jun-01	Jul-01	Aug-01	Sep-01	Total
Average	-0.03%	-0.03%	0.19%	0.16%	-0.03%	-1.98%	-0.20%
Std Dev	0.50%	0.38%	0.64%	0.32%	0.36%	10.03%	3.54%
N	26	29	37	25	40	22	179
Most Neg.	-1.03%	-0.74%	-0.65%	-0.38%	-0.80%	-46.78%	-46.78%
Most Pos.	1.35%	0.84%	2.43%	0.79%	0.97%	1.50%	2.43%

Table 10. Average Percent Recovery for Nitrate and Sulfate Spikes

Analyte:		NO3 Spk Recov		Units:		Percent Spike Recovery	
Type:		Nylon Filter		Inst:		S3A	
Date:	Apr-01	May-01	Jun-01	Jul-01	Aug-01	Sep-01	Total
Average	100.20%	100.05%	99.27%	99.85%	99.17%	100.36%	99.76%
Std Dev	1.13%	1.12%	0.86%	0.74%	0.60%	2.14%	1.24%
N	25	30	28	31	40	27	181
Min	98.49%	98.01%	97.64%	97.87%	97.95%	98.31%	97.64%
Max	102.13%	102.83%	100.64%	101.29%	100.63%	109.00%	109.00%

Analyte:		NO3 Spk Recov		Units:		Percent Spike Recovery	
Type:		Quartz Filter		Inst:		S3A	
Date:	Apr-01	May-01	Jun-01	Jul-01	Aug-01	Sep-01	Total
Average	101.29%	100.53%	100.91%	----	----	----	100.89%
Std Dev	2.13%	1.29%	1.01%	----	----	----	1.38%
N	4	5	6	----	----	----	15
Min	99.61%	98.86%	99.49%	----	----	----	98.86%
Max	104.39%	102.27%	102.30%	----	----	----	104.39%

Analyte:		NO3 Spk Recov		Units:		Percent Spike Recovery	
Type:		Teflon Filter		Inst:		S3A	
Date:	Apr-01	May-01	Jun-01	Jul-01	Aug-01	Sep-01	Total
Average	99.29%	101.51%	101.49%	100.70%		102.87%	101.07%
Std Dev	0.94%	1.11%	0.36%	0.62%		2.04%	1.40%
N	3	2	4	7		3	19
Min	98.35%	100.73%	101.09%	99.87%		100.54%	98.35%
Max	100.23%	102.30%	101.90%	101.42%		104.36%	104.36%

Analyte:		NO3 Spk Recov		Units:		Percent Spike Recovery	
Type:		All Filters		Inst:		S3A	
Date:	Apr-01	May-01	Jun-01	Jul-01	Aug-01	Sep-01	Total
Average	100.25%	100.19%	99.76%	100.01%	99.17%	100.61%	99.96%
Std Dev	1.31%	1.16%	1.19%	0.79%	0.60%	2.23%	1.33%
N	32	37	38	38	40	30	215
Min	98.35%	98.01%	97.64%	97.87%	97.95%	98.31%	97.64%
Max	104.39%	102.83%	102.30%	101.42%	100.63%	109.00%	109.00%

Analyte:		SO4 Spk Recov		Units:		Percent Spike Recovery	
Type:		Nylon Filter		Inst:		S3A	
Date:	Apr-01	May-01	Jun-01	Jul-01	Aug-01	Sep-01	Total
Average	100.47%	100.34%	99.67%	100.40%	100.07%	100.92%	100.29%
Std Dev	0.99%	1.03%	0.86%	0.89%	0.85%	1.88%	1.16%
N	25	30	28	31	40	27	181
Min	97.78%	97.54%	97.66%	98.31%	98.19%	98.86%	97.54%
Max	101.99%	102.52%	100.82%	102.16%	101.79%	108.40%	108.40%

Table 10 (continued).

Analyte: SO4 Spk Recov		Units: Percent Spike Recovery					
Type: Quartz Filter							
Inst: S3A							
Date:	Apr-01	May-01	Jun-01	Jul-01	Aug-01	Sep-01	Total
Average	100.47%	100.25%	100.71%	----	----	----	100.50%
Std Dev	0.71%	1.38%	1.11%	----	----	----	1.07%
N	4	5	6	----	----	----	15
Min	99.79%	97.98%	99.53%	----	----	----	97.98%
Max	101.41%	101.71%	102.14%	----	----	----	102.14%

Analyte: SO4 Spk Recov		Units: Percent Spike Recovery					
Type: Teflon Filter							
Inst: S3A							
Date:	Apr-01	May-01	Jun-01	Jul-01	Aug-01	Sep-01	Total
Average	100.50%	101.23%	99.65%	100.12%	----	101.16%	100.36%
Std Dev	0.25%	0.57%	1.07%	0.41%	----	1.27%	0.88%
N	3	2	4	7	----	3	19
Min	100.31%	100.83%	98.42%	99.69%	----	99.81%	98.42%
Max	100.78%	101.64%	100.79%	100.91%	----	102.33%	102.33%

Analyte: SO4 Spk Recov		Units: Percent Spike Recovery					
Type: All Filters							
Inst: S3A							
Date:	Apr-01	May-01	Jun-01	Jul-01	Aug-01	Sep-01	Total
Average	100.48%	100.38%	99.83%	100.35%	100.07%	100.94%	100.31%
Std Dev	0.90%	1.06%	0.98%	0.83%	0.85%	1.81%	1.13%
N	32	37	38	38	40	30	215
Min	97.78%	97.54%	97.66%	98.31%	98.19%	98.86%	97.54%
Max	101.99%	102.52%	102.14%	102.16%	101.79%	108.40%	108.40%

Table 11. Filter and Reagent Blank Values for Nitrate and Sulfate

Analyte: Nitrate Units: ug/ml							
Type: N BLANK							
Inst: S3A							
Date:	Apr-01	May-01	Jun-01	Jul-01	Aug-01	Sep-01	Total
Average	0.0139	0.0019	0.0000	0.0018	0.0024	----	0.0045
Std Dev	0.0157	0.0045	0.0000	0.0052	0.0057	----	0.0099
N	11	6	9	8	12	----	46
Min	0.0000	0.0000	0.0000	0.0000	0.0000	----	0.0000
Max	0.0489	0.0111	0.0000	0.0148	0.0147	----	0.0489

Analyte: Nitrate Units: ug/ml							
Type: REAGENT BLANK DI H2O							
Inst: S3A							
Date:	Apr-01	May-01	Jun-01	Jul-01	Aug-01	Sep-01	Total
Average	0.0099	0.0054	0.0064	0.0000	0.0000	0.0000	0.0040
Std Dev	0.0174	0.0094	0.0113	0.0000	0.0000	0.0000	0.0106
N	27	23	24	22	20	19	135
Min	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
Max	0.0587	0.0247	0.0305	0.0000	0.0000	0.0000	0.0587

Analyte: Nitrate Units: ug/ml							
Type: REAGENT BLANK ELUENT							
Inst: S3A							
Date:	Apr-01	May-01	Jun-01	Jul-01	Aug-01	Sep-01	Total
Average	0.0012	0.0071	0.0013	0.0009	0.0013	0.0000	0.0018
Std Dev	0.0048	0.0095	0.0052	0.0035	0.0054	0.0000	0.0056
N	17	13	15	16	17	15	93
Min	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
Max	0.0197	0.0210	0.0200	0.0139	0.0222	0.0000	0.0222

Analyte: Sulfate Units: ug/ml							
Type: N BLANK							
Inst: S3A							
Date:	Apr-01	May-01	Jun-01	Jul-01	Aug-01	Sep-01	Total
Average	0.0125	0.0000	0.0041	0.0094	0.0080	----	0.0075
Std Dev	0.0225	0.0000	0.0081	0.0145	0.0112	----	0.0143
N	11	6	9	8	12	----	46
Min	0.0000	0.0000	0.0000	0.0000	0.0000	----	0.0000
Max	0.0559	0.0000	0.0196	0.0378	0.0323	----	0.0559

Table 11 (continued)

Analyte: Sulfate Units: ug/ml							
Type: REAGENT BLANK DI H2O							
Inst: S3A							
Date:	Apr-01	May-01	Jun-01	Jul-01	Aug-01	Sep-01	Total
Average	0.0123	0.0156	0.0049	0.0060	0.0105	0.0086	0.0097
Std Dev	0.0236	0.0196	0.0115	0.0138	0.0164	0.0120	0.0172
N	27	23	24	22	20	19	135
Min	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
Max	0.0930	0.0589	0.0495	0.0429	0.0626	0.0375	0.0930

Analyte: Sulfate Units: ug/ml							
Type: REAGENT BLANK ELUENT							
Inst: S3A							
Date:	Apr-01	May-01	Jun-01	Jul-01	Aug-01	Sep-01	Total
Average	0.0116	0.0365	0.0075	0.0048	0.0090	0.0046	0.0116
Std Dev	0.0198	0.0397	0.0098	0.0088	0.0165	0.0112	0.0218
N	17	13	15	16	17	15	93
Min	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
Max	0.0620	0.1275	0.0253	0.0248	0.0639	0.0402	0.1275

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 12 presents the average percent recovery value for sodium for both QA and QC samples for the instrument used for these measurements. The average recovery for the QA samples over the six month period ranged from 100.2% to 103.1%. The average recovery for the QC samples ranged from 100.0% to 101.6%.

Table 13 presents the average percent recovery value for ammonium for both QA and QC samples for the instrument used for these measurements. The average recovery for the QA samples over the six month period ranged from 99.6% to 105.5%. The average recovery for the QC samples ranged from 98.9% to 101.1%.

Table 14 presents the average percent recovery value for potassium for both QA and QC samples for the instrument used for these measurements. The average recovery for the QA samples over the six month period ranged from 98.5% to 100.4%. The average recovery for the QC samples ranged from 99.8% to 101.4%.

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

Analyte:		Na		Units:		Percent Recovery	
Type:		0.4 PPM QA		Inst:		D6C	
Date:	Apr-01	May-01	Jun-01	Jul-01	Aug-01	Sep-01	Total
Average	103.06%	101.91%	101.99%	101.67%	101.62%	103.11%	102.17%
Std Dev	1.41%	1.70%	1.71%	0.67%	1.13%	3.62%	1.87%
N	22	25	27	22	23	16	135
Min	100.85%	98.78%	99.41%	99.88%	99.21%	98.78%	98.78%
Max	106.94%	106.22%	106.80%	102.52%	103.47%	112.62%	112.62%

Analyte:		Na		Units:		Percent Recovery	
Type:		4.0 PPM QA		Inst:		D6C	
Date:	Apr-01	May-01	Jun-01	Jul-01	Aug-01	Sep-01	Total
Average	100.91%	100.18%	100.34%	100.90%	100.77%	100.78%	100.64%
Std Dev	0.84%	0.94%	1.95%	0.75%	0.82%	1.72%	1.27%
N	11	14	17	16	18	13	89
Min	100.05%	98.81%	94.85%	99.93%	99.33%	96.15%	94.85%
Max	102.82%	101.86%	103.41%	103.03%	102.48%	103.08%	103.41%

Analyte:		Na		Units:		Percent Recovery	
Type:		2.0 PPM QC		Inst:		D6C	
Date:	Apr-01	May-01	Jun-01	Jul-01	Aug-01	Sep-01	Total
Average	100.72%	100.22%	101.55%	100.25%	100.49%	100.95%	100.70%
Std Dev	0.92%	1.16%	2.08%	1.56%	1.08%	2.05%	1.58%
N	22	26	27	23	22	17	137
Min	99.76%	98.44%	95.63%	98.63%	97.84%	97.17%	95.63%
Max	103.52%	103.20%	107.57%	106.66%	103.30%	104.44%	107.57%

Analyte:		Na		Units:		Percent Recovery	
Type:		5.0 PPM QC		Inst:		D6C	
Date:	Apr-01	May-01	Jun-01	Jul-01	Aug-01	Sep-01	Total
Average	100.31%	100.43%	100.68%	100.00%	100.29%	100.11%	100.31%
Std Dev	0.48%	0.99%	1.57%	0.71%	0.48%	1.61%	1.06%
N	14	13	19	19	19	13	97
Min	99.62%	98.89%	95.86%	98.66%	99.35%	96.12%	95.86%
Max	101.07%	101.77%	103.38%	101.38%	101.13%	102.24%	103.38%

Table 13. Average Percent Recovery for Ammonium QA and QC Samples

Analyte:		NH4		Units:		Percent Recovery	
Type:		0.4 PPM QA		Inst:		D6C	
Date:	Apr-01	May-01	Jun-01	Jul-01	Aug-01	Sep-01	Total
Average	99.97%	98.18%	101.47%	102.79%	103.23%	105.54%	101.61%
Std Dev	2.21%	2.61%	2.84%	1.31%	1.12%	2.04%	3.11%
N	22	25	27	22	23	16	135
Min	95.93%	92.58%	93.90%	100.26%	101.44%	102.91%	92.58%
Max	104.52%	102.59%	104.87%	105.57%	104.88%	109.94%	109.94%

Analyte:		NH4		Units:		Percent Recovery	
Type:		4.0 PPM QA		Inst:		D6C	
Date:	Apr-01	May-01	Jun-01	Jul-01	Aug-01	Sep-01	Total
Average	100.13%	100.11%	100.03%	99.76%	99.64%	99.67%	99.87%
Std Dev	2.29%	1.74%	1.30%	1.18%	1.26%	2.06%	1.59%
N	11	14	17	16	18	13	89
Min	97.14%	96.77%	98.20%	98.17%	97.82%	95.63%	95.63%
Max	106.33%	102.49%	102.90%	102.93%	103.23%	103.69%	106.33%

Analyte:		NH4		Units:		Percent Recovery	
Type:		2.0 PPM QC		Inst:		D6C	
Date:	Apr-01	May-01	Jun-01	Jul-01	Aug-01	Sep-01	Total
Average	99.47%	98.93%	101.04%	100.15%	100.50%	101.06%	100.16%
Std Dev	1.85%	2.08%	2.13%	1.48%	0.83%	1.70%	1.90%
N	22	26	27	23	22	17	137
Min	96.43%	95.52%	95.20%	98.13%	98.96%	97.97%	95.20%
Max	105.51%	103.34%	107.50%	105.40%	102.36%	104.22%	107.50%

Analyte:		NH4		Units:		Percent Recovery	
Type:		5.0 PPM QC		Inst:		D6C	
Date:	Apr-01	May-01	Jun-01	Jul-01	Aug-01	Sep-01	Total
Average	100.71%	101.08%	100.52%	99.89%	100.30%	100.27%	100.42%
Std Dev	1.43%	1.30%	1.30%	1.09%	0.69%	1.72%	1.27%
N	14	13	19	19	19	13	97
Min	98.77%	98.82%	97.67%	98.26%	99.11%	97.24%	97.24%
Max	104.79%	103.26%	102.38%	101.84%	101.32%	102.25%	104.79%

Table 14. Average Percent Recoveries for Potassium QA and QC Samples

Analyte:		K						Units:	Percent Recovery
Type:		0.4 PPM QA							
Inst:		D6C							
Date:	Apr-01	May-01	Jun-01	Jul-01	Aug-01	Sep-01	Total		
Average	100.28%	99.72%	99.56%	99.58%	99.60%	100.42%	99.82%		
Std Dev	2.21%	1.77%	1.46%	0.60%	1.11%	2.52%	1.68%		
N	22	25	27	22	23	16	135		
Min	94.46%	95.93%	96.33%	98.14%	97.71%	98.26%	94.46%		
Max	105.13%	103.56%	102.29%	100.84%	101.82%	108.15%	108.15%		

Analyte:		K						Units:	Percent Recovery
Type:		4.0 PPM QA							
Inst:		D6C							
Date:	Apr-01	May-01	Jun-01	Jul-01	Aug-01	Sep-01	Total		
Average	99.23%	98.54%	99.55%	99.72%	99.60%	99.76%	99.42%		
Std Dev	1.19%	0.87%	0.94%	0.79%	0.84%	1.48%	1.07%		
N	11	14	17	16	18	13	89		
Min	96.83%	96.81%	98.33%	98.53%	98.44%	96.54%	96.54%		
Max	101.93%	100.03%	101.82%	101.46%	101.13%	102.10%	102.10%		

Analyte:		K						Units:	Percent Recovery
Type:		2.0 PPM QC							
Inst:		D6C							
Date:	Apr-01	May-01	Jun-01	Jul-01	Aug-01	Sep-01	Total		
Average	99.84%	99.83%	101.43%	100.66%	100.83%	101.08%	100.60%		
Std Dev	1.17%	1.47%	2.03%	1.50%	0.60%	1.51%	1.57%		
N	22	26	27	23	22	17	137		
Min	97.72%	98.03%	98.49%	99.07%	99.75%	98.52%	97.72%		
Max	102.71%	102.47%	107.66%	106.81%	102.26%	104.34%	107.66%		

Analyte:		K						Units:	Percent Recovery
Type:		5.0 PPM QC							
Inst:		D6C							
Date:	Apr-01	May-01	Jun-01	Jul-01	Aug-01	Sep-01	Total		
Average	99.91%	100.46%	100.39%	100.34%	100.65%	100.55%	100.39%		
Std Dev	0.97%	0.81%	1.12%	0.72%	0.90%	1.38%	0.99%		
N	14	13	19	19	19	13	97		
Min	98.25%	99.27%	98.29%	99.53%	98.39%	97.50%	97.50%		
Max	101.62%	102.32%	103.34%	101.76%	102.03%	102.64%	103.34%		

Table 15 shows relative percent different (RPD) values for replicate measurements of sodium, ammonium, and potassium at concentrations <0.050 ppm (approximately the limit of quantitation) and at concentrations >0.050 ppm. For measured concentrations <0.050 ppm, the average RPD value for the instrument used over the six month period ranged from -12.4% to 3.3% for sodium, from -11.1% to 7.2% for ammonium, and from -2.3% to 1.9% for potassium. For measured concentrations >0.050 ppm, the average RPD value ranged from -3.3% to -0.65% for sodium, from -0.31% to 1.74% for ammonium, and from 0.04% to 5.1% for potassium. Higher than usual RPDs for sodium occurred in September 2001, concurrent with the observation of higher RPDs for sulfate ion and a nylon filter erosion problem. Experiments were performed in the laboratory in an attempt to identify and eliminate the source of the problem. These experiments are discussed in Section 2.2.5.

Table 16 shows average percent recovery for spikes of sodium, ammonium, and potassium by filter type over the six month period. There was no significant difference in the spike recoveries of sodium, ammonium, or potassium for the three different filter types. The average recovery values for all filter types ranged from 99.4% to 100.4% for sodium, 98.6% to 100.1% for ammonium, and 97.0% to 99.5% for potassium.

Table 17 presents filter (N BLANK) and reagent blank values for sodium, ammonium, and potassium for the instrument used for these measurements. The highest average sodium values over the six month period were 0.0151 ppm for the nylon filter blanks (25 mL extract) and 0.0070 ppm for reagent blank deionized water. The highest average ammonium values were 0.0060 ppm (25 mL extract) for the nylon filter blanks and 0.0096 for reagent blank deionized water. The highest average potassium values were 0.0018 ppm for nylon filter blanks (25 mL extract) and 0.0017 ppm for reagent blank deionized water.

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 or more filters were found in one petri dish. The filters were extracted and analyzed as one, and this was noted on the data report for that batch of samples. Also, as a result of the filter erosion occurring when field samples were extracted, it was necessary to filter each affected extract prior to injection into the ion chromatograph. All analysis results for extracts that required filtration are flagged in the database.

Table 15. Relative Percent Difference for Replicate Sodium, Ammonium, and Potassium Measurements at Concentrations >0.050 ppm and <0.050 ppm

Analyte:		RPD Na		Units:		Relative Percent Difference	
Type:		Na < 0.05 ppm		Inst:		D6C	
Date:	Apr-01	May-01	Jun-01	Jul-01	Aug-01	Sep-01	Total
Average	-12.39%	-1.43%	-9.32%	0.32%	3.26%	-9.31%	-3.73%
Std Dev	41.97%	13.75%	24.35%	17.15%	12.67%	41.31%	25.56%
N	15	15	18	22	24	11	105
Most Neg.	-148.52%	-28.04%	-103.51%	-52.54%	-19.96%	-106.88%	-148.52%
Most Pos.	32.85%	21.93%	5.57%	26.58%	41.52%	33.72%	41.52%

Analyte:		RPD Na		Units:		Relative Percent Difference	
Type:		Na > 0.05 ppm		Inst:		D6C	
Date:	Apr-01	May-01	Jun-01	Jul-01	Aug-01	Sep-01	Total
Average	-1.65%	-1.65%	-0.65%	-0.95%	-3.33%	-2.12%	-1.63%
Std Dev	3.34%	2.08%	2.31%	5.80%	12.08%	20.00%	9.14%
N	17	21	24	17	16	16	111
Most Neg.	-11.78%	-5.26%	-6.80%	-21.55%	-35.52%	-32.51%	-35.52%
Most Pos.	3.92%	2.01%	3.67%	4.72%	8.99%	53.86%	53.86%

Analyte:		RPD NH4		Units:		Relative Percent Difference	
Type:		NH4 < 0.05 ppm		Inst:		D6C	
Date:	Apr-01	May-01	Jun-01	Jul-01	Aug-01	Sep-01	Total
Average	7.22%	0.81%	7.22%	-2.27%	----	-11.14%	1.47%
Std Dev	0.91%	0.62%	16.85%	21.08%	----	28.75%	16.78%
N	2	4	7	3	----	3	19
Most Neg.	6.57%	0.31%	-4.83%	-24.74%	----	-43.13%	-43.13%
Most Pos.	7.87%	1.67%	44.60%	17.06%	----	12.56%	44.60%

Analyte:		RPD NH4		Units:		Relative Percent Difference	
Type:		NH4 > 0.05 ppm		Inst:		D6C	
Date:	Apr-01	May-01	Jun-01	Jul-01	Aug-01	Sep-01	Total
Average	-0.27%	0.17%	-0.31%	-0.10%	-0.01%	1.74%	0.16%
Std Dev	1.19%	1.24%	1.28%	0.97%	1.02%	8.51%	3.38%
N	24	28	31	27	35	24	169
Most Neg.	-3.27%	-3.84%	-4.40%	-1.92%	-3.96%	-2.65%	-4.40%
Most Pos.	2.13%	2.75%	1.30%	1.81%	2.91%	41.02%	41.02%

Analyte:		RPD K		Units:		Relative Percent Difference	
Type:		K < 0.05 ppm		Inst:		D6C	
Date:	Apr-01	May-01	Jun-01	Jul-01	Aug-01	Sep-01	Total
Average	-0.69%	-2.25%	-1.29%	-0.36%	1.91%	-1.37%	-0.48%
Std Dev	5.16%	6.09%	3.92%	2.85%	3.54%	10.39%	5.72%
N	21	23	31	29	37	25	166
Most Neg.	-9.31%	-17.09%	-11.81%	-7.25%	-3.12%	-48.48%	-48.48%
Most Pos.	12.75%	6.90%	5.12%	5.43%	12.41%	9.22%	12.75%

Table 15 (continued).

Analyte:		RPD K		Units:		Relative Percent Difference	
Type:		K > 0.05 ppm		Inst:		D6C	
Date:	Apr-01	May-01	Jun-01	Jul-01	Aug-01	Sep-01	Total
Average	5.10%	1.74%	0.40%	0.04%	----	0.25%	1.22%
Std Dev	2.33%	5.16%	2.76%	1.51%	----	1.09%	3.25%
N	3	5	7	3	----	5	23
Most Neg.	2.65%	-6.65%	-4.33%	-1.64%	----	-0.80%	-6.65%
Most Pos.	7.30%	5.83%	3.46%	1.29%	----	2.06%	7.30%

Table 16. Average Percent Recovery for Sodium, Ammonium, and Potassium Spikes

Analyte:		Sodium		Units:		pct spike recovery	
Type:		Nylon filter		Inst:		D6C	
Date:	Apr-01	May-01	Jun-01	Jul-01	Aug-01	Sep-01	Total
Average	99.9%	99.2%	99.4%	100.3%	99.5%	100.1%	99.7%
Std Dev	1.3%	1.3%	2.2%	0.8%	1.4%	1.9%	1.6%
N	20	25	24	28	38	25	160
Min	97.27%	96.49%	92.45%	98.52%	95.71%	96.18%	92.45%
Max	102.37%	102.36%	102.09%	102.47%	102.99%	103.35%	103.35%

Analyte:		Sodium		Units:		pct spike recovery	
Type:		Quartz Filter		Inst:		D6C	
Date:	Apr-01	May-01	Jun-01	Jul-01	Aug-01	Sep-01	Total
Average	97.9%	98.9%	99.5%	----	----	----	98.9%
Std Dev	2.3%	0.6%	0.5%	----	----	----	1.3%
N	4	5	6	----	----	----	15
Min	95.26%	98.03%	98.64%	----	----	----	95.26%
Max	100.19%	99.57%	100.14%	----	----	----	100.19%

Analyte:		Sodium		Units:		pct spike recovery	
Type:		Teflon Filter		Inst:		D6C	
Date:	Apr-01	May-01	Jun-01	Jul-01	Aug-01	Sep-01	Total
Average	99.8%	99.1%	99.6%	100.8%	----	95.6%	99.4%
Std Dev	1.2%		0.3%	0.7%	----	0.6%	1.9%
N	3	1	5	7	----	3	19
Min	98.82%	99.15%	99.33%	99.80%	----	94.97%	94.97%
Max	101.21%	99.15%	100.12%	101.79%	----	96.07%	101.79%

Table 16 (continued).

Analyte: Sodium		Units: pct spike recovery					
Type: All Filters							
Inst: D6C							
Date:	Apr-01	May-01	Jun-01	Jul-01	Aug-01	Sep-01	Total
Average	99.6%	99.1%	99.4%	100.4%	99.5%	99.7%	99.6%
Std Dev	1.6%	1.2%	1.8%	0.8%	1.4%	2.3%	1.6%
N	27	31	35	35	38	28	194
Min	95.26%	96.49%	92.45%	98.52%	95.71%	94.97%	92.45%
Max	102.37%	102.36%	102.09%	102.47%	102.99%	103.35%	103.35%

Analyte: Ammonium		Units: pct spike recovery					
Type: Nylon filter							
Inst: D6C							
Date:	Apr-01	May-01	Jun-01	Jul-01	Aug-01	Sep-01	Total
Average	99.1%	98.7%	99.5%	100.0%	99.5%	100.2%	99.5%
Std Dev	2.6%	1.8%	1.6%	1.3%	1.2%	1.3%	1.7%
N	20	25	24	28	38	25	160
Min	95.83%	95.18%	95.28%	96.69%	96.38%	96.87%	95.18%
Max	107.34%	100.95%	101.80%	102.48%	102.77%	103.13%	107.34%

Analyte: Ammonium		Units: pct spike recovery					
Type: Quartz Filter							
Inst: D6C							
Date:	Apr-01	May-01	Jun-01	Jul-01	Aug-01	Sep-01	Total
Average	99.5%	98.6%	96.6%	----	----	----	98.0%
Std Dev	4.8%	4.0%	1.1%	----	----	----	3.4%
N	4	5	6	----	----	----	15
Min	95.21%	92.48%	95.52%	----	----	----	92.48%
Max	105.78%	102.31%	98.25%	----	----	----	105.78%

Analyte: Ammonium		Units: pct spike recovery					
Type: Teflon Filter							
Inst: D6C							
Date:	Apr-01	May-01	Jun-01	Jul-01	Aug-01	Sep-01	Total
Average	98.9%	97.4%	99.6%	100.2%	----	97.9%	99.3%
Std Dev	0.3%		0.5%	1.5%	----	1.3%	1.4%
N	3	1	5	7	----	3	19
Min	98.57%	97.43%	98.98%	97.44%	----	96.41%	96.41%
Max	99.07%	97.43%	100.33%	101.93%	----	98.87%	101.93%

Analyte: Ammonium		Units: pct spike recovery					
Type: All Filters							
Inst: D6C							
Date:	Apr-01	May-01	Jun-01	Jul-01	Aug-01	Sep-01	Total
Average	99.1%	98.6%	99.0%	100.1%	99.5%	100.0%	99.4%
Std Dev	2.8%	2.2%	1.8%	1.3%	1.2%	1.5%	1.9%
N	27	31	35	35	38	28	194
Min	95.21%	92.48%	95.28%	96.69%	96.38%	96.41%	92.48%
Max	107.34%	102.31%	101.80%	102.48%	102.77%	103.13%	107.34%

Table 16 (continued).

Analyte: Potassium		Units: pct spike recovery					
Type: Nylon filter							
Inst: D6C							
Date:	Apr-01	May-01	Jun-01	Jul-01	Aug-01	Sep-01	Total
Average	97.2%	97.8%	98.5%	99.6%	98.8%	99.5%	98.7%
Std Dev	1.9%	1.7%	1.7%	1.0%	1.1%	1.3%	1.6%
N	20	25	24	28	38	25	160
Min	93.73%	94.76%	94.91%	97.24%	95.77%	97.03%	93.73%
Max	101.45%	101.81%	103.04%	101.52%	101.71%	101.87%	103.04%

Analyte: Potassium		Units: pct spike recovery					
Type: Quartz Filter							
Inst: D6C							
Date:	Apr-01	May-01	Jun-01	Jul-01	Aug-01	Sep-01	Total
Average	96.3%	98.3%	97.6%	----	----	----	97.5%
Std Dev	0.9%	1.5%	0.9%	----	----	----	1.3%
N	4	5	6	----	----	----	15
Min	95.42%	96.69%	96.49%	----	----	----	95.42%
Max	97.12%	100.66%	98.43%	----	----	----	100.66%

Analyte: Potassium		Units: pct spike recovery					
Type: Teflon Filter							
Inst: D6C							
Date:	Apr-01	May-01	Jun-01	Jul-01	Aug-01	Sep-01	Total
Average	97.0%	96.3%	98.0%	99.1%	----	96.3%	97.9%
Std Dev	1.4%		0.9%	0.4%	----	0.8%	1.3%
N	3	1	5	7	----	3	19
Min	96.01%	96.32%	96.96%	98.38%	----	95.37%	95.37%
Max	98.58%	96.32%	98.99%	99.42%	----	96.87%	99.42%

Analyte: Potassium		Units: pct spike recovery					
Type: All Filters							
Inst: D6C							
Date:	Apr-01	May-01	Jun-01	Jul-01	Aug-01	Sep-01	Total
Average	97.0%	97.9%	98.3%	99.5%	98.8%	99.2%	98.5%
Std Dev	1.7%	1.7%	1.5%	0.9%	1.1%	1.6%	1.6%
N	27	31	35	35	38	28	194
Min	93.73%	94.76%	94.91%	97.24%	95.77%	95.37%	93.73%
Max	101.45%	101.81%	103.04%	101.52%	101.71%	101.87%	103.04%

**Table 17. Filter and Regent Blank Values for Sodium,
Ammonium, and Potassium**

Analyte: Sodium Units: ug/ml							
Type: N BLANK							
Inst: D6C							
Date:	Apr-01	May-01	Jun-01	Jul-01	Aug-01	Sep-01	Total
Average	0.0040	-0.0016	0.0089	0.0151	0.0062	----	0.0069
Std Dev	0.0086	0.0060	0.0092	0.0135	0.0143	----	0.0118
N	11	6	9	9	12	----	47
Min	-0.0033	-0.0081	0.0000	-0.0009	-0.0100	----	-0.0100
Max	0.0211	0.0091	0.0245	0.0397	0.0348	----	0.0397

Analyte: Sodium Units: ug/ml							
Type: REAGENT BLANK DI H2O							
Inst: D6C							
Date:	Apr-01	May-01	Jun-01	Jul-01	Aug-01	Sep-01	Total
Average	0.0016	0.0040	0.0070	0.0039	0.0026	0.0020	0.0036
Std Dev	0.0072	0.0052	0.0085	0.0072	0.0132	0.0170	0.0101
N	26	23	26	24	20	19	138
Min	-0.0059	-0.0088	-0.0017	-0.0048	-0.0099	-0.0343	-0.0343
Max	0.0219	0.0154	0.0393	0.0254	0.0494	0.0516	0.0516

Analyte: Ammonium Units: ug/ml							
Type: N BLANK							
Inst: D6C							
Date:	Apr-01	May-01	Jun-01	Jul-01	Aug-01	Sep-01	Total
Average	0.0010	0.0000	-0.0018	-0.0161	-0.0125	----	-0.0064
Std Dev	0.0034	0.0000	0.0027	0.0013	0.0022	----	0.0075
N	11	6	9	9	12	----	47
Min	0.0000	0.0000	-0.0058	-0.0175	-0.0153	----	-0.0175
Max	0.0113	0.0000	0.0000	-0.0146	-0.0092	----	0.0113

Analyte: Ammonium Units: ug/ml							
Type: REAGENT BLANK DI H2O							
Inst: D6C							
Date:	Apr-01	May-01	Jun-01	Jul-01	Aug-01	Sep-01	Total
Average	0.0096	0.0096	0.0035	-0.0061	-0.0102	-0.0082	0.0004
Std Dev	0.0122	0.0187	0.0113	0.0063	0.0040	0.0065	0.0137
N	26	23	26	24	20	19	138
Min	0.0000	0.0000	-0.0127	-0.0188	-0.0171	-0.0205	-0.0205
Max	0.0313	0.0629	0.0297	0.0000	-0.0026	0.0016	0.0629

Analyte: Potassium Units: ug/ml							
Type: N BLANK							
Inst: D6C							
Date:	Apr-01	May-01	Jun-01	Jul-01	Aug-01	Sep-01	Total
Average	0.0011	0.0018	0.0000	0.0000	0.0000	----	0.0005
Std Dev	0.0036	0.0044	0.0000	0.0000	0.0000	----	0.0023
N	11	6	9	9	12	----	47
Min	0.0000	0.0000	0.0000	0.0000	0.0000	----	0.0000
Max	0.0120	0.0108	0.0000	0.0000	0.0000	----	0.0120

Table 17 (continued).

Analyte: Potassium		Units: ug/ml					
Type: REAGENT BLANK DI H2O							
Inst: D6C							
Date:	Apr-01	May-01	Jun-01	Jul-01	Aug-01	Sep-01	Total
Average	0.0017	0.0006	0.0009	0.0000	0.0004	0.0003	0.0007
Std Dev	0.0049	0.0028	0.0046	0.0000	0.0017	0.0057	0.0038
N	26	23	26	24	20	19	138
Min	0.0000	0.0000	0.0000	0.0000	0.0000	-0.0120	-0.0120
Max	0.0167	0.0133	0.0235	0.0000	0.0077	0.0140	0.0235

2.2.5 Corrective Actions Taken

Beginning in September 2001, it was observed that the relative percent differences for replicate analyses were higher than usual for sodium and sulfate. A contamination problem was suspected, and experiments were carried out to identify and eliminate the source of the problem. All tubing in the ion chromatographs was replaced from the autosampler to the separator column, the chromatographs were flushed with a dilute bleach solution, the injection valves were cleaned, and the autosampler vials were subjected to a more rigorous cleaning procedure.

At the same time, it was observed during the nylon filter extraction procedure that material (apparently nylon) was being removed from some of the filters, leaving bare (transparent) areas on the filter substrate. The ion extraction procedure involves sonication of the filter in the extraction solution followed by shaking overnight on a reciprocating shaker. The filter material that was removed settled to the bottom of the extraction vessel as a white particulate. Since the filter pre-washing procedure is very similar to the sample extraction procedure, it was suspected that the filter loss could begin during washing. A closer inspection of a batch of filters as they were washed revealed that this was the case. To rule out problems with the ultrasonic bath used for filter extraction, another ultrasonic bath was used; filter loss was observed with the second bath also. The filter supplier was notified, and filters from a different lot were requested. However, the only filters in stock were from the same lot that showed filter material loss. The manufacturer suggested that the affected filters could have been cut from an area of the nylon sheet that had not been properly bonded. Since a large number of filters from this lot had not shown the filter loss problem, and to maintain continuity in the PM2.5 sampling network while a new filter lot was being prepared, the available filters were carefully screened by sonicating a few filters selected from each box of 100 to determine the boxes that were acceptable.

As a result of the filter erosion occurring when field samples were extracted, it was necessary to filter each affected extract prior to injection into the ion chromatograph. This was accomplished using a 5-mL disposable plastic syringe fitted with a Gelman IC Acrodisc® 13 mm syringe filter with a 0.45 µm membrane. All analysis results for extracts that required filtration are flagged in the database.

The manufacturer of the nylon filters agreed to replace the defective filters with new filters from a different lot. When the replacement filters are received, they will be carefully tested.

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 18**.

Table 18. Summary of OC/EC Checks, Acceptance Criteria, and Corrective Actions

QC Element	Frequency	Acceptance Criteria	Corrective Action
Method Detection Limit	annually	$MDL \leq 0.5 \mu\text{g C/cm}^2$	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 $\leq 0.3 \mu\text{g C/cm}^2$	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) ≥ 0.99 [with force-fit through 0,0]	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 $10 \mu\text{g C/cm}^2$ – Less than 10% RPD, (2) TC Values 5 - $10 \mu\text{g C/cm}^2$ – Less than 15% RPD, (3) TC Values less than $5 \mu\text{g C/cm}^2$ – Within $0.5 \mu\text{g C/cm}^2$.	Flag analysis results for that filter with non-uniform filter deposit (LFU) flag.

2.3.2 Statistical Summary of QC Results

The OC/EC Laboratory had two carbon analyzers (one designated as the New analyzer and the other as the Retrofit analyzer) on April 1, 2001. The New analyzer was removed from service and replaced with the instrument currently designated the Second analyzer on June 6, 2001. The Third analyzer was also placed in service on June 6, 2001. The statistical summaries in this section contain data from four OC/EC analyzers: New, Retrofit, Second, and Third.

The method detection limit for total carbon (TC) is determined annually. Both the New and the Retrofit OC/EC carbon analyzers met the required limit of $\leq 0.5 \mu\text{g C/cm}^2$ with MDLs of $0.13 \mu\text{g C/cm}^2$ for the New analyzer and $0.16 \mu\text{g C/cm}^2$ for the Retrofit analyzer on March 16, 2001. The MDL for the Third analyzer was determined to be $0.18 \mu\text{g C/cm}^2$ on June 5, 2001; and the MDL for the Second analyzer was determined to be $0.11 \mu\text{g C/cm}^2$ on June 6, 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.

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

Figure 1 shows measured TC for daily instrument blanks run on the New, Retrofit, Second, and Third OC/EC analyzers during the reporting period (April 1 through September 30, 2001). The instrument blank must be $\leq 0.3 \mu\text{g C/cm}^2$ (bold line at the top of **Figure 1**). Mean and standard deviation of blank responses by instrument over the reporting period are summarized in **Table 19**.

Table 19. Mean and Standard Deviation of Blank Responses by Instrument Over the Reporting Period

	OC/EC Analyzer			
	New	Retrofit	Second	Third
No. of Instrument Blanks	39	122	81	77
Mean Response ($\mu\text{g C/cm}^2$)	0.061	0.032	0.026	0.022
Standard Deviation	0.042	0.030	0.023	0.020

None of the daily instrument blanks run on any of the four instruments exceeded the acceptance criterion of $\leq 0.3 \mu\text{g C/cm}^2$.

Figure 2 shows linearity (as R^2 , forced-fit through the origin) for all three-point calibrations run on all four instruments during the reporting period. All four instruments met the $R^2 \geq 0.99$ (heavy line in **Figure 2**) requirement for every three-point calibration.

Percent recovery of standards is used to make sure the instruments are functioning properly and are still calibrated correctly. **Figures 3a, 3b, 3c, and 3d** show percent recovery on the New, Retrofit, Second, and Third analyzers, respectively, for each of the three (low, middle, and high) calibration standards, as well as the average percent recovery for the three, used for each three-point calibration. All four instruments met the 90-110% criterion (heavy lines in figures) for recovery for all three standards in every three-point calibration during the reporting period.

Response factors for the flame ionization detector (FID) are used to monitor FID performance. **Figures 4a, 4b, 4c, and 4d** 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, Retrofit, Second, and Third instruments, respectively, during the reporting period. FID response is affected by slight changes in flow rate for hydrogen and other gases, but use of the internal methane standard at the end of every analysis compensates for such changes. The efficiency of the methanator on the Retrofit analyzer began to diminish during April 2001, and the methanator was replaced on May 1, 2001; at which time, the FID response factor increased significantly. The shift in FID response did not affect the data produced because both the carbon volatilized from the filter and the methane internal standard were oxidized to CO₂ before entering the methanator and thus were converted to CH₄ with the same efficiency by the methanator. The ratio of FID area counts for the internal standard to the known mass of carbon in the internal standard injection loop is calculated separately for each analysis and used to calculate the mass of carbon volatilized from the filter punch during that analysis as shown in the following equation.

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

Figure 5 shows the slopes of three-point calibration plots with force-fit through the origin for all four OC/EC analyzers during the reporting period. The slope for the Retrofit analyzer increased dramatically after replacement of its methanator on May 1, 2001. The end of the preceding paragraph explains why changing the methanator did not affect measured values.

Figure 6 shows percent recovery for all daily calibration checks run on all four instruments during the reporting period. All daily calibration checks met the acceptance criterion of 90% to 110% recovery.

Duplicate measurements are used to monitor the uniformity of filter loading and to indicate instrument stability. The acceptance criteria for duplicate measurements (in the Table above) are based on a significant absolute uncertainty at low ($< 5 \mu\text{g C}/\text{cm}^2$) TC loadings and the relative uncertainty at higher TC loadings. **Figures 7a, 7b, 7c, and 7d** show relative percent difference of duplicate measurements versus filter concentration ($\mu\text{g C}/\text{cm}^2$) for the New,

Retrofit, Second, and Third instruments, respectively, during the reporting period. Text boxes beside each figure show total number of duplicates run on that instrument and the numbers of filters that passed and that failed the appropriate duplicate criterion. Filters that failed to meet the appropriate duplicate acceptance criterion were flagged as having a nonuniform filter deposit (LFU).

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 is extremely rare.

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 Corrective Actions Taken

No corrective actions were taken during the period April 1, 2001, through September 30, 2001.

2.3.5 Validation of OC/EC Analyzers

RTI's New OC/EC analyzer malfunctioned and was removed from service in early June. The New analyzer was replaced by Sunset Laboratory with an analyzer, designated as RTI's Second analyzer, on 6 June 2001. RTI purchased a new Sunset Laboratory carbon aerosol analyzer, designated as RTI's Third analyzer, which was also placed in service on 6 June 2001. The Second and Third analyzers were thoroughly checked out in the OC/EC Lab by both the Sunset Laboratory technician and RTI's primary analyst. After both the Second and Third instruments successfully met all criteria required for analysis of samples, separate punches from 14 PM_{2.5} filters were analyzed on the Retrofit, the Second, and the Third instruments. Results for TC between all possible paired combinations of instruments (i.e., Retrofit with Second, Retrofit with Third, and Second with Third) were compared using the criteria (table in Section 2.3.1) used for duplicate punches run on the same instrument. The results of the comparison are shown in **Table 20**. With 14 of 14, 13 of 14, and 12 of 14 filter measurements passing the appropriate duplicate criterion for the Retrofit-Second, Retrofit-Third, and Second-Third comparisons, respectively, the results clearly indicate that the three instruments yield essentially the same values for TC.

Table 20. Duplicate Criteria for TC

Comparison	No. Failed Dups/No. Total Dups		
	Retrofit	Second	Third
Versus Retrofit	---	0/14 = 0%	1/14 = 7.1%
Versus Second	0/14 = 0%	---	2/14 = 14.3%
Versus Third	1/14 = 7.1%	2/14 = 14.3%	---
This Instrument Only (4/1/01-9/30/01)	14/238 = 5.9%	6/166 = 3.6%	6/158 = 3.8%

NOTE: The New instrument had 5/67 or 7.5% of duplicates failing to meet the criteria in the current reporting period and 18/403 or 4.5% over its lifetime at RTI.

NOTE: The Retrofit instrument, which has been in service since the beginning of the contract, has had 30/558 or 5.4% of duplicates failing to meet the criteria over its lifetime at RTI.

The results of the validation study illustrate an anomaly in the current duplicate criteria for filters with loadings just below $5 \mu\text{g C/cm}^2$ (shown by the downward dip in the heavy criteria lines at $\text{TC} = 5 \mu\text{g C/cm}^2$ in **Figures 7a through 7d**). The one filter that failed the Retro-Third comparison and one of the 2 filters that failed the Second-Third comparison had average TC loadings slightly below $5 \mu\text{g C/cm}^2$ ($4.89 \mu\text{g C/cm}^2$ and $4.95 \mu\text{g C/cm}^2$, respectively) and RPDs of 11.31% and 13.55%, respectively. If either filter had an average loading of just $5.00 \mu\text{g C/cm}^2$ (0.11 and $0.05 \mu\text{g C/cm}^2$ higher, respectively) and the RPD had remained the same, that filter would have passed the criterion (within 15% RPD) applied to duplicates with an average loading in the range 5 - $10 \mu\text{g C/cm}^2$. The criterion for duplicates with average loading below $5 \mu\text{g C/cm}^2$ is agreement "within $0.5 \mu\text{g C/cm}^2$," which corresponds to 10% of $5 \mu\text{g C/cm}^2$. Thus, the criterion for duplicates with average loading just below $5 \mu\text{g C/cm}^2$ is more stringent than the criterion for duplicates with an average loading of $5 \mu\text{g C/cm}^2$.

A suggested change in the criterion for duplicates from filters with average loading below $5 \mu\text{g C/cm}^2$ to "within $0.75 \mu\text{g C/cm}^2$ " is proposed in Section 2.3.6 and illustrated by a heavy dashed line in **Figures 7a through 7d**. This change would hold the absolute uncertainty for these lightly-loaded filters to an absolute amount equal to the currently accepted 15% RPD applied when the average loading is $5.00 \mu\text{g C/cm}^2$. If the proposed criterion is applied to the data from the validation study, only one filter in one comparison (the Second-Third comparison) fails to meet the appropriate duplicate criterion.

2.3.6 Suggested Changes to OC/EC SOP and QAPP

The two changes below are proposed for both the OC/EC SOP and the QAPP for the PM2.5 Chemical Speciation Program.

Duplicate Criteria. The criterion for duplicates from filters with average TC loading below $5 \mu\text{g C/cm}^2$ should be changed from "within $0.5 \mu\text{g C/cm}^2$ " to "within $0.75 \mu\text{g C/cm}^2$."

This change, which is illustrated by a heavy dashed line in **Figures 7a through 7d**, is necessary to be consistent with the 15% RPD criterion applied to filters with an average loading of $5 \mu\text{g C/cm}^2$ (i.e., 15% of $5 \mu\text{g C/cm}^2$ is $0.75 \mu\text{g C/cm}^2$, not $0.5 \mu\text{g C/cm}^2$).

Calcium Carbonate Standard Analysis. The frequency of qualitative analysis of solid calcium carbonate standard (which is used to determine the time of evolution of carbonate during the analysis or the position of the carbonate peak in the thermogram) should be changed to once per year or whenever an MDL is determined. The calcium carbonate peak, if it appears at all in thermograms of $\text{PM}_{2.5}$, is not large enough to allow accurate measurement of its area the boundaries of which must be set manually. More frequent qualitative analysis of solid calcium carbonate standard is not necessary for a species that is not seen in sufficient quantity to allow accurate measurement by OC/EC analysis and whose position on the thermogram should not change significantly.

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 21**.

Table 21. 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 using standard samples. 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. The data used to monitor precision are presented in **Figures 8 through 14**.

The low number in **Figure 8** is in error. The actual value was 92.6 percent. Average recoveries for all test elements are within 5 percent of expected and all values are within the range of 90 to 100 percent of expected values as summarized in **Table 22**. Changes with time are noted to be significant for Si(0), Se(4), and Cd(5). From the figure, only Si(0) appears to be of any significant concern. A jump in recovery about August 1 occurred. The changes per year are less than 10 percent and will be monitored. The recovery for these elements appear to be within the uncertainty in unknown after correction for mass absorption and spectral overlap.

Table 22. Summary of Chester QC Precision Recovery Data, 4/1 through 9/30/01.

Percent Recoveries

Element	Avg.	Std Dev	% RSD	Max	Min	R	Slope/Year	Slope Uncert.	Slope > +/-0.00 ?
Si(0)	102.91	1.561	1.52%	106.33	92.63	0.6507	8.51%	0.66%	Significant
Si(1)	100.91	1.485	1.47%	103.99	95.70	0.0518	0.64%	0.83%	
Ti(2)	103.36	1.026	0.99%	105.91	100.60	-0.0183	-0.16%	0.57%	
Fe(3)	102.05	1.024	1.00%	104.56	98.35	-0.1825	-1.56%	0.56%	
Se(4)	102.19	1.395	1.37%	104.62	96.22	-0.4301	-5.03%	0.70%	Significant
Pb(4)	101.48	1.419	1.40%	105.50	93.78	0.1438	1.71%	0.78%	
Cd(5)	100.14	1.175	1.17%	103.02	95.13	-0.3910	-3.85%	0.60%	Significant

N=227 for all data

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 15 through 27** show recovery for 12 select elements spanning the range of the 48 elements normally measured. All recovery values for all elements ranged between 91 and 108 percent as shown in **Table 23**.

Table 23. Recovery Determined from Analysis of NIST Standard Reference Material Filters

Element	Range	% Recovery
Al	94 -	106
Si*	99 -	109
Si**	96 -	105
S	94 -	102
K	94 -	98
Ca	102 -	108
Ti	91 -	95
V	92 -	98
Mn	100 -	109
Fe	99 -	103
Cu	95 -	103
Zn	94 -	101
Pb	99 -	103

* SRM 1832

* SRM 1833

2.4.2.3 Replicates – Ten percent of the filters are reanalyzed and the results for select elements are compared. **Figures 28 through 33** 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 0.999, 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 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: There were many anomalous data points for the R&P samplers. **Corrective Action:** RTI investigated the handling of these modules. A new procedure was implemented and all SHAL workers were retrained in the processing of the R&P modules.

Problem: EPA asked RTI to investigate the high mass values for blank filters (see Section 1.6 for more information). **Corrective Action:** RTI identified the major cause of the high masses for Teflon filters as the white Delrin rings in the MET ONE samplers. RTI replaced the white Delrin rings with blue poly rings for the cassettes holding the Teflon filters in the MET ONE modules.

Problem: The XRF laboratory was not analyzing and returning filters promptly. **Corrective Action:** The primary subcontractor, Chester LabNet (Labcor) has purchased a second XRF to support this program. A second subcontractor, Cooper Environmental Services (CES), has been added to perform XRF analyses. Also, RTI has purchased an XRF for analysis of PM_{2.5} filters. When all three laboratories are ready and meet EPA's criteria, the sample backlog will be reduced quickly.

Problem: Nylon filters were disintegrating when being extracted for ions in a sonicator. **Corrective Action:** A bad batch of nylon filters was supplied by the manufacturer. Only those filters which do not show signs of deterioration following initial washing are being used until a new batch can be obtained.

2.6 Denuder Refurbishment Laboratory

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

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

2.6.1 Operational Summary

Denuders for the Andersen and URG speciation samplers are being cleaned and then coated with magnesium oxide. They are replaced at the sites at 3-month intervals. The last replacement was in early October 2001; the next scheduled change-out is early January 2002.

MetOne aluminum honeycomb denuders are also coated with magnesium oxide. Because the MetOne denuders are part of the sampling module and six sets of modules are in circulation to each site, these denuders are refurbished at 18-month intervals. A major change-out of MetOne denuders occurred in July, 2001, for those modules that had been in use for 18 months to that point. RTI ordered uncoated aluminum honeycomb denuder substrates from MetOne, cleaned them with solvent and deionized water, and then coated them with magnesium oxide. This change-out is the first where RTI-coated MetOne denuders were used; all earlier MetOne denuders had been supplied by the manufacturer.

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

No XAD-4 resin coated denuders (for removal of organic vapors) have been ordered thus far under the project by EPA/OAQPS.

2.6.2 Problems and Corrective Actions

The only significant problem encountered in the reporting period of operation has been the receipt of broken or loose denuders. One URG denuder arrived at RTI broken. It was repaired using denuder task funds at half the cost of a new assembly. The other URG denuder arrived with the glass sleeves detached from its aluminum pipe casing. This denuder was repaired by the manufacturer (URG) at no cost. The site operators continue to be alerted to the proper procedures for packaging and shipping whenever a replacement denuder is sent to them.

2.6.3 Quality Assurance Activities

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

- Obstruction-free annuli. 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 by scraping 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 is repeated and the tapping test 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 1.0 g of magnesium oxide. The typical Andersen annular denuder retains 0.7 g of magnesium oxide. The amount retained by double-coating the Met One aluminum honeycomb denuder was approximately 1.1 g.

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. Continuing improvements in our QC and QA review process were made by addition of additional checks and automating checks to improve efficiency and effectiveness.

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 affected data users:

Problem: Several events were processed and results delivered to the client before the field data had been entered. This resulted in missing concentration data (due to the lack of field sampling volume information). **Corrective Action:** Reporting software has been modified to

prevent any scheduled routine sampling event (i.e., non-blank event) from being automatically reported without having data from the correct number of sampling channels (for that type of sampler) entered. Samples that legitimately have missing data (not supplied on form or sample not run) may be manually overridden for processing.

2.8 Quality Assurance and Data Validation

2.8.1 QA Activities

QA activities directly related to data validation are described in the PM_{2.5} 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
 - Application of Level 1 outlier screening criteria
- Review of each data batch before it is sent to AIRS
 - Verification of data attribution to the correct site, POC, and date
 - Verification that changes requested by the state monitoring agencies have been correctly made by the Data Processing personnel
 - Review of data format to be sure that records and individual fields are of the correct length
- Troubleshooting of sample and data problems that cross the boundaries between laboratories, the SHAL, and/or the data processing function

2.8.2 Data Validation Procedures

The full scope of the Level 0 and Level 1 procedures carried out by RTI before data are delivered to the state monitoring agencies each month are described in the Laboratory QAPP (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 are being 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:** Contamination from Delrin canister rings used by the MetOne SASS sampler has been identified as a significant source of erroneous mass measurements. See the July 18, 2001 report (Attachment A). RTI is continuing to work with the manufacturers, EPA, and the monitoring agencies to identify and fix any other 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 16 through 21, or approximately March through July, 2001. **Table 24** summarizes the delivery batch by delivery date covered by this report. 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.

Table 24. Delivery Batch by Delivery Date

Delivery Batch Number	Report Date	Earliest Sample	Last Sample
16	5/15/2001	1/27/2001	4/10/2001
17	6/19/2001	3/14/2001	5/10/2001
18	7/16/2001	3/17/2001	6/12/2001
19	8/15/2001	3/5/2001	7/6/2001
20	9/17/2001	2/15/2001	8/11/2001
21	10/15/2001	6/21/2001	9/10/2001

The number of blanks run during this period are summarized in **Table 25**. 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 25. Summary of Blanks Reported in Batches 15 through 21

Blank Type	Delivery Batch	Count of Blanks
Field Blank	16	43
Field Blank	17	68
Field Blank	18	57
Field Blank	19	98
Field Blank	20	76
Field Blank	21	59
Trip Blank	16	55
Trip Blank	17	3
Trip Blank	18	9
Trip Blank	19	49
Trip Blank	20	77
Trip Blank	21	21
Unsampled Blank	16	16
Unsampled Blank	17	21
Unsampled Blank	18	19
Unsampled Blank	19	4
Unsampled Blank	20	6
Unsampled Blank	21	6

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 26 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 26. Summary of Percent Valid AIRS Data by Delivery Batch.

Location Name	POC	16	17	18	19	20	21
20th St. Fire Station	5		90.6%	90.6%			
Air Monitoring, VA DEQ	5	90.6%	90.6%	77.7%	90.6%	90.6%	90.6%
Aldine	5	88.0%	63.5%	57.2%	87.0%	90.6%	77.2%
Allen Park	5	90.6%	79.3%	69.7%	90.6%	90.0%	79.3%
Alpine	5	18.1%	30.2%	75.3%	40.5%	89.1%	90.6%
Arendtsville	5						90.6%
Army Reserve Center	5		90.6%	68.0%	88.7%	90.6%	89.3%
Arnold	5			75.5%	66.6%	81.1%	30.2%
Bakersfield-California Ave	5					90.6%	90.6%
Bakersfield-California Ave (Collocated)	6					79.7%	90.6%
Baxter Water Treatment Plant	5						90.1%
Bayland Park	5	60.3%	57.2%	75.3%	58.6%	77.1%	54.5%
Beacon Hill	6	90.8%	90.8%	86.7%	90.8%	9.2%	90.8%
Bismarck Residential	5		90.6%	68.0%	90.6%	90.6%	90.6%
Blair Street	6	73.6%	90.6%	81.1%	90.6%	90.6%	90.6%
Boyd Park	5	90.6%	90.6%	90.6%	81.9%	90.6%	90.6%
Burlington	5	90.6%	88.4%	90.6%	90.6%	90.6%	90.6%
Camden	5					90.6%	90.6%
Capitol	5				63.1%		90.8%
Chamizal	5	90.8%	90.8%	86.1%	90.8%	9.2%	75.6%
Channelview	5	68.9%	77.7%	67.1%	81.3%	77.4%	83.1%
Chester	5					90.6%	88.3%
Chicopee	5	80.3%	6.2%	74.7%	79.4%	9.2%	76.7%
Com ED	5			90.8%	90.8%		62.8%
Commerce City	5	88.7%	90.6%	74.2%	90.6%	90.6%	77.7%
Conroe Airport	5	88.3%	80.6%	80.7%	56.4%	4.7%	12.9%
Cornell Elementary	5		82.8%	90.6%	68.0%	90.6%	90.6%
CPW	5	90.6%	77.7%	90.6%	89.9%	90.6%	90.6%
Deer Park	6	76.9%	90.5%	82.2%	60.5%	9.2%	90.8%
Deer Park (Collocated)	7	85.1%	90.8%	86.6%	64.8%	9.2%	90.8%
Dona Park	5	88.3%	79.7%	90.6%	90.6%	88.3%	90.6%
Dover	5					90.6%	90.6%

Table 26 (continued)

El Cajon	5				90.6%	90.6%	90.6%
Elizabeth Lab	5				90.6%	90.6%	89.3%
Essex	5	90.6%	90.6%	89.6%	78.3%	85.2%	90.6%
Fargo NW	5						90.6%
Florence	5						90.6%
Fresno - First Street	5	90.6%	90.6%	69.7%	87.7%	84.0%	75.4%
G.T. Craig	5	90.6%	70.5%	30.2%	70.5%	90.6%	79.3%
G.T. Craig - Collocated	6		60.4%	75.3%	75.5%	83.7%	79.3%
Galveston Airport	5	81.5%	90.6%	66.8%	76.7%	90.6%	90.6%
Garinger High School	5					76.2%	82.1%
Garringer High School	5	75.5%	81.1%	90.6%	36.3%		
Georgetown	5	75.6%		90.8%	69.6%		90.8%
Grant School Site	5					90.6%	90.6%
Greensburg	5						90.6%
Guaynabo	5	45.3%	90.6%	77.7%	90.6%	89.4%	79.3%
Gulfport	5	90.6%	90.6%	90.6%	90.6%	90.6%	90.6%
Guthrie	5		90.6%				
Hamshire	5	90.6%	90.6%	90.6%	90.6%	90.6%	90.6%
Hawthorne	5	80.6%	90.6%	80.6%	90.6%	90.1%	90.6%
Hazelwood	5						90.6%
Hinton	5	90.8%	63.1%	90.8%	90.5%	48.5%	90.8%
HRM 3#	5	90.4%	70.5%	90.6%	73.4%	90.6%	60.4%
IS 52	5	80.1%	90.6%	82.1%	90.6%	90.1%	
Jefferson Elementary (10th and Vine)	5	90.6%	90.6%	69.8%	79.3%	90.1%	80.6%
JFK Center	5					72.5%	90.6%
Karnack	5						58.7%
Lake Clifton	5						57.7%
Lawrenceville	6						90.6%
Lewis	5	82.1%	90.6%	90.6%	90.6%	90.6%	69.7%
Lindon	5					60.4%	68.0%
Mauriceville	5			90.6%	90.6%	90.6%	90.6%
McMillan Reservoir	5	14.1%	45.3%	88.7%	77.3%	90.0%	80.3%
MLK	5					90.6%	90.6%
New Brunswick	5	90.6%	90.6%	90.6%	90.6%	90.6%	90.6%
New Brunswick (Collocated)	6					90.6%	90.6%
North Birmingham	5	90.6%	90.6%	80.6%	90.6%	84.7%	90.6%

Table 26 (continued)

NY Botanical Gardens	6	90.6%	89.7%	80.5%	89.8%	84.2%	88.3%
Osborn	5	90.6%	55.6%	60.0%	90.6%	74.0%	73.8%
Peoria Site 1127	5	90.6%	90.6%	90.6%	90.6%	85.5%	90.6%
PHILA - AMS Laboratory	7	90.6%	90.6%	90.6%	80.6%	90.6%	
Philips	5	90.6%	90.6%	90.6%	90.6%	77.7%	79.3%
Phoenix Supersite	7	90.6%	90.6%	90.6%	90.6%	73.4%	90.6%
Pinnacle State Park	5	88.7%	90.6%	90.0%	90.6%	90.6%	66.6%
Portland - SE Lafayette	6	90.6%	90.6%	90.6%	87.7%	84.0%	88.4%
Queens College	6	7.0%	90.6%	90.6%	90.6%	90.1%	90.6%
Reno	5			90.6%	65.6%	85.2%	90.6%
Riverside-Rubidoux	5					90.6%	90.6%
Riverside-Rubidoux (Collocated)	6					90.6%	90.6%
Rochester Fire Headquarters	5	90.6%	90.6%	80.4%	90.6%	90.6%	90.6%
Roxbury (Boston)	5	90.6%	90.6%	60.4%	70.3%	62.7%	62.7%
Sacramento - Del Paso Manor	5	90.6%	90.6%	81.1%	72.5%	83.2%	88.4%
San Jose - Fourth Street	5	90.6%	90.6%	90.6%	90.6%	90.6%	77.7%
SER-DNR Headquarters	5	90.6%	90.6%	90.6%	90.6%	79.3%	90.6%
South DeKalb	5	90.6%	90.6%	90.6%	70.5%	84.1%	90.6%
Southfield	5	69.9%	60.4%		90.6%	90.6%	90.6%
Springfield Pumping Station	5		90.6%	90.6%	90.6%	90.6%	90.6%
Sun Metro	5	90.4%	90.6%	90.6%	90.6%	90.6%	90.6%
Washington Park	5	90.6%	90.6%	90.6%	90.6%	90.6%	88.9%
Whiteface	5				9.4%	90.6%	90.6%
Woolworth St	5				90.6%	90.6%	60.4%

Figures 1 through 33 are contained in the following pages.

Figure 1. OC/EC Instrument Blanks

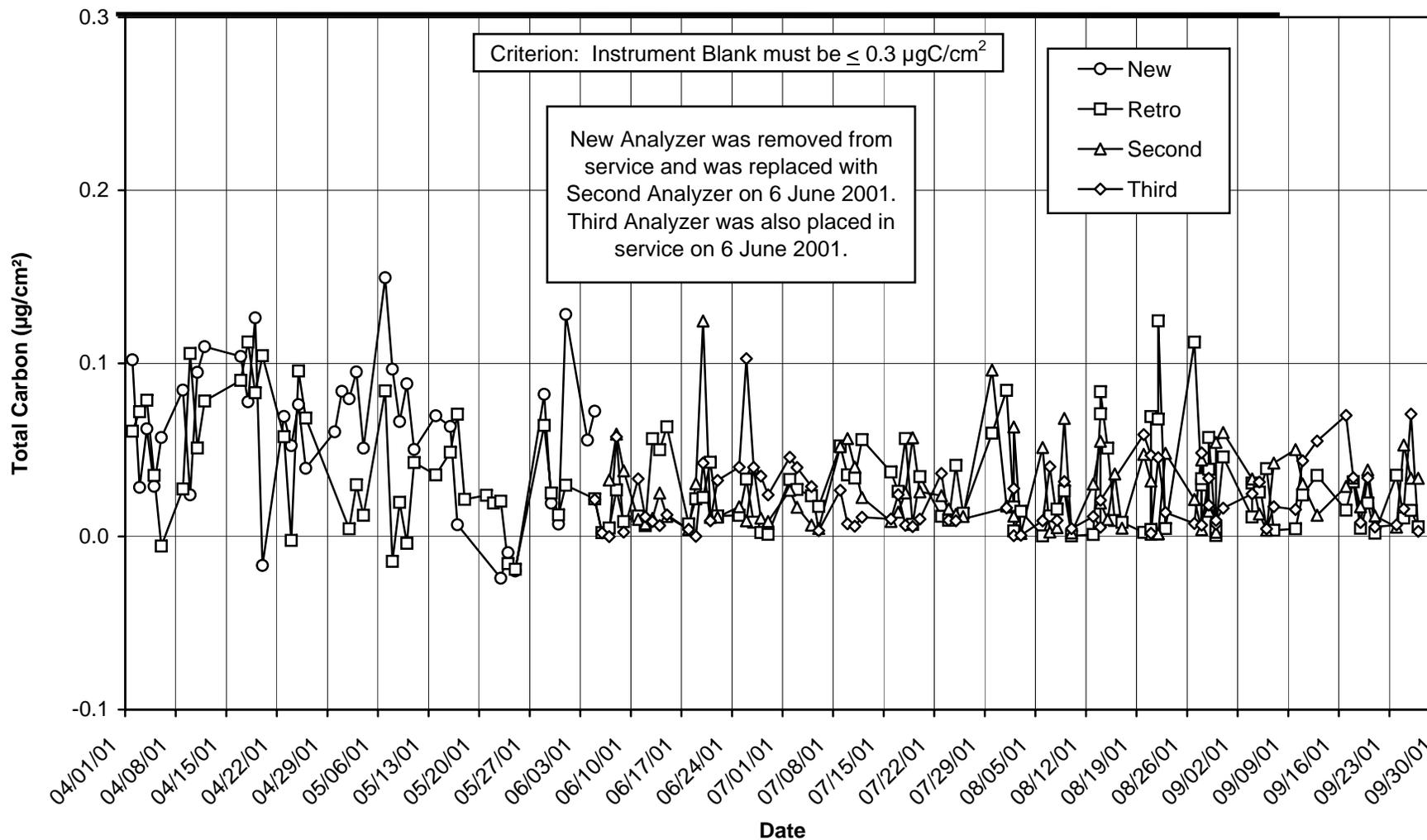


Figure 2. Linearity of Three-Point Calibrations

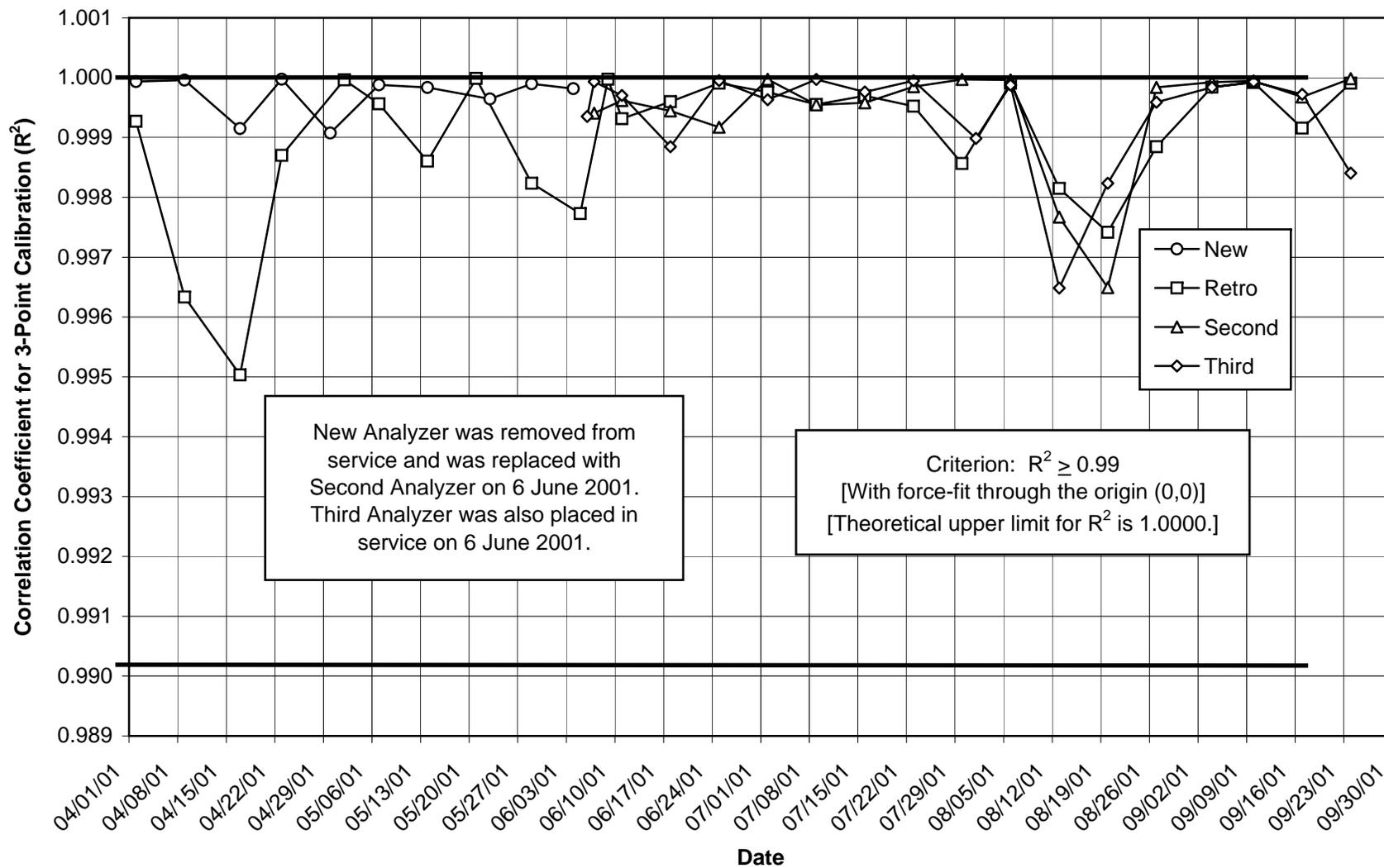


Figure 3a. Percent Recoveries for Three-Point Calibration Standards on the New OC/EC Analyzer

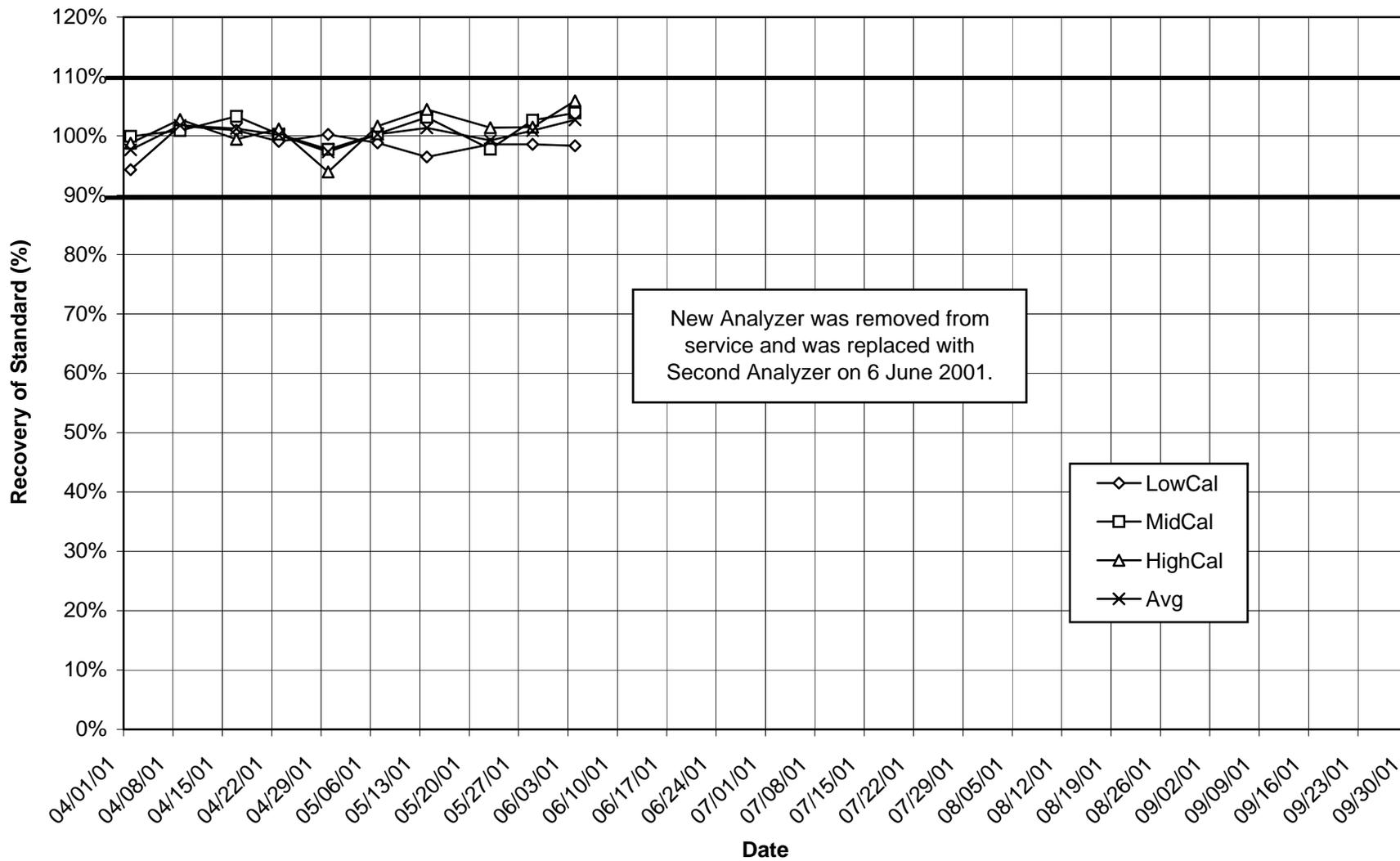


Figure 3b. Percent Recoveries for Three-Point Calibration Standards on the Retrofit OC/EC Analyzer

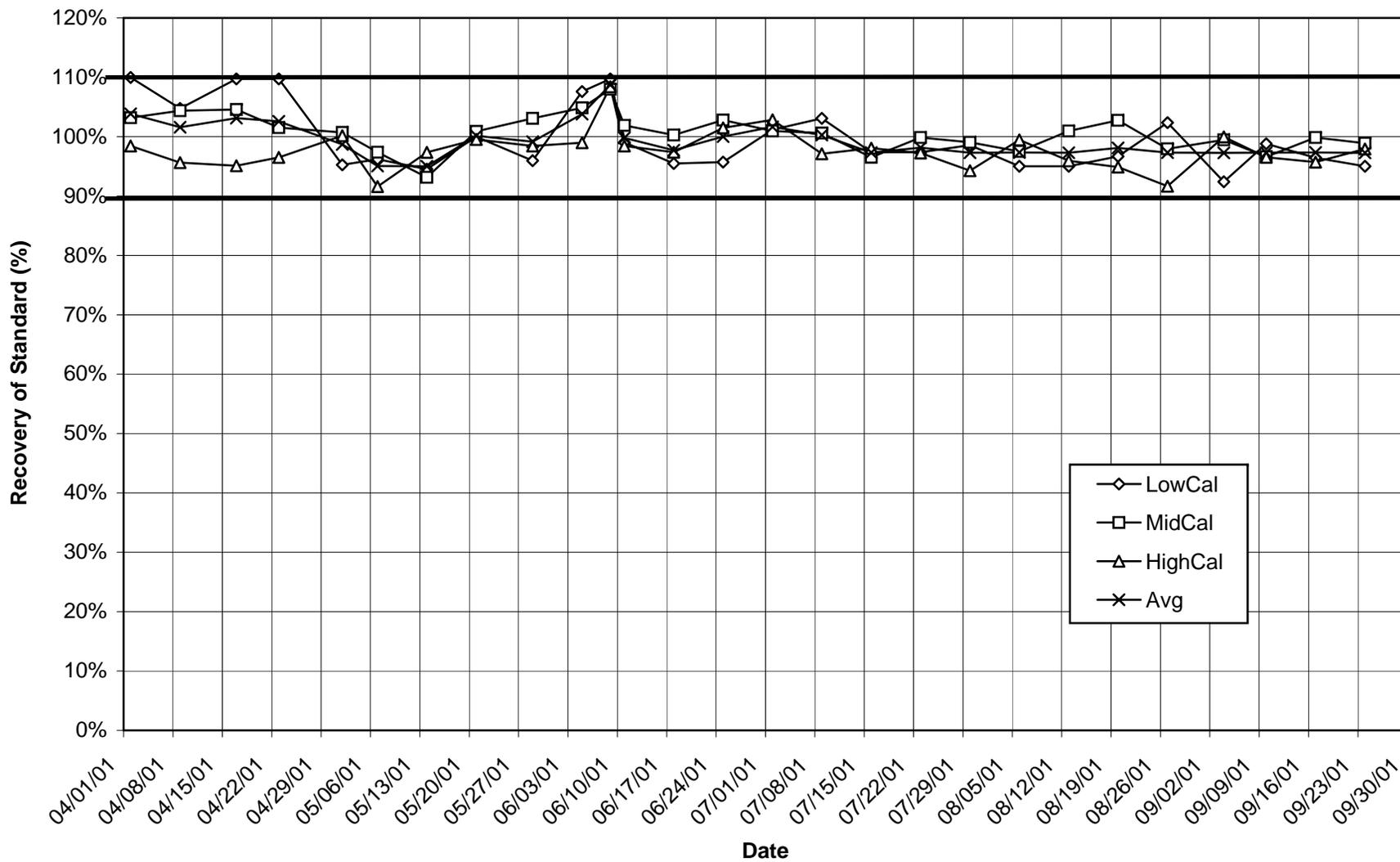


Figure 3c. Percent Recoveries for Three-Point Calibration Standards on the Second OC/EC Analyzer

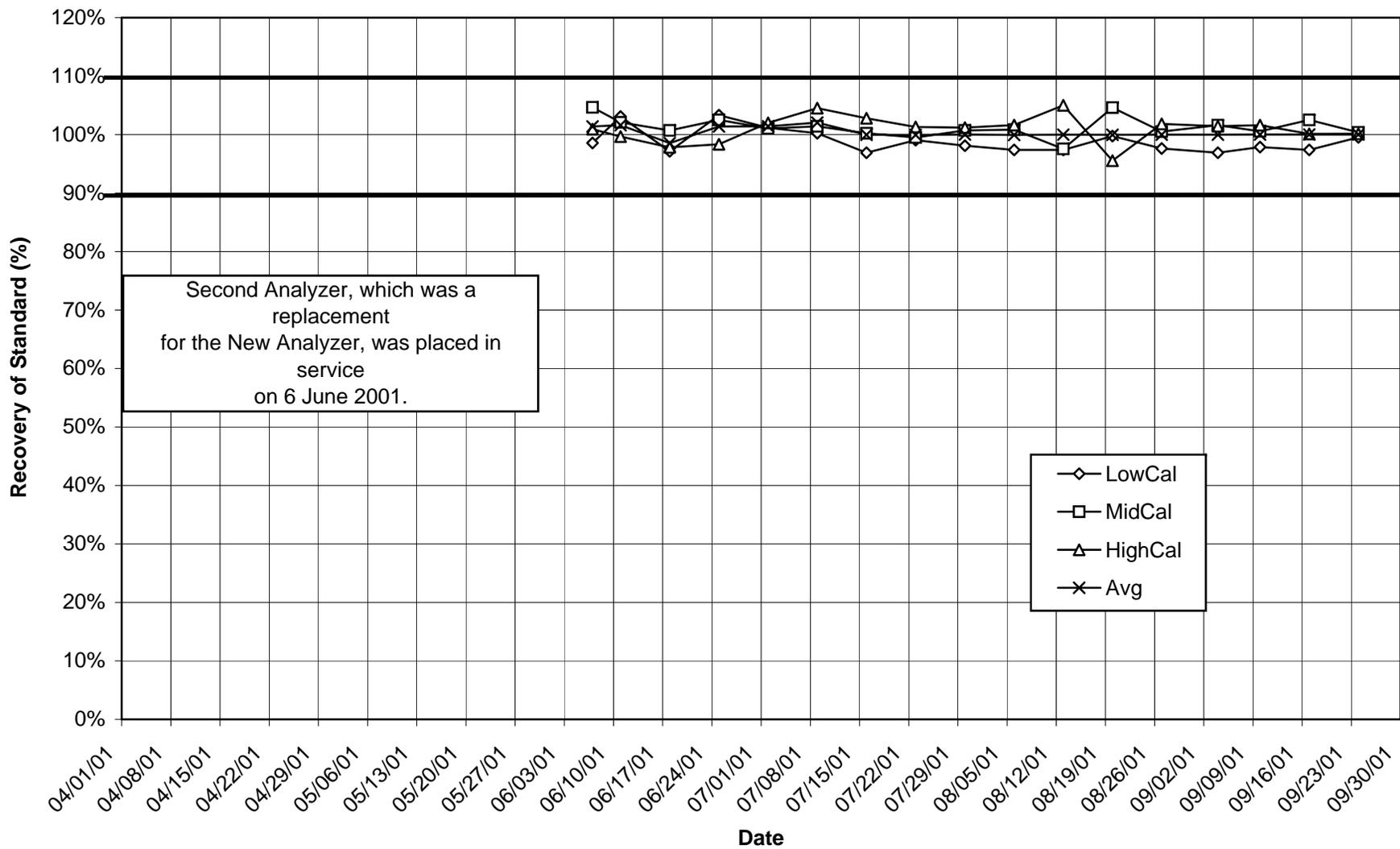


Figure 3d. Percent Recoveries for Three-Point Calibration Standards on the Third OC/EC Analyzer

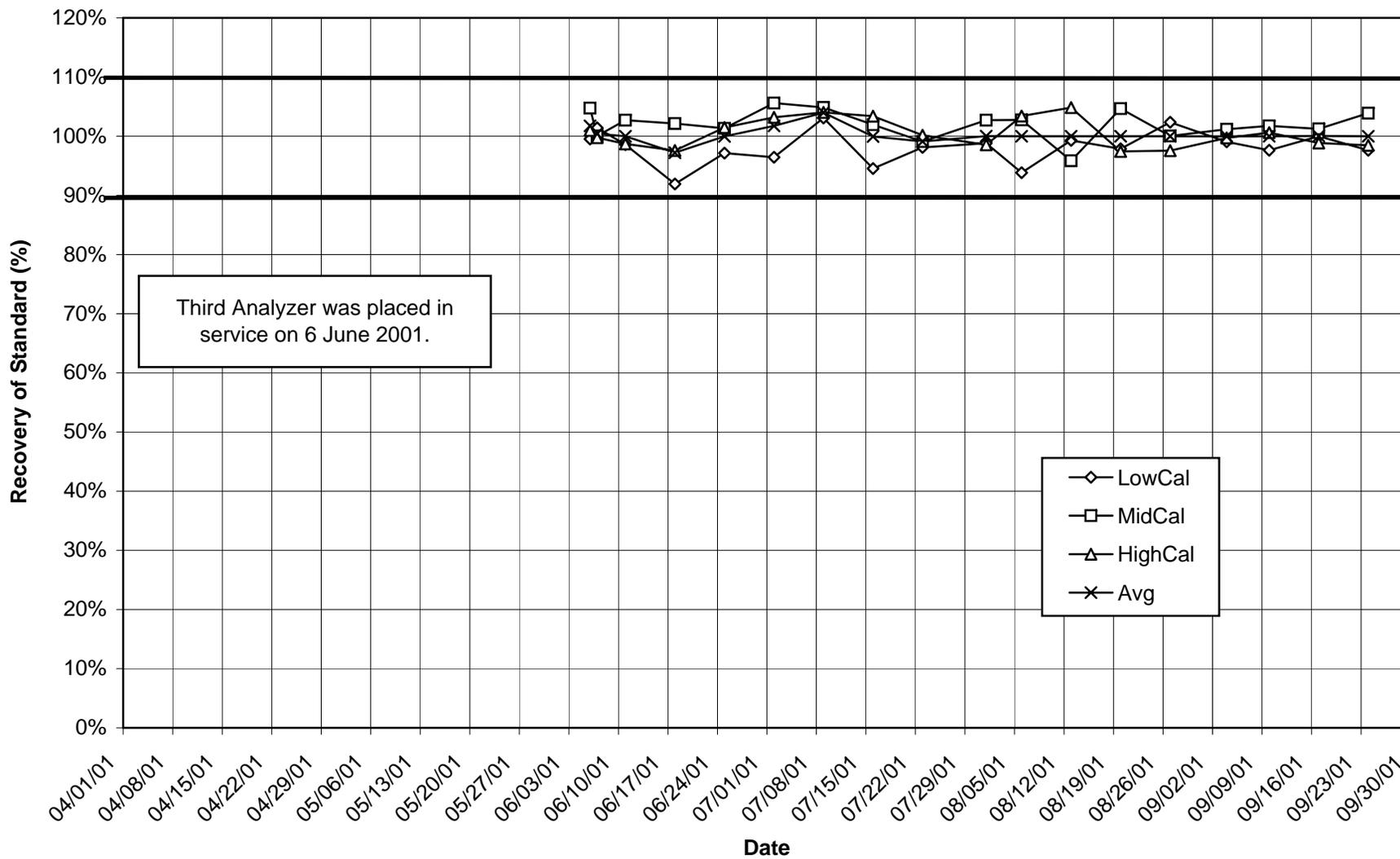


Figure 4a. FID Response Factors for Three-Point Calibration Standards on the New OC/EC Analyzer

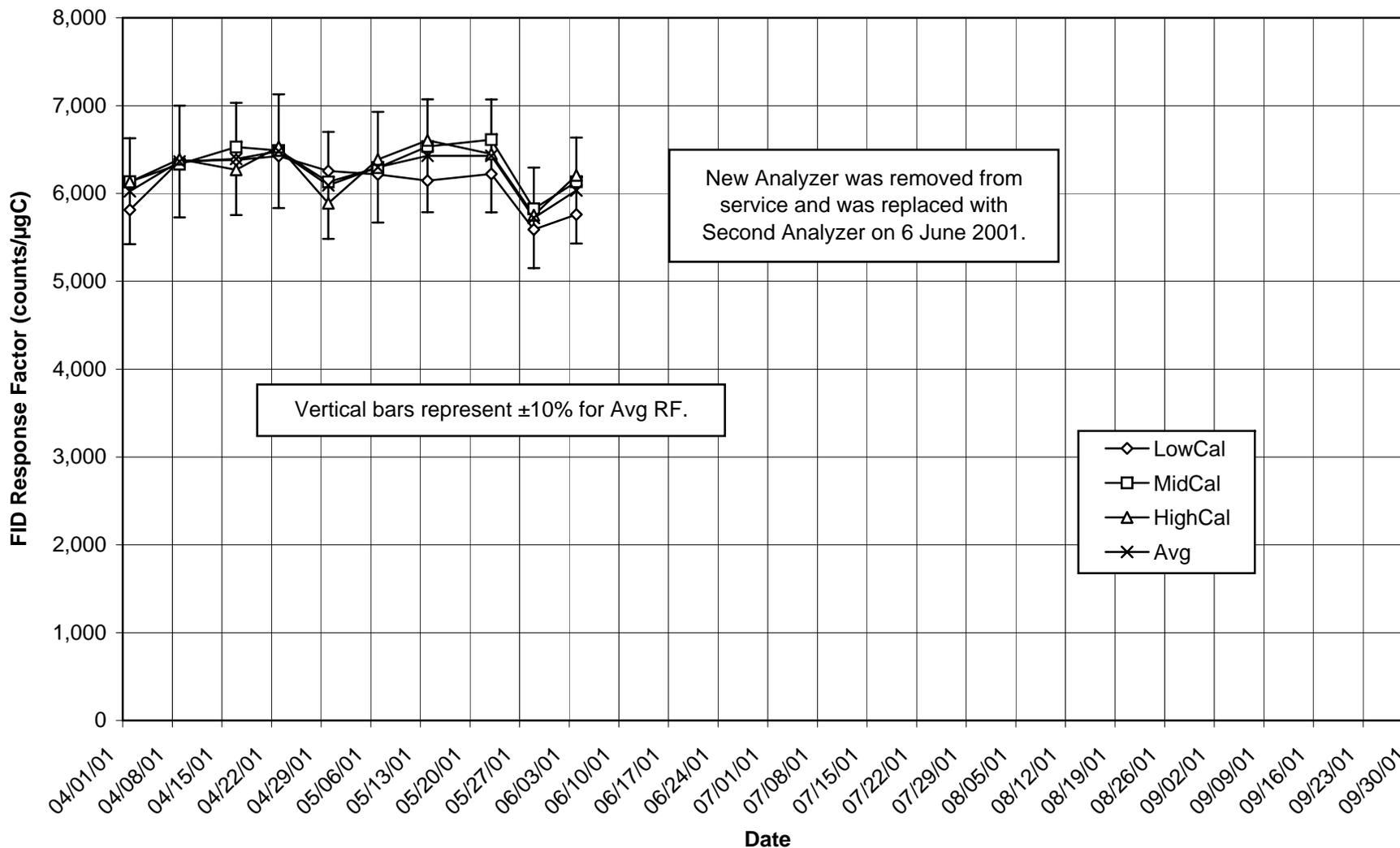


Figure 4b. FID Response Factors for Three-Point Calibration Standards on the Retrofit OC/EC Analyzer

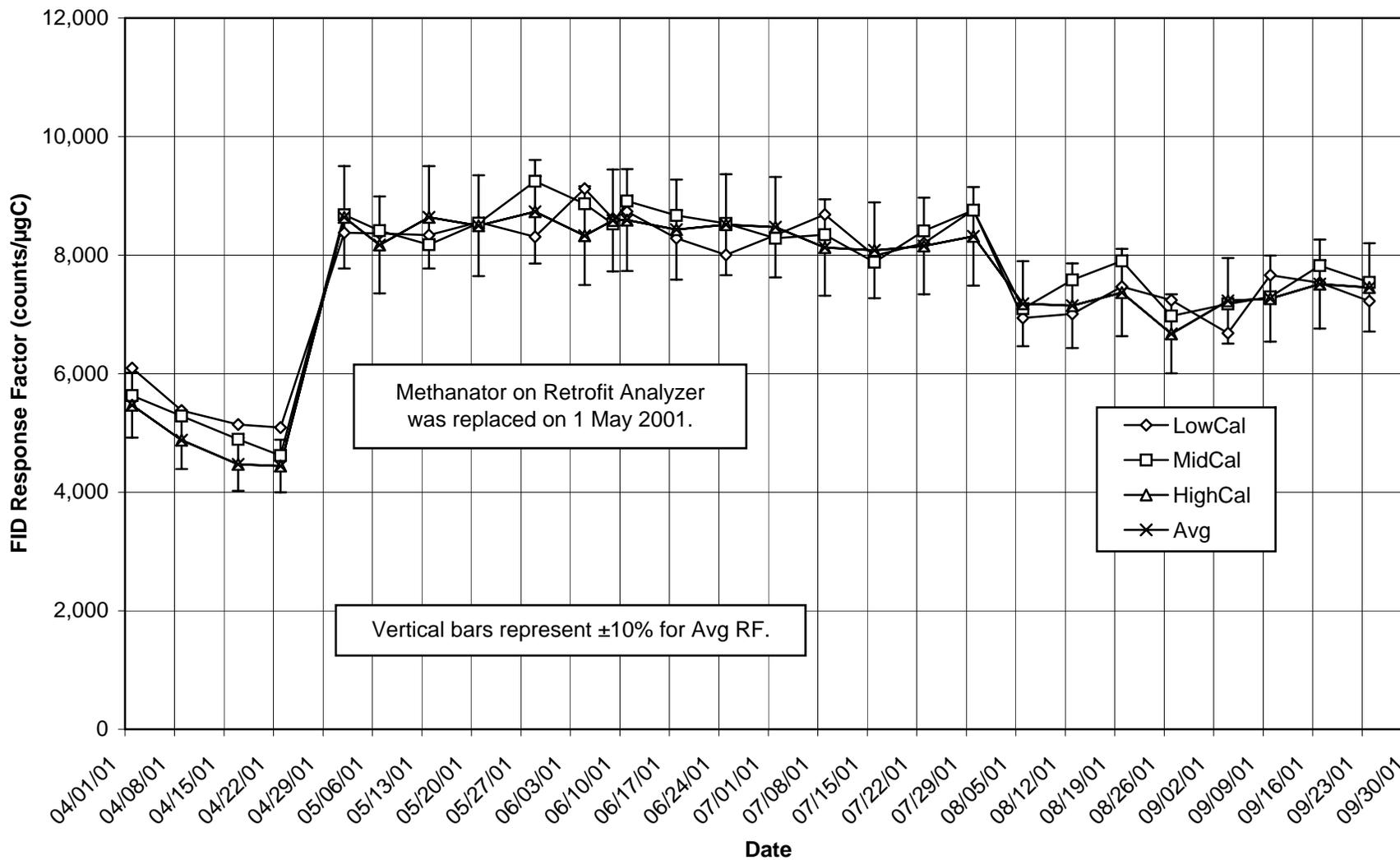


Figure 4c. FID Response Factors for Three-Point Calibration Standards on the Second OC/EC Analyzer

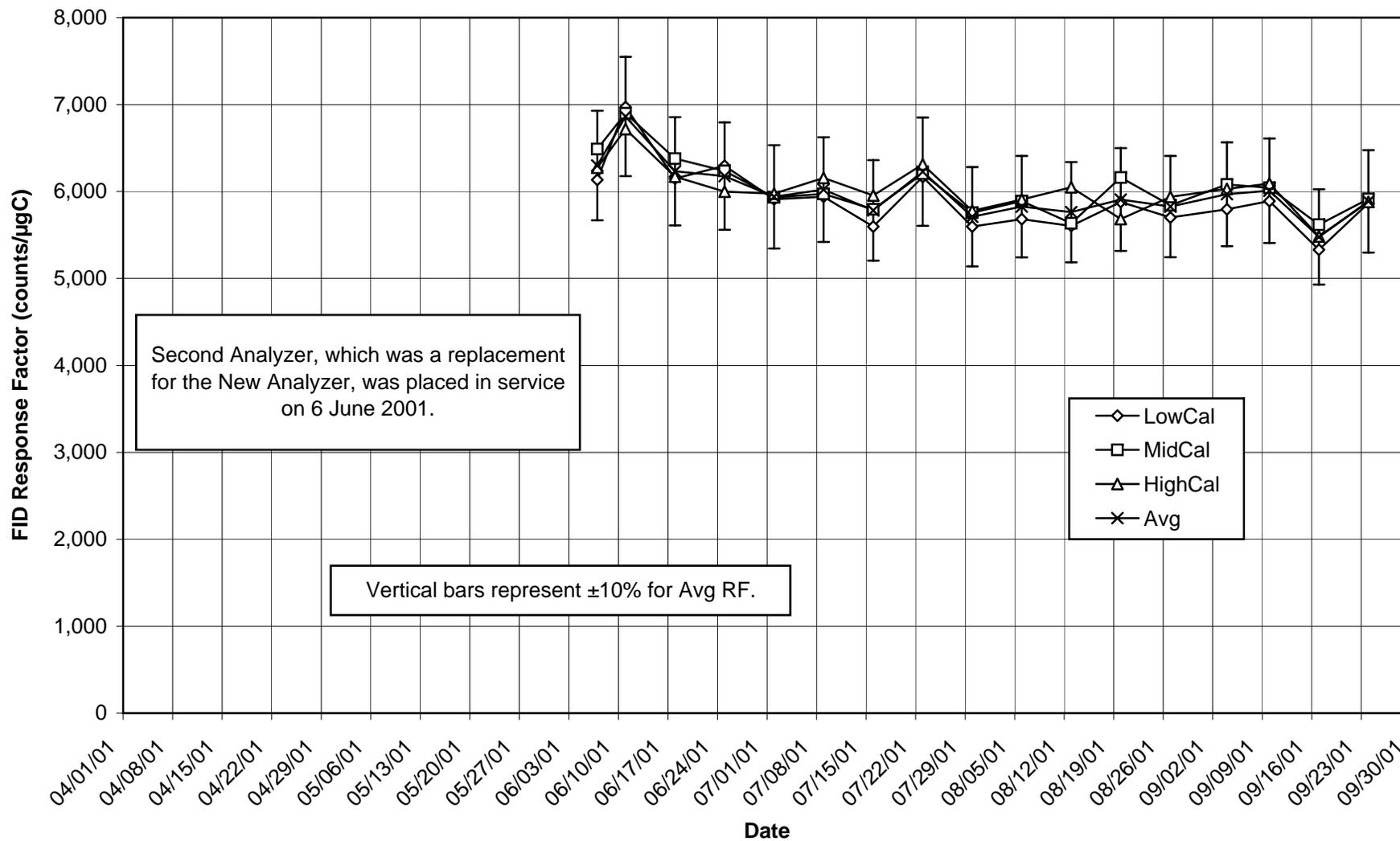


Figure 4d. FID Response Factors for Three-Point Calibration Standards on the Third OC/EC Analyzer

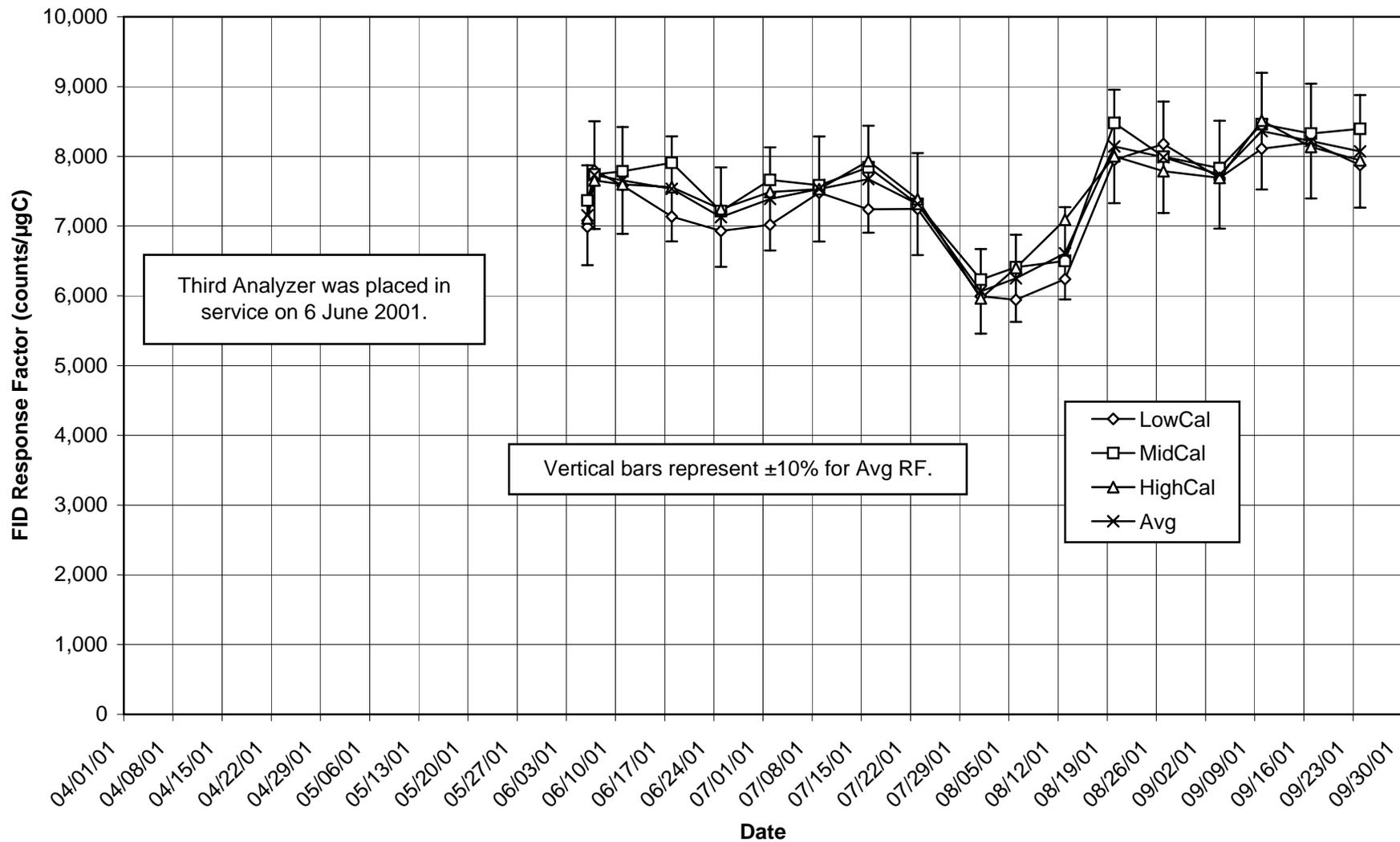


Figure 5. Slopes of Calibration Plots for Three-Point Calibrations With Force-Fit Through Origin (0,0)

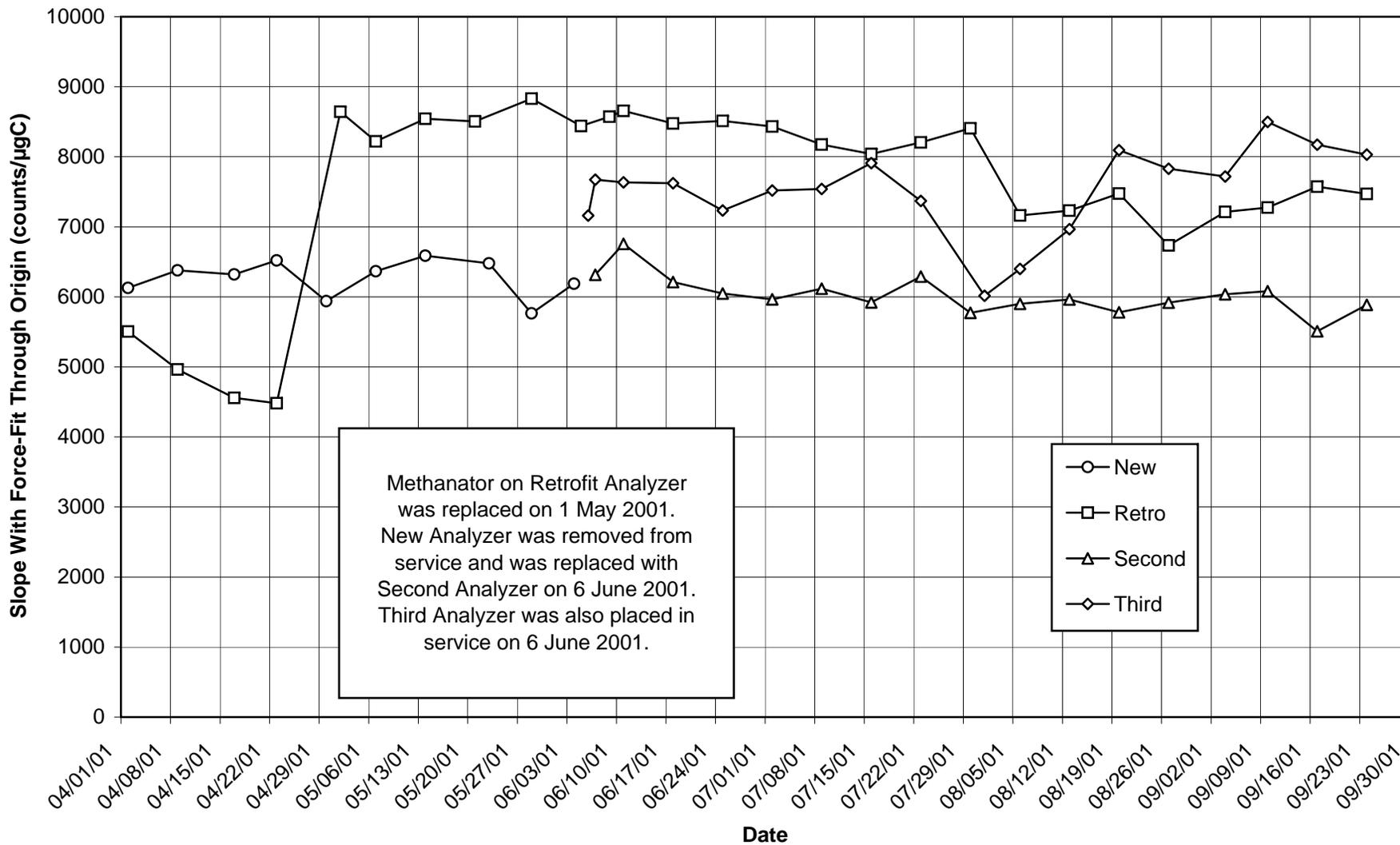


Figure 6. Daily Calibration Checks

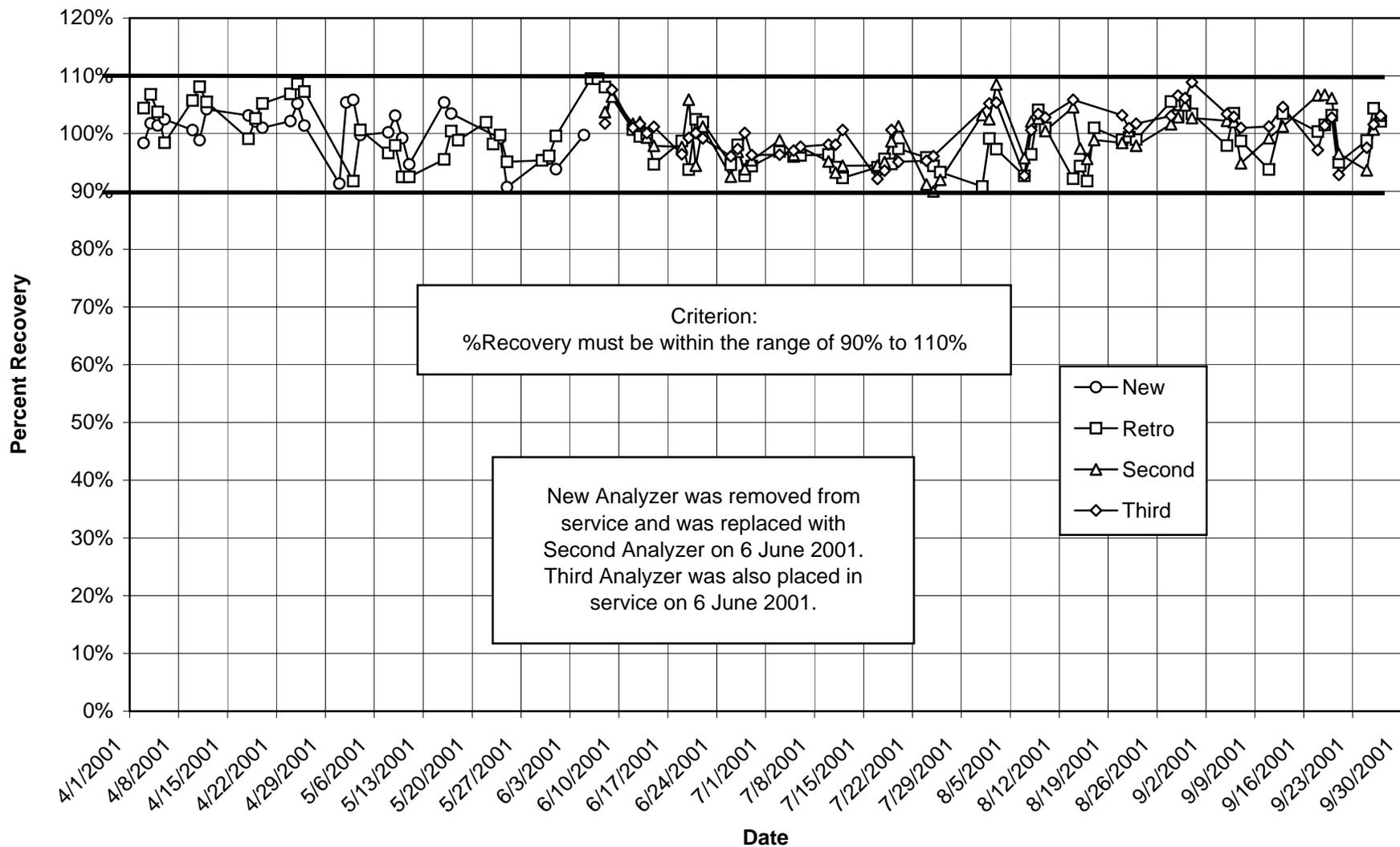


Figure 7a: Relative Percent Difference of Duplicates vs. Average Value for TC on New OC/EC Analyzer - April 1, 2001, through June 4, 2001

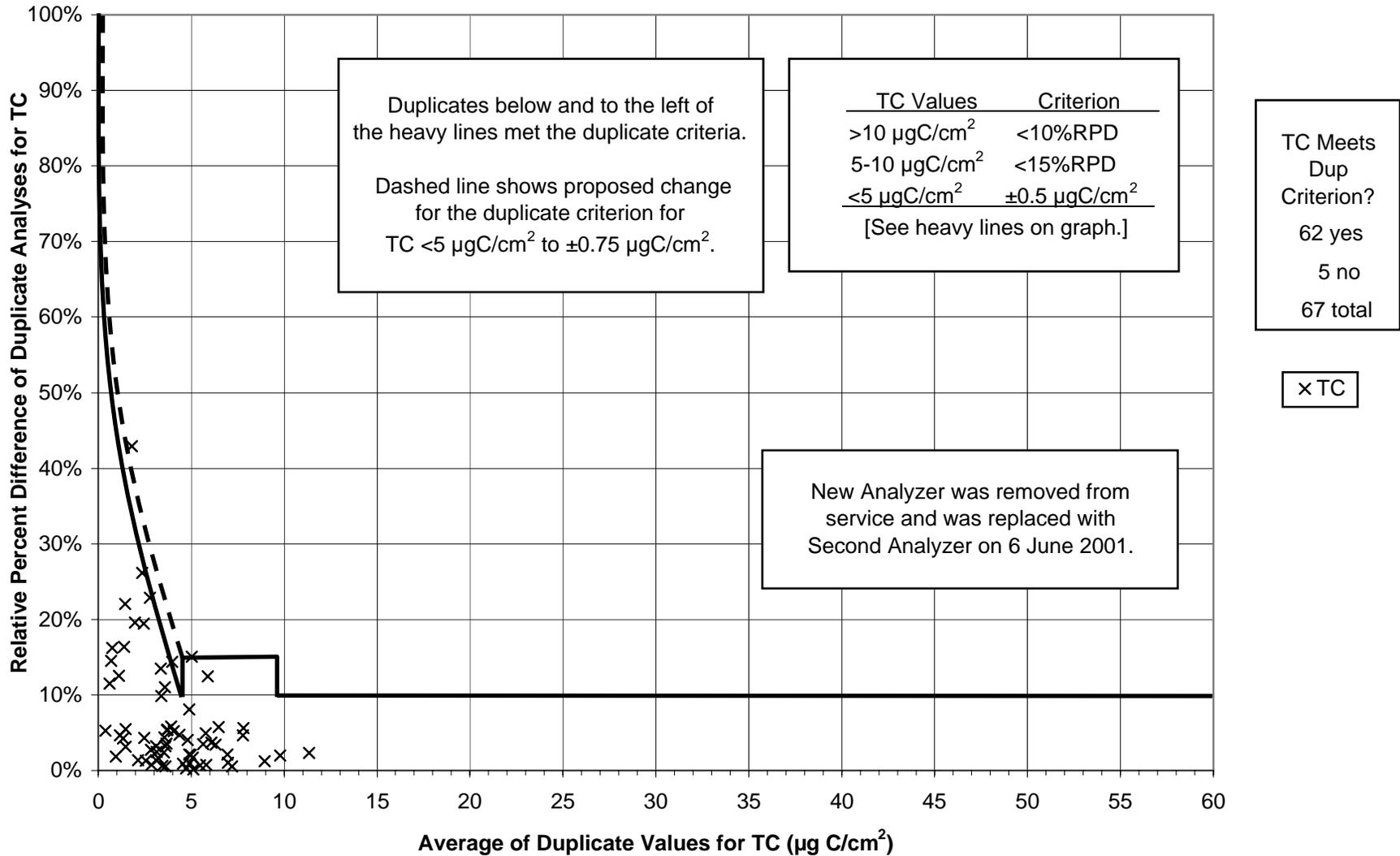


Figure 7b: Relative Percent Difference of Duplicates vs. Average Value for TC on Retrofit OC/EC Analyzer - April 1, 2001, through September 30, 2001

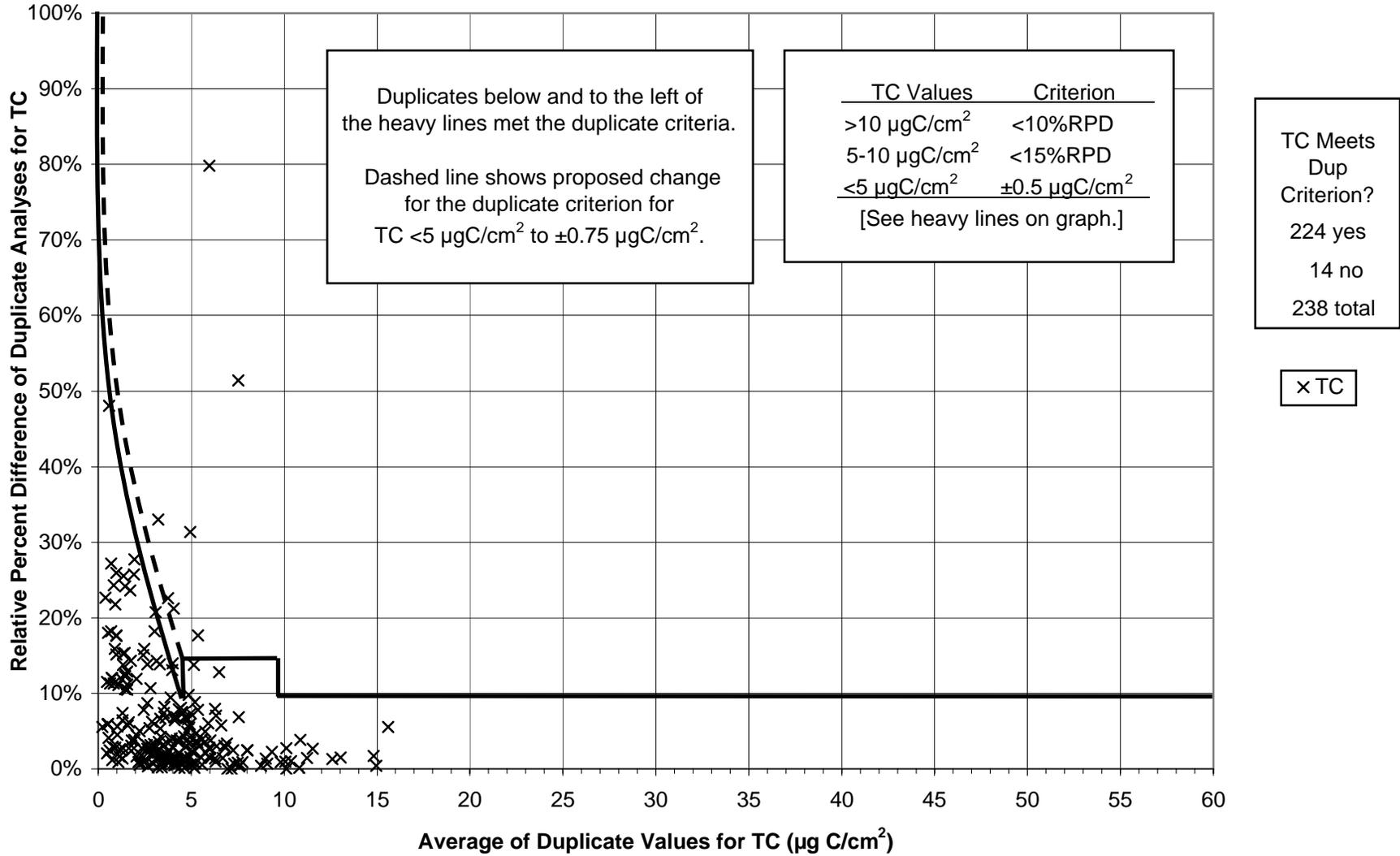


Figure 7c: Relative Percent Difference of Duplicates vs. Average Value for TC on Second OC/EC Analyzer - June 6, 2001, through September 30, 2001

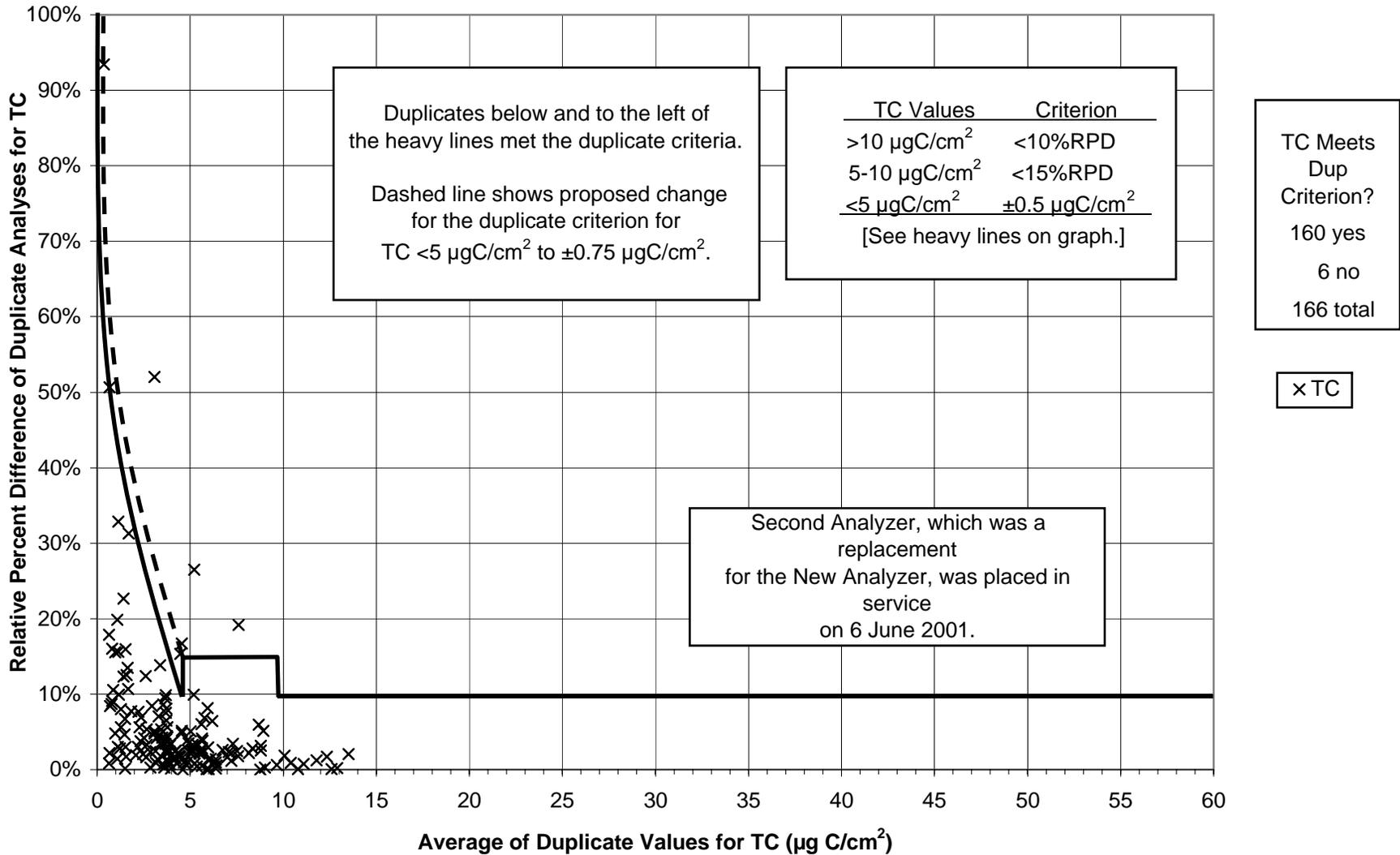
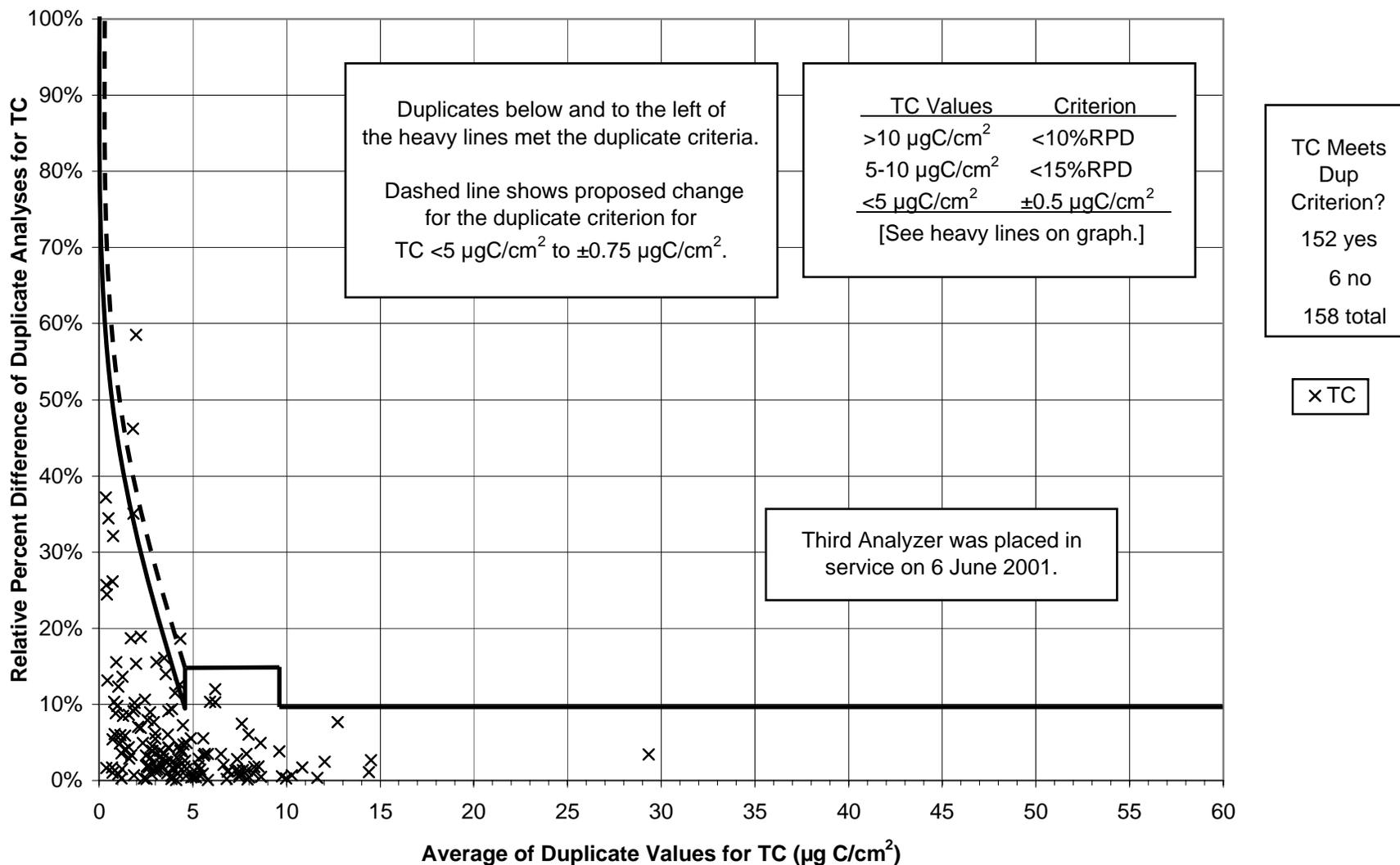
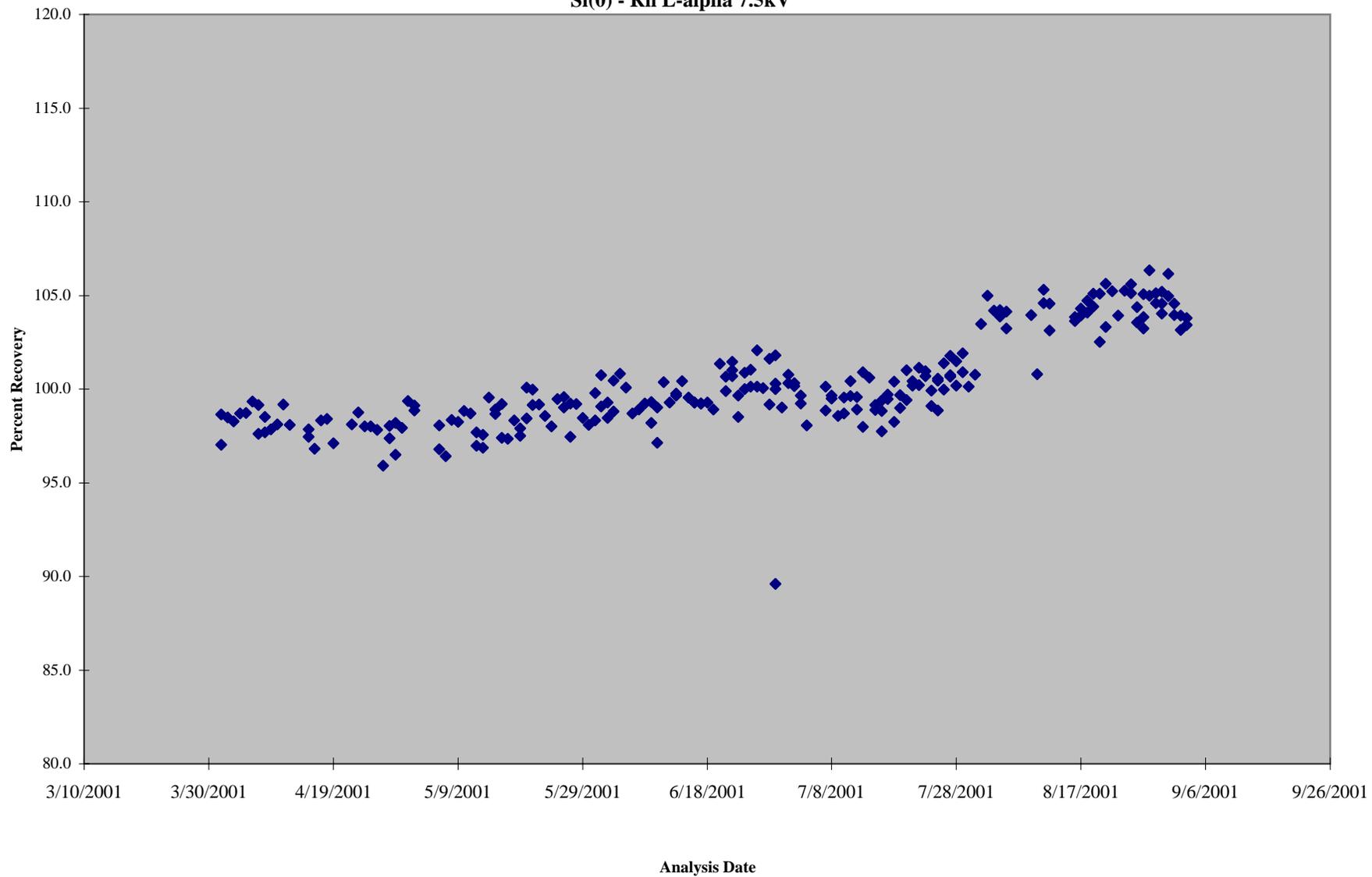


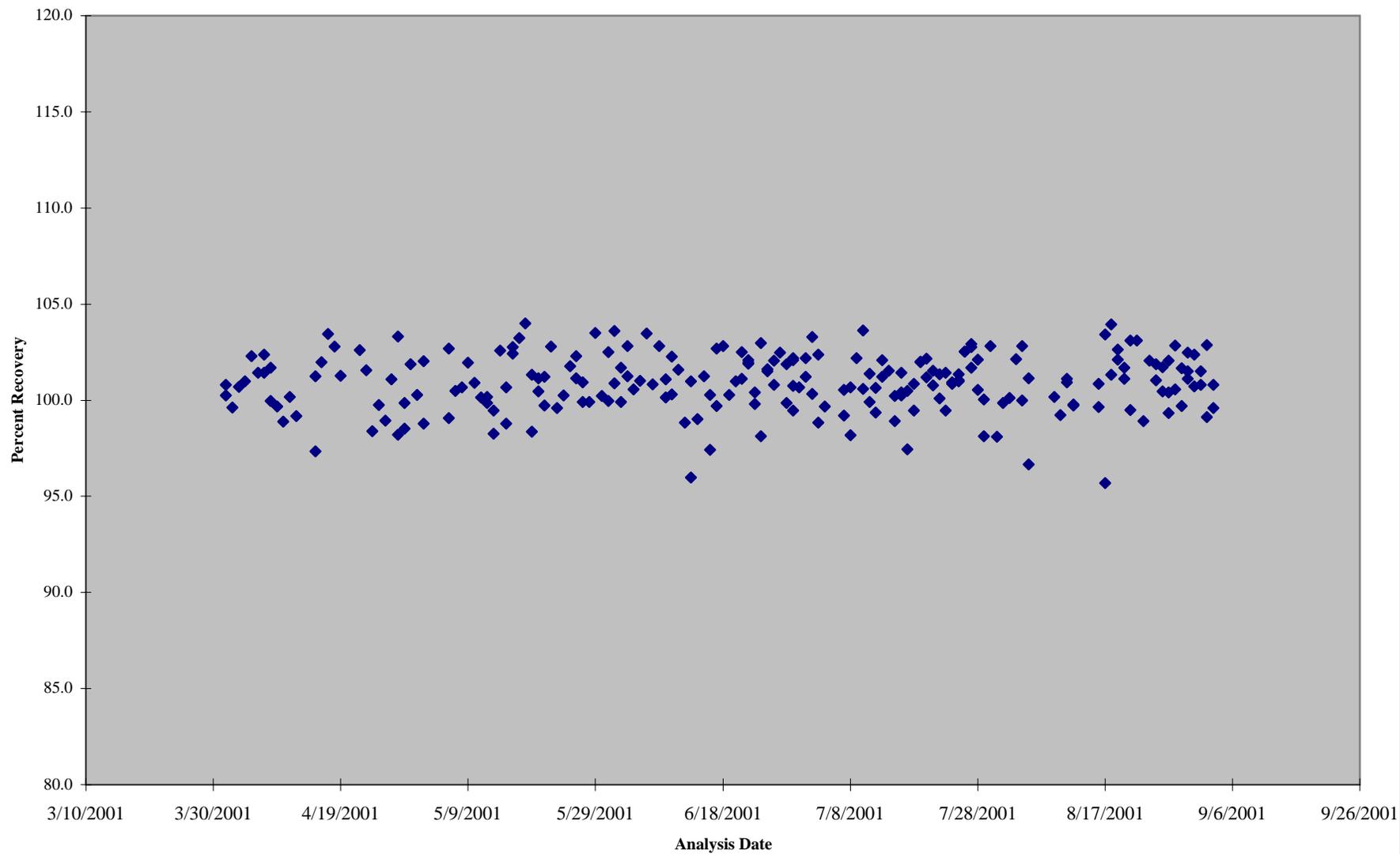
Figure 7d: Relative Percent Difference of Duplicates vs. Average Value for TC on Third OC/EC Analyzer - June 6, 2001, through September 30, 2001



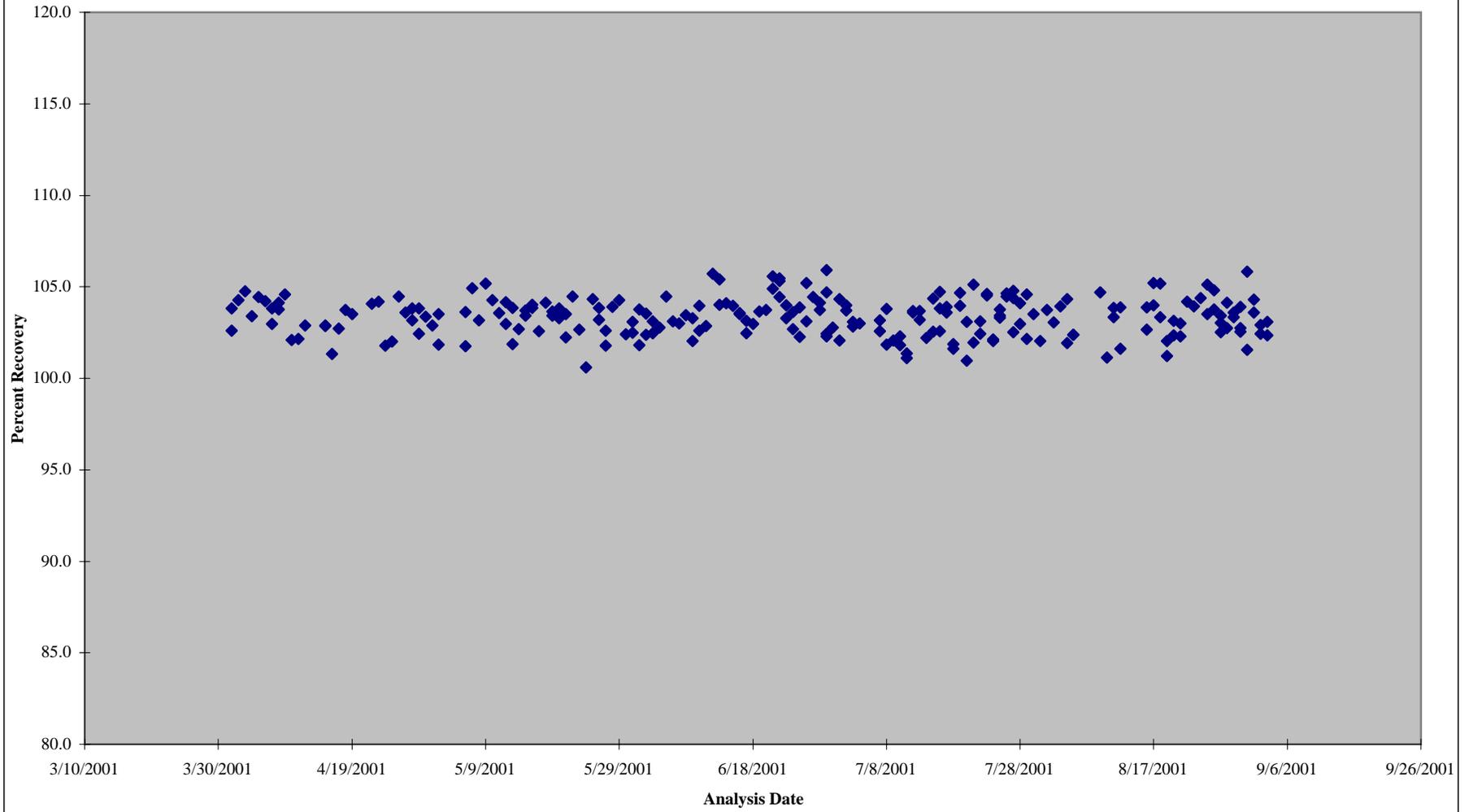
**Figure 8. Recovery Precision for
Si(0) - Rh L-alpha 7.5kV**



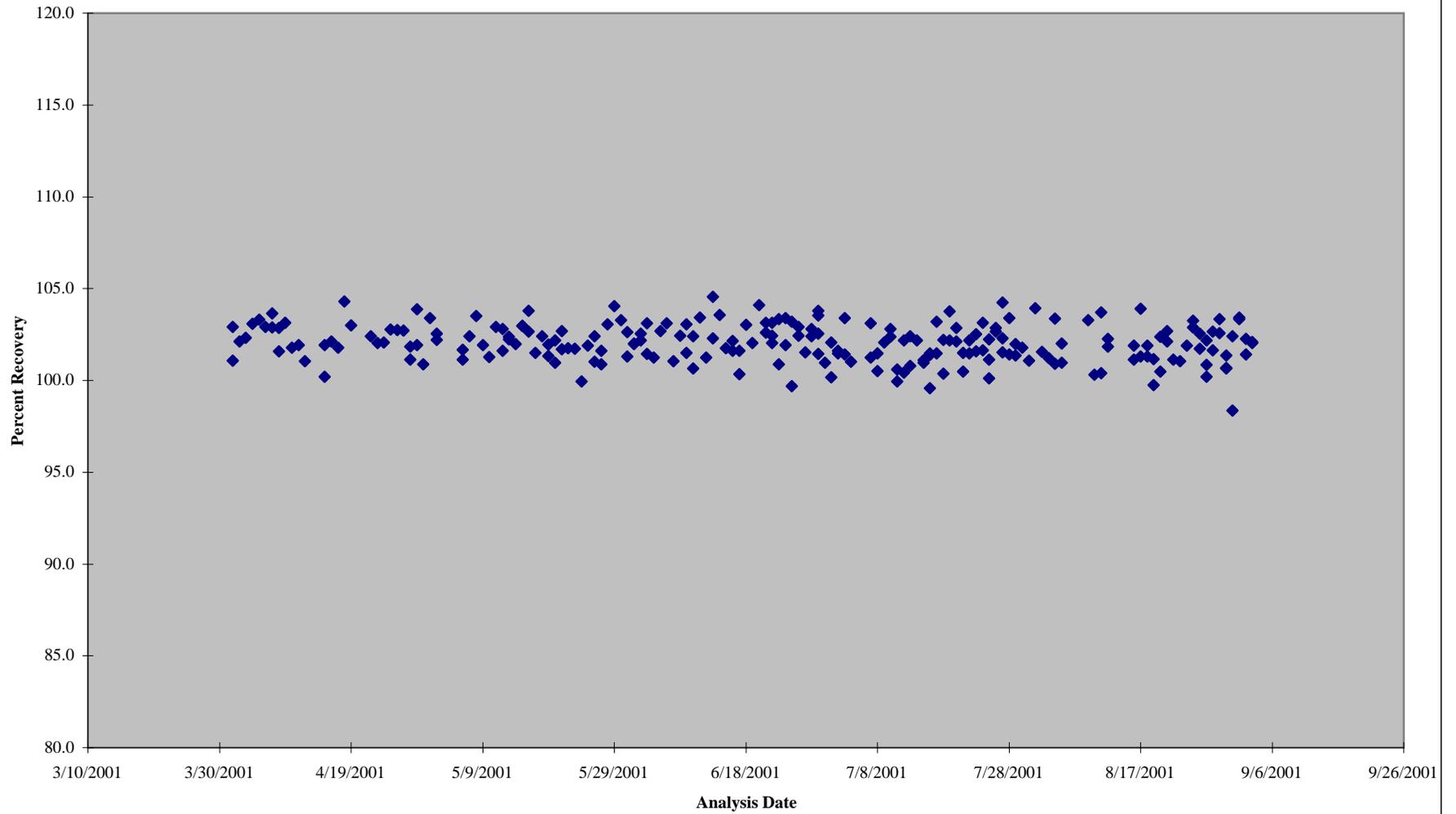
**Figure 9. Recovery Precision for
Si(1) - Ti target 25kV**



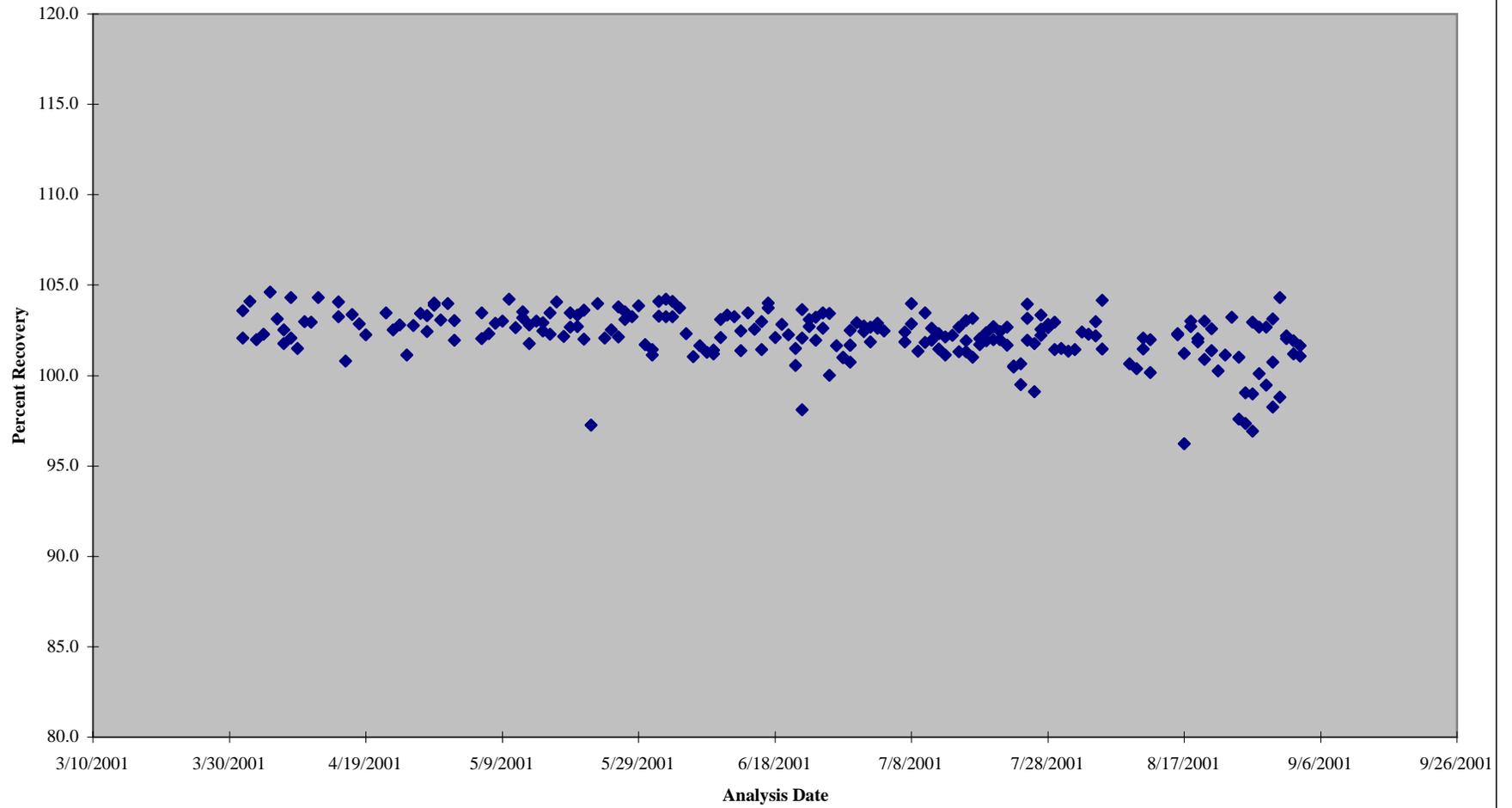
**Figure 10. Recovery Precision for
Ti(2) - Fe target 35mA**



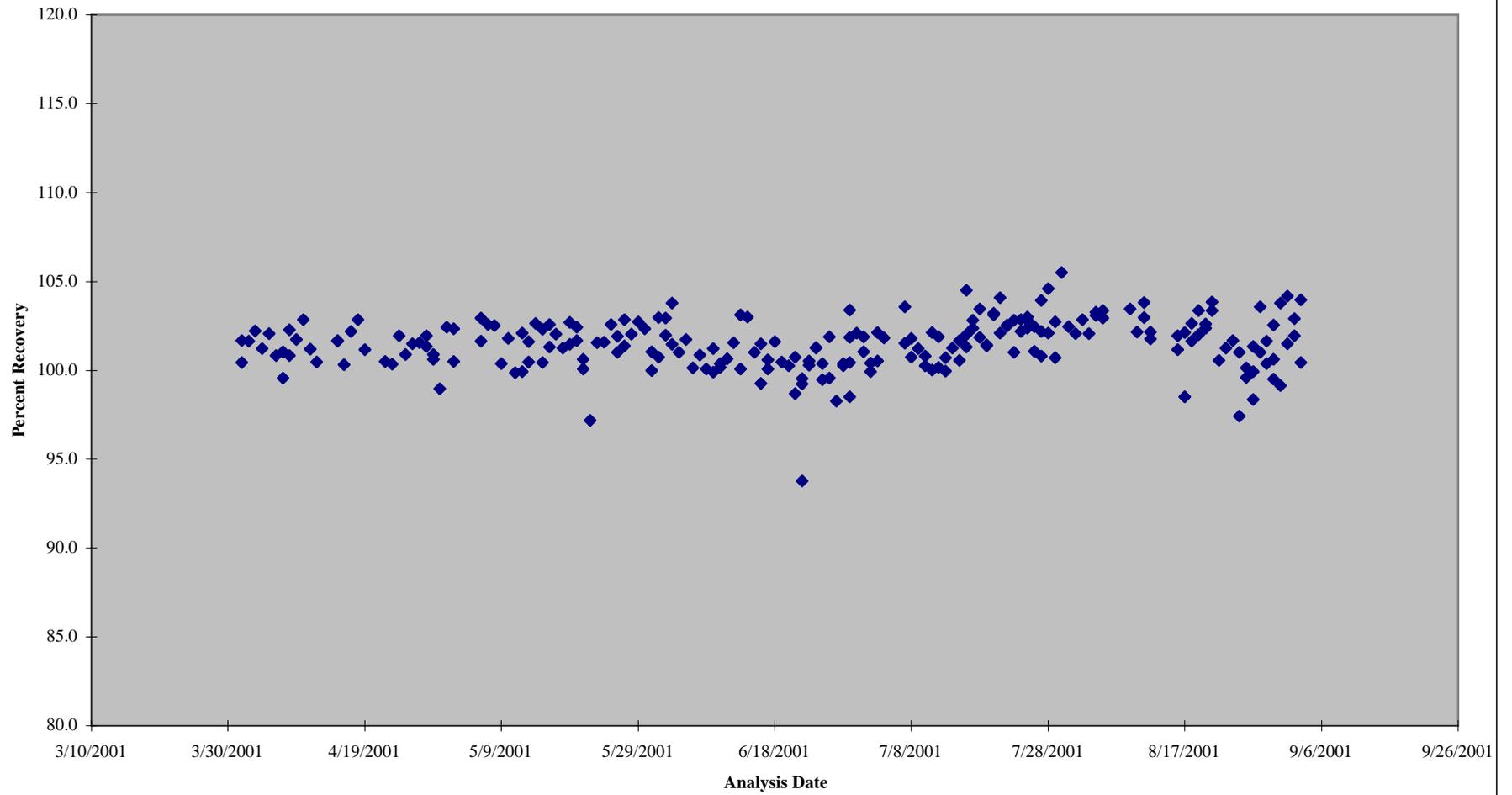
**Figure 11. Recovery Precision for
Fe(3) - Ge target 35mA**



**Figure 12. Recovery Precision for
Se(4) - Rh K-alpha 35kV**



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



**Figure 14. Recovery Precision for
Cd(5) W filter 55kV**

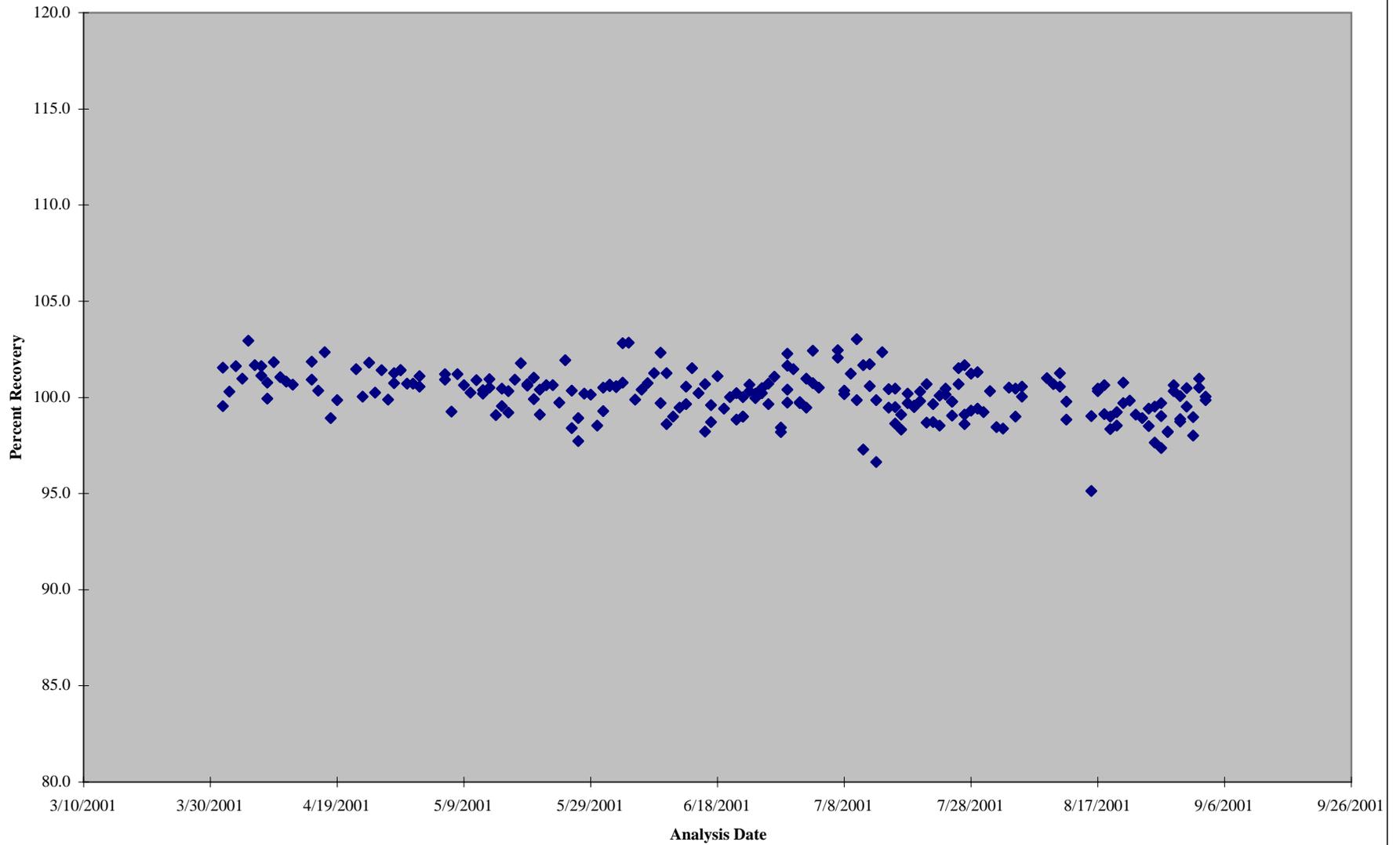


Figure 15. Recovery for Aluminum (AL) in NIST SRM 1832

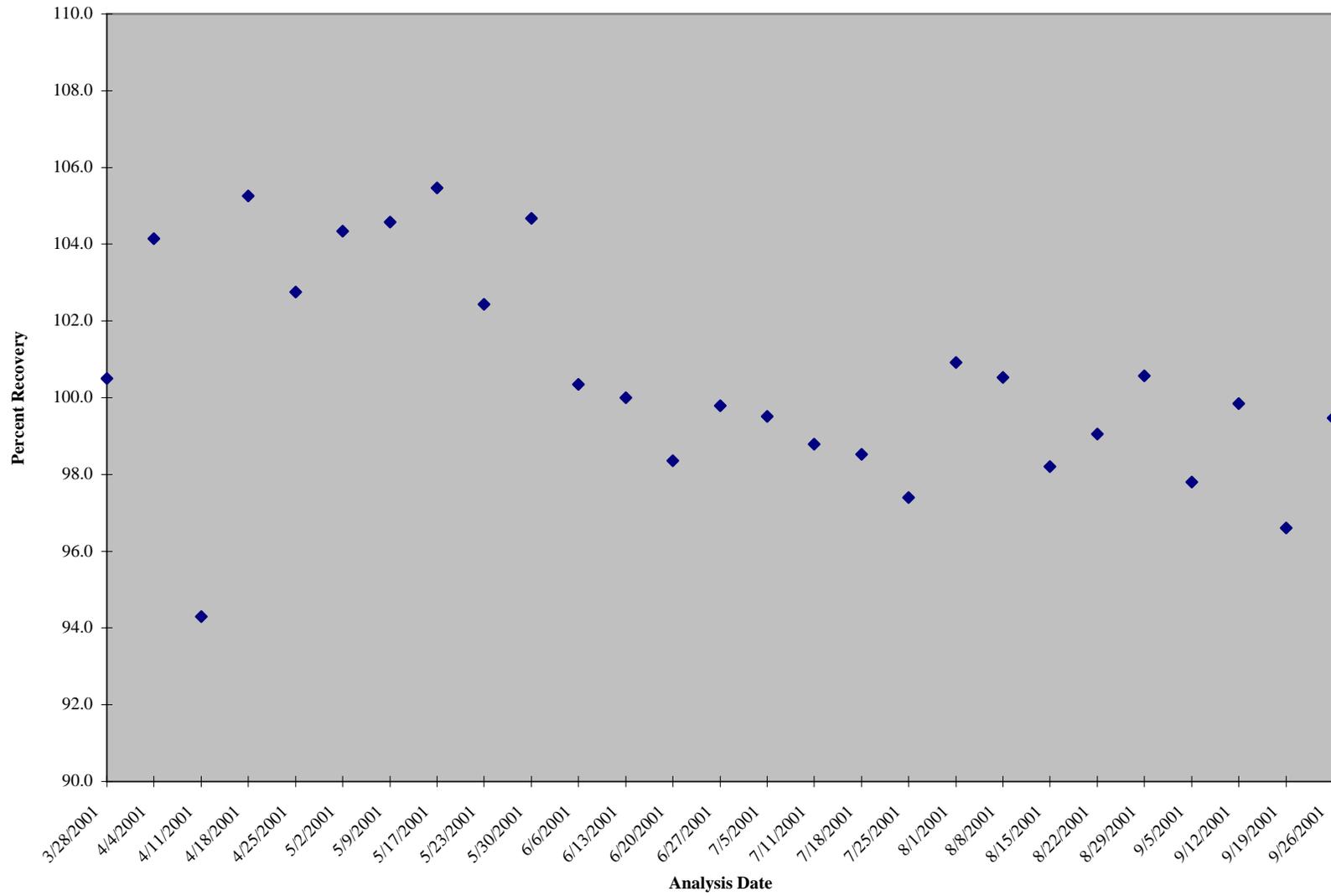


Figure 16. Recovery of Silicon (Si) in NIST SRM 1832

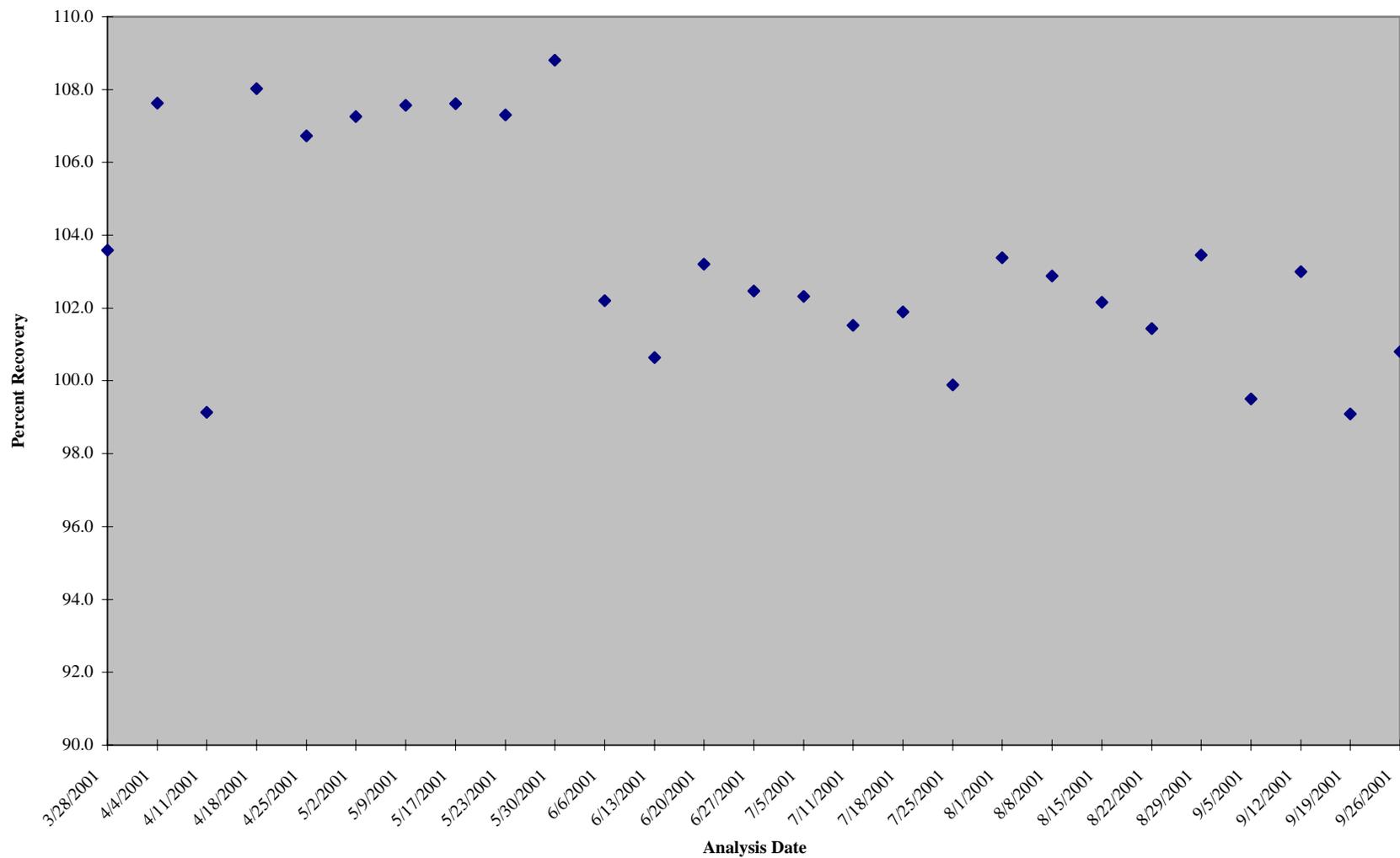


Figure 17. Recovery of Silicon (Si) in NIST SRM 1833

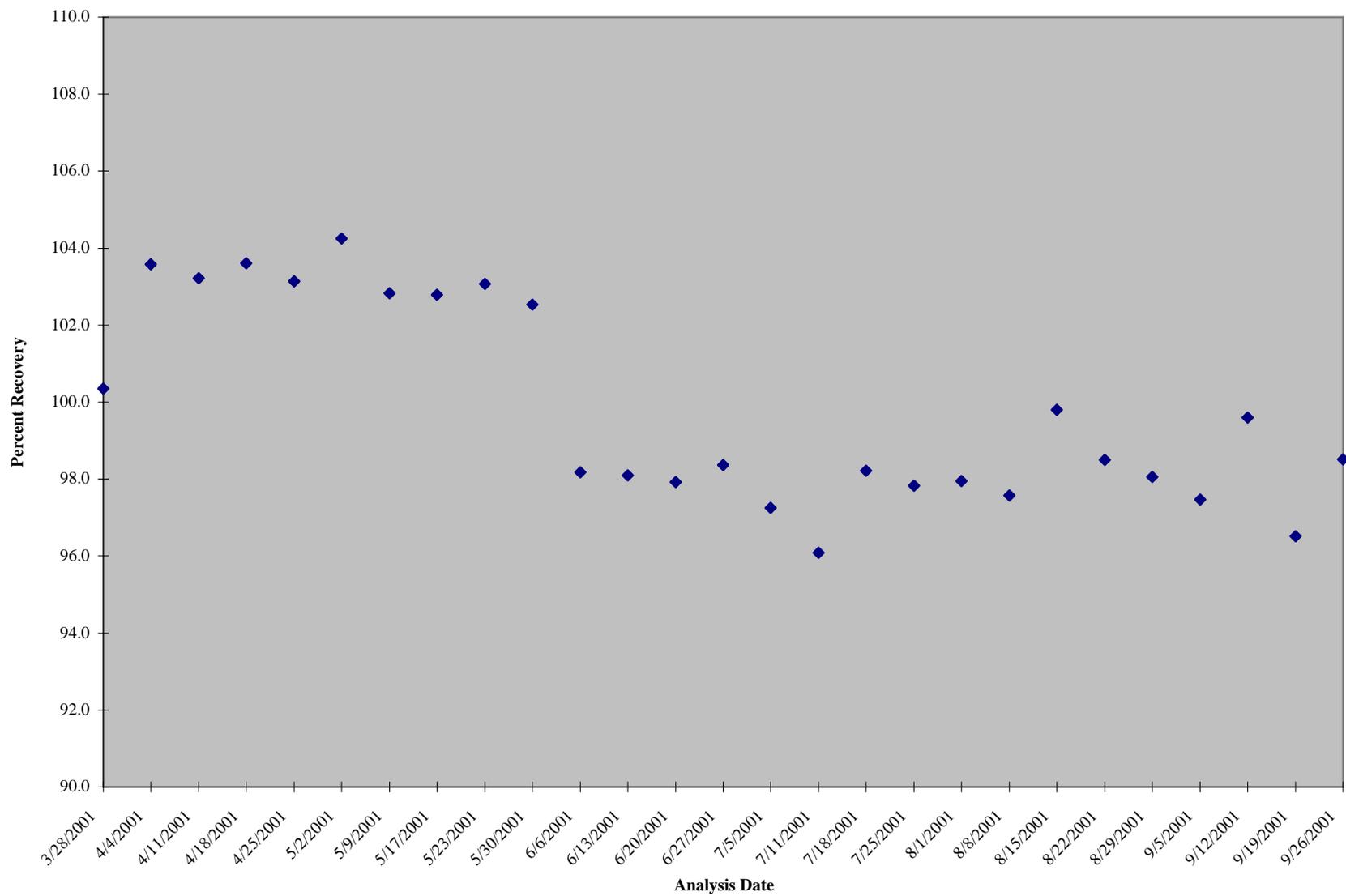


Figure 18. Recovery for Sulfur (S) in NIST SRM 2708

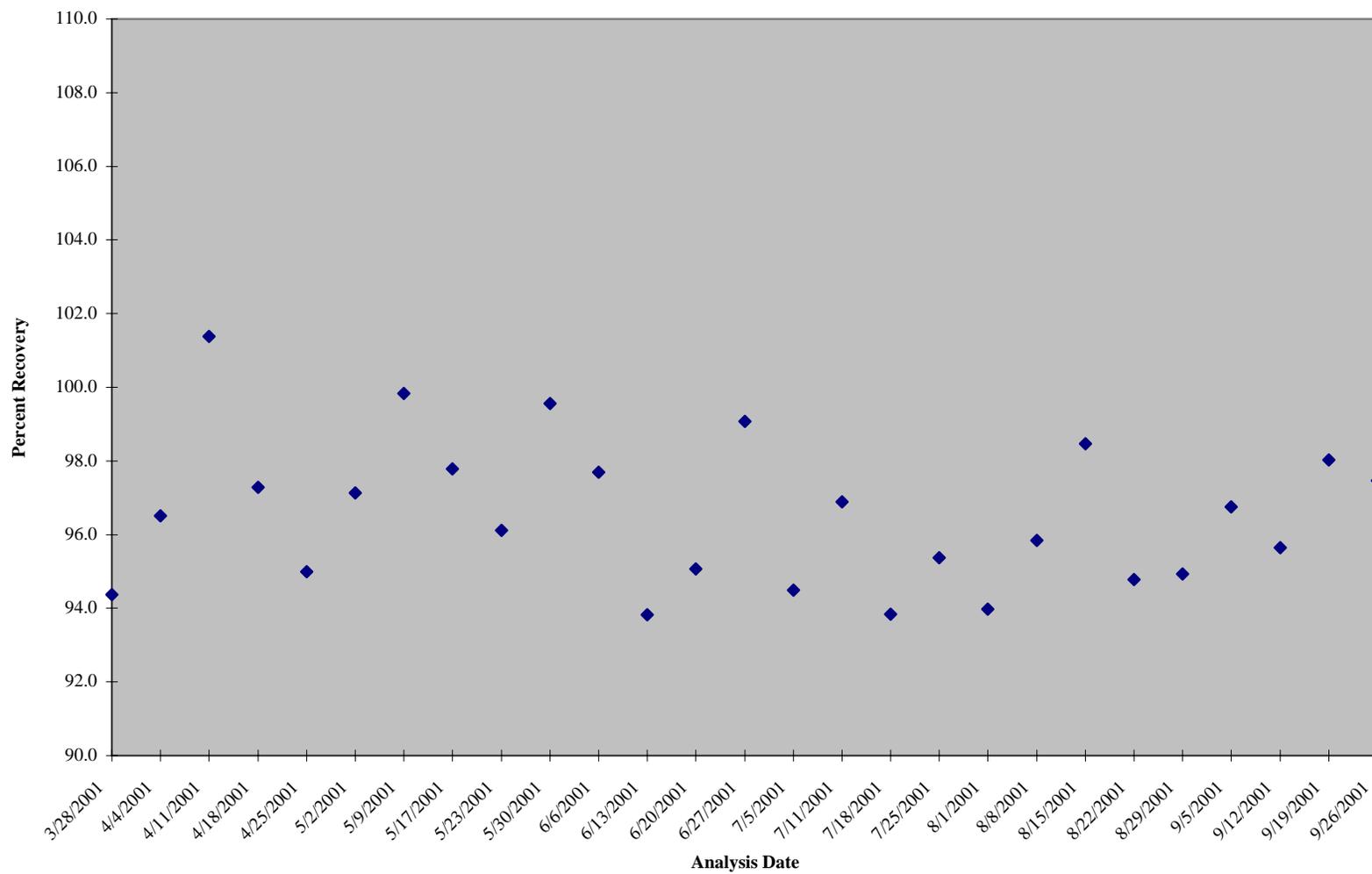


Figure 19. Recovery for Potassium (K) in NIST SRM 1833

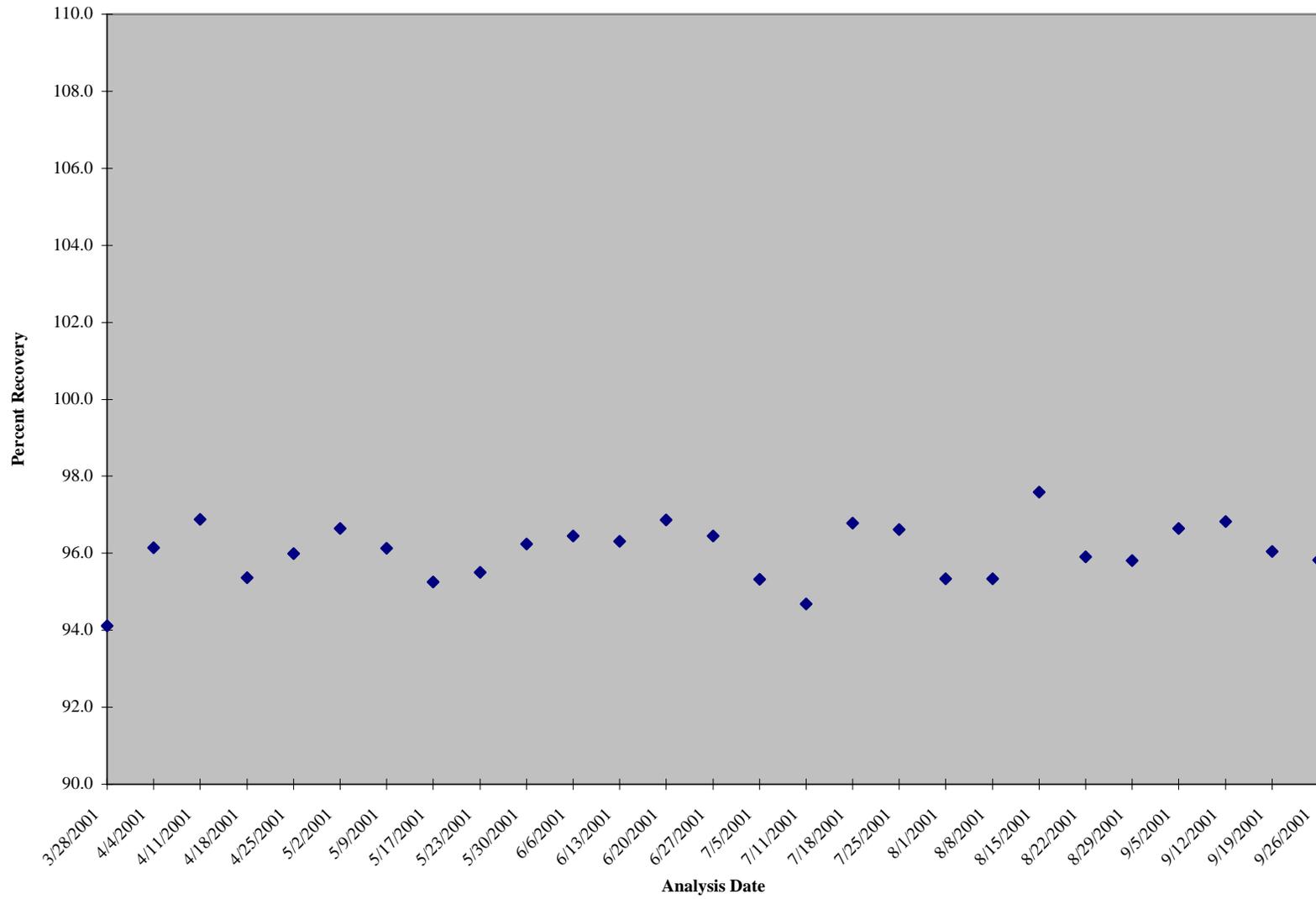


Figure 20. Recovery for Calcium (Ca) in NIST SRM 1832

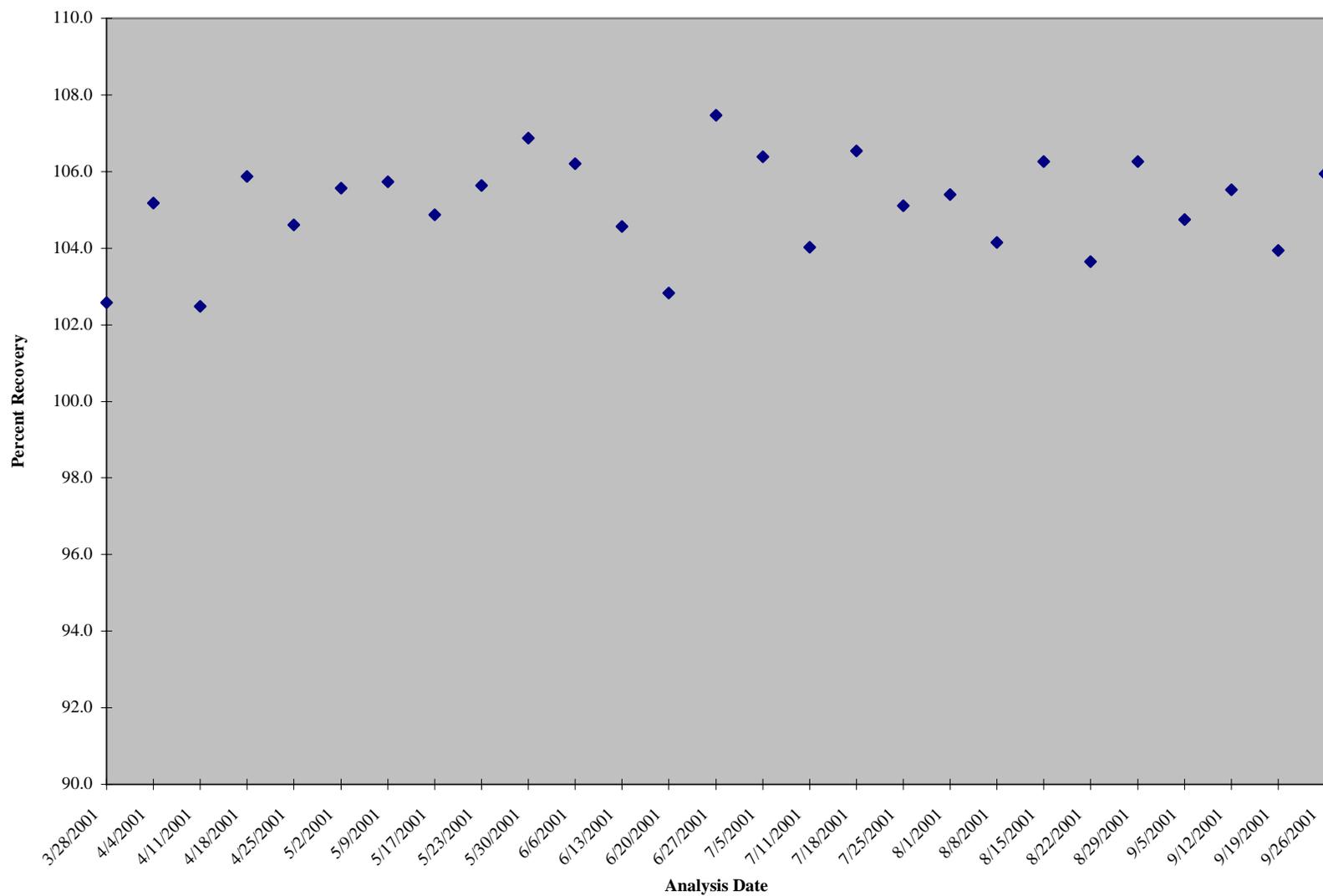


Figure 21. Recovery for Titanium (Ti) in NIST SRM 1833

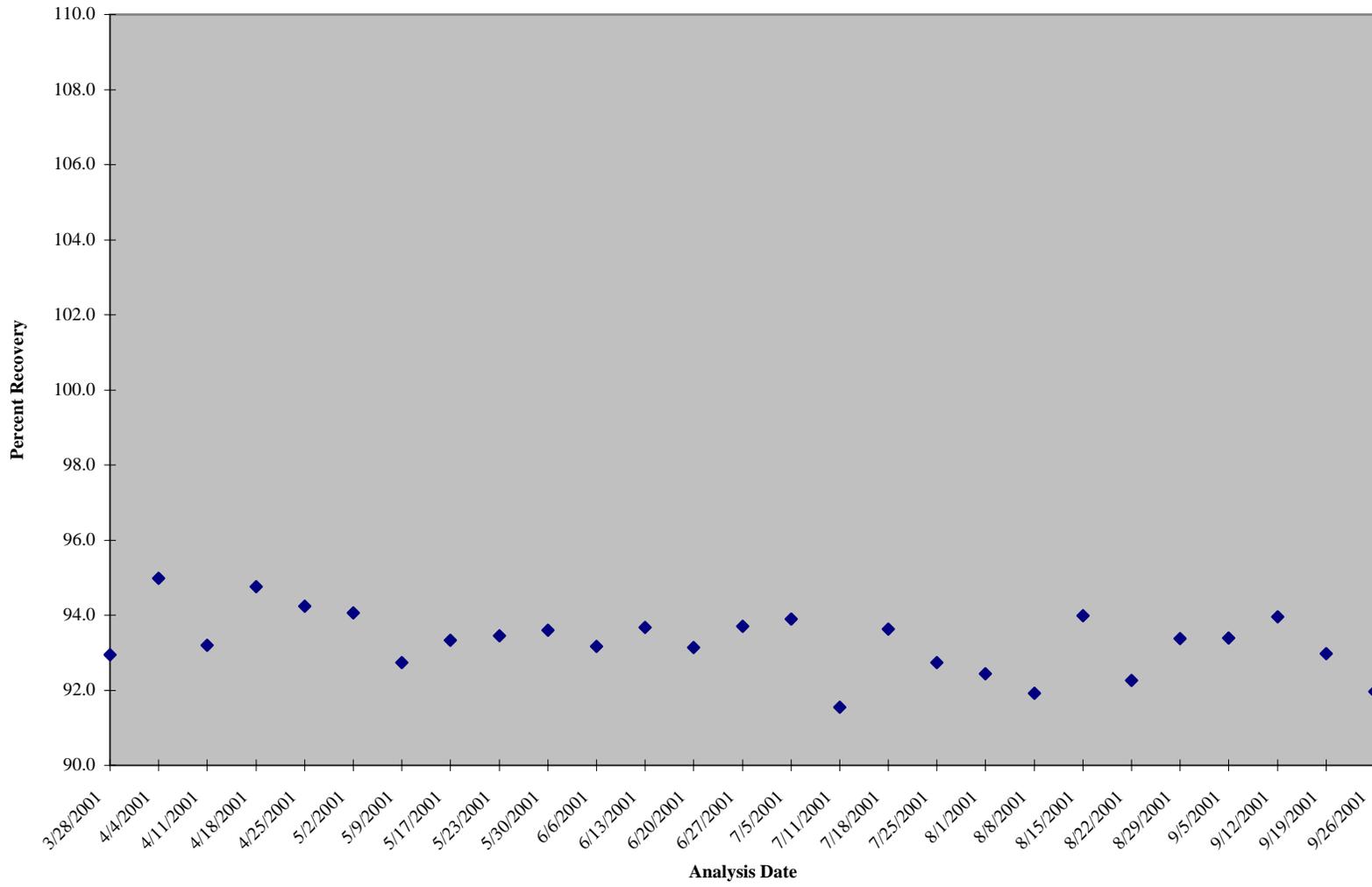


Figure 22. Recovery of Vanadium (V) in NIST SRM 1832

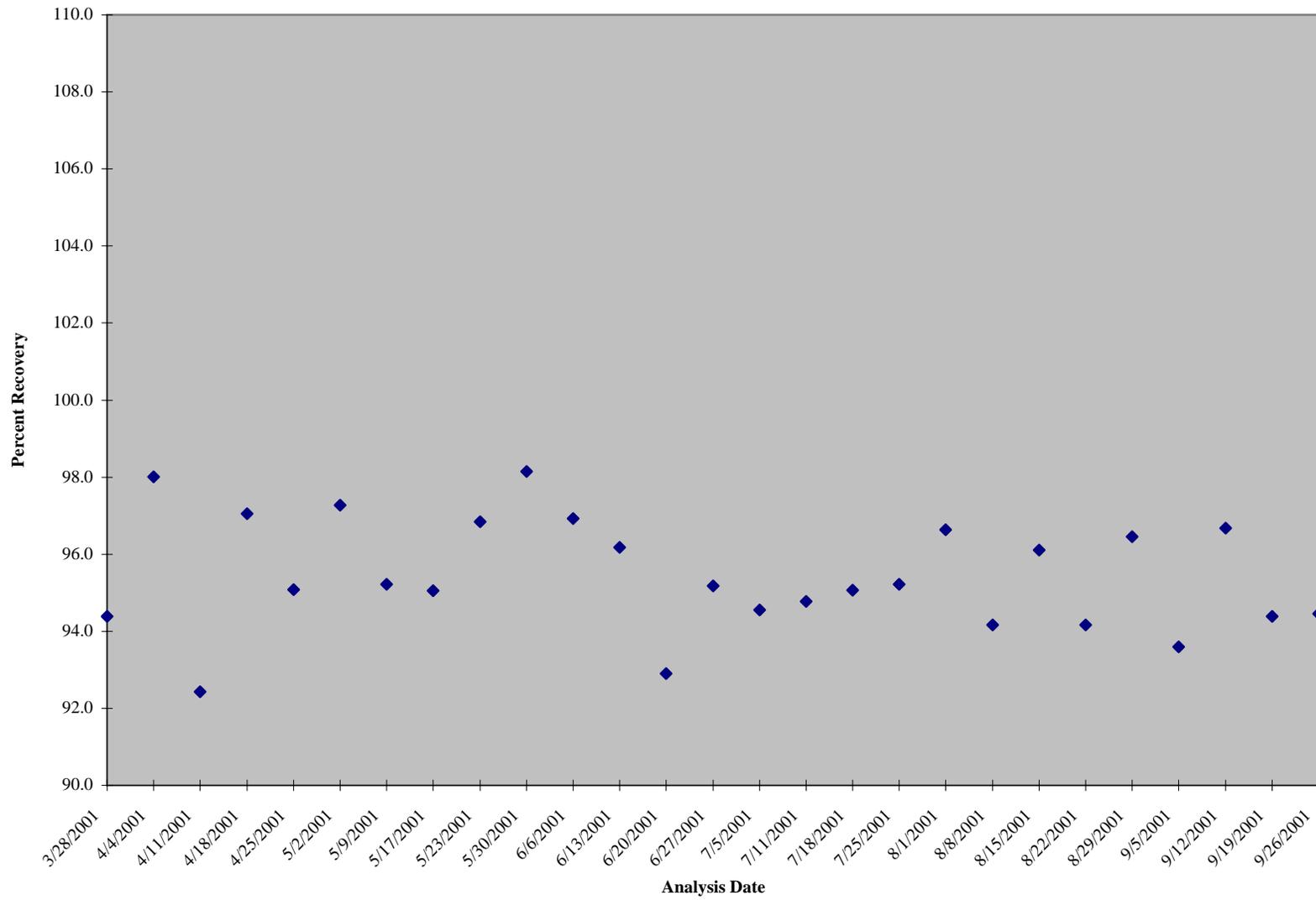


Figure 23. Recovery of Manganese (Mn) in NIST SRM 1832

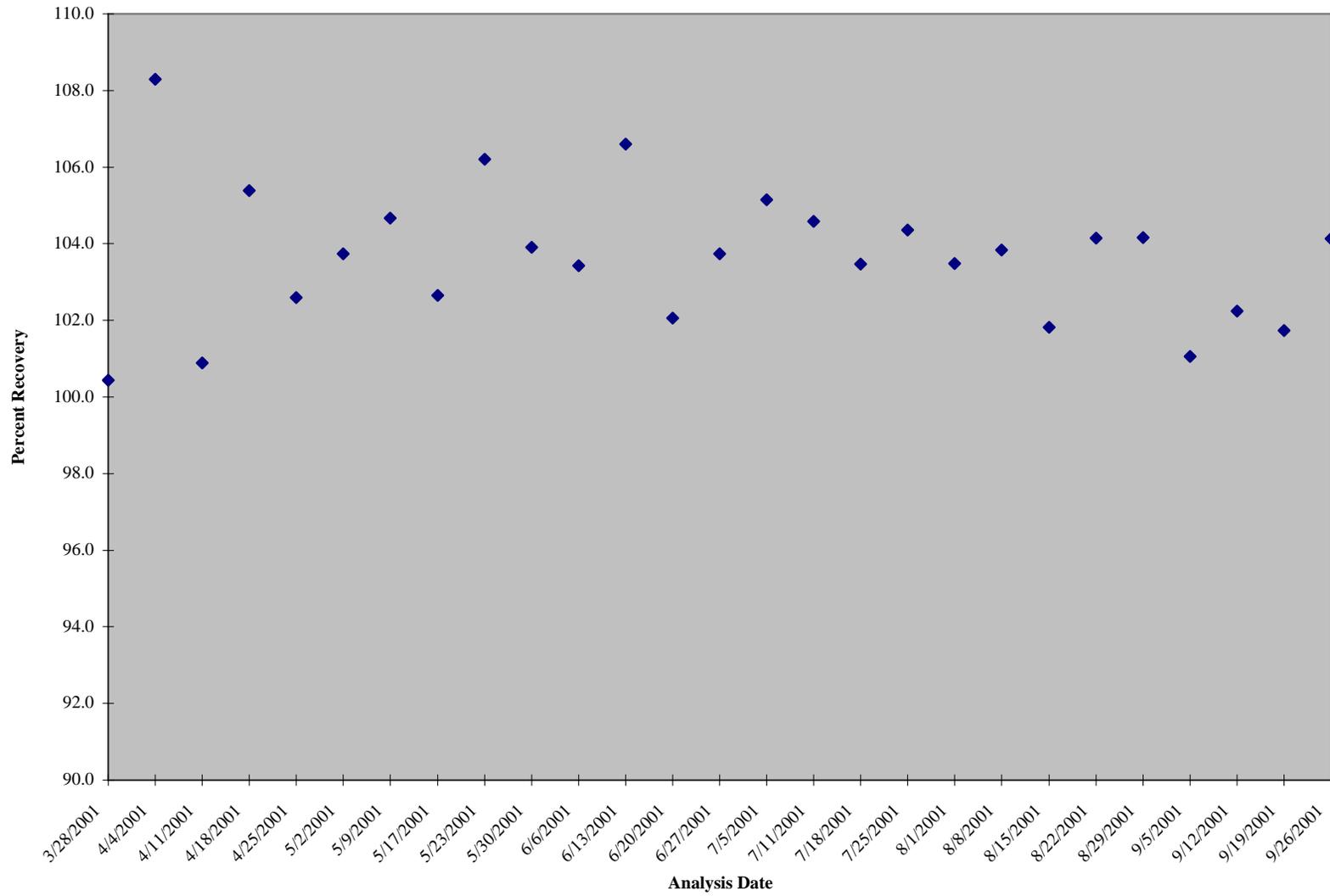


Figure 24. Recovery of Iron (Fe) in NIST SRM 1833

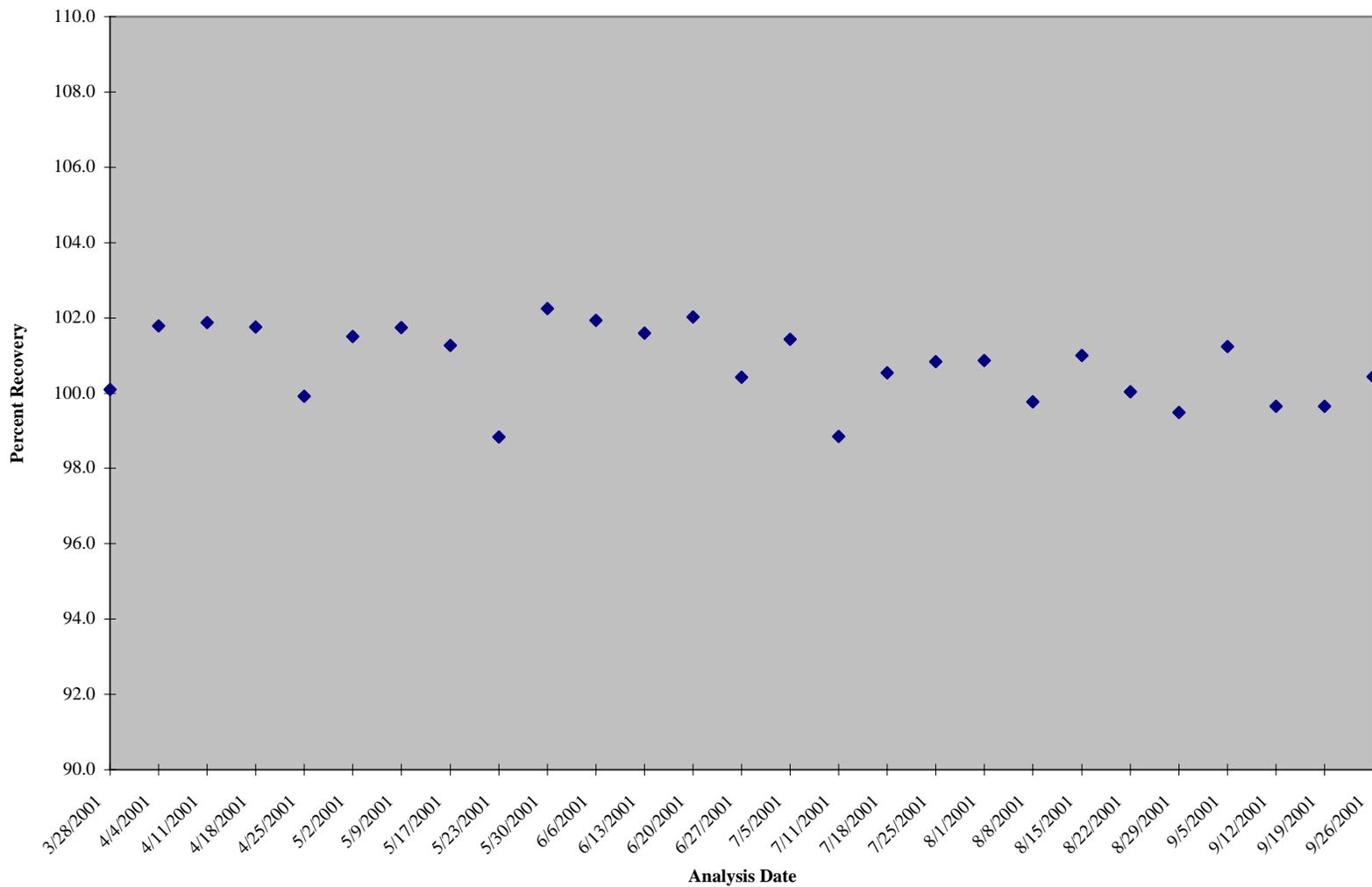


Figure 25. Recovery of Copper (cu) in NIST SRM 1832

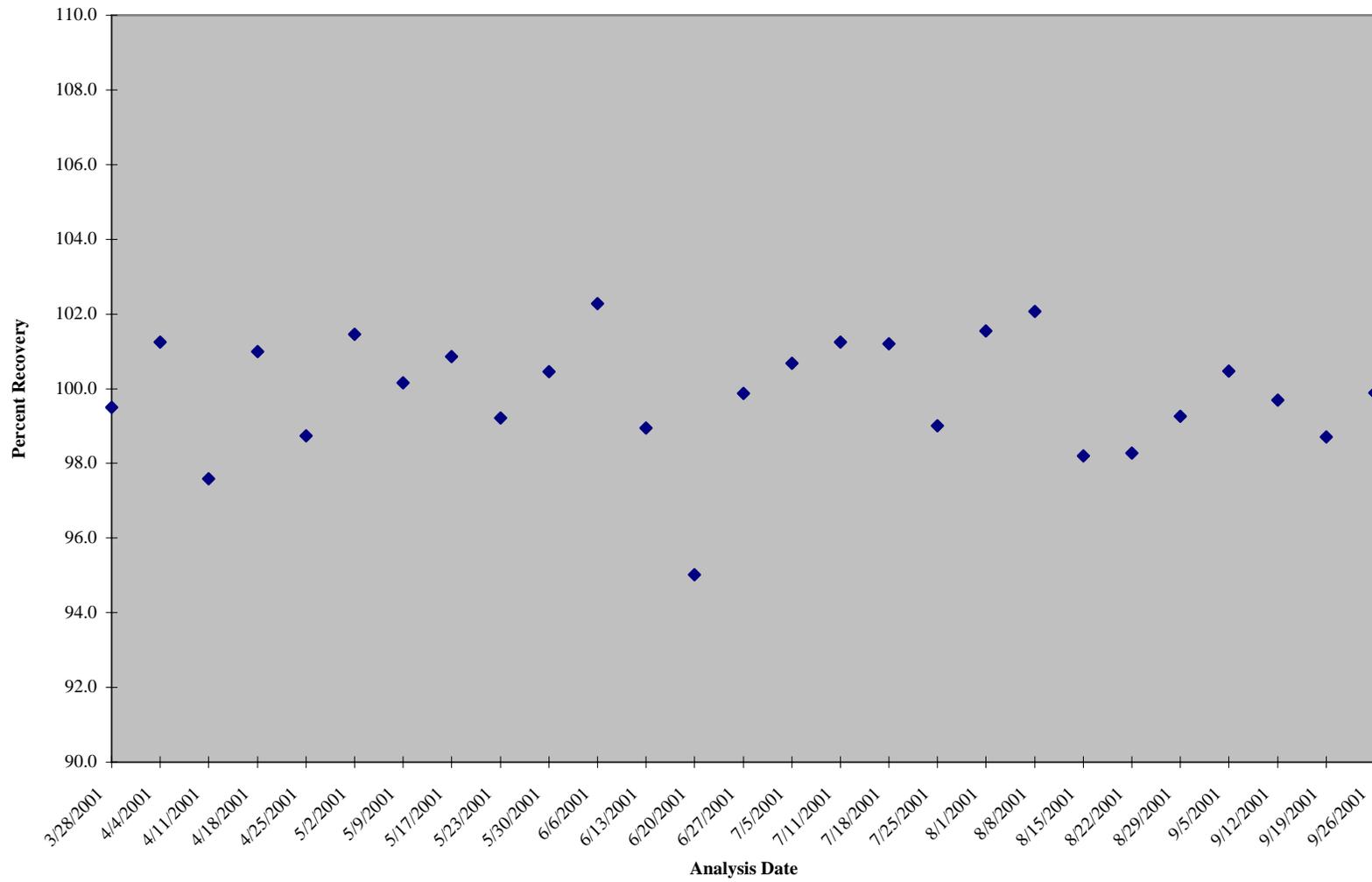


Figure 26. Recovery of Zinc (Zn) in NIST SRM 1833

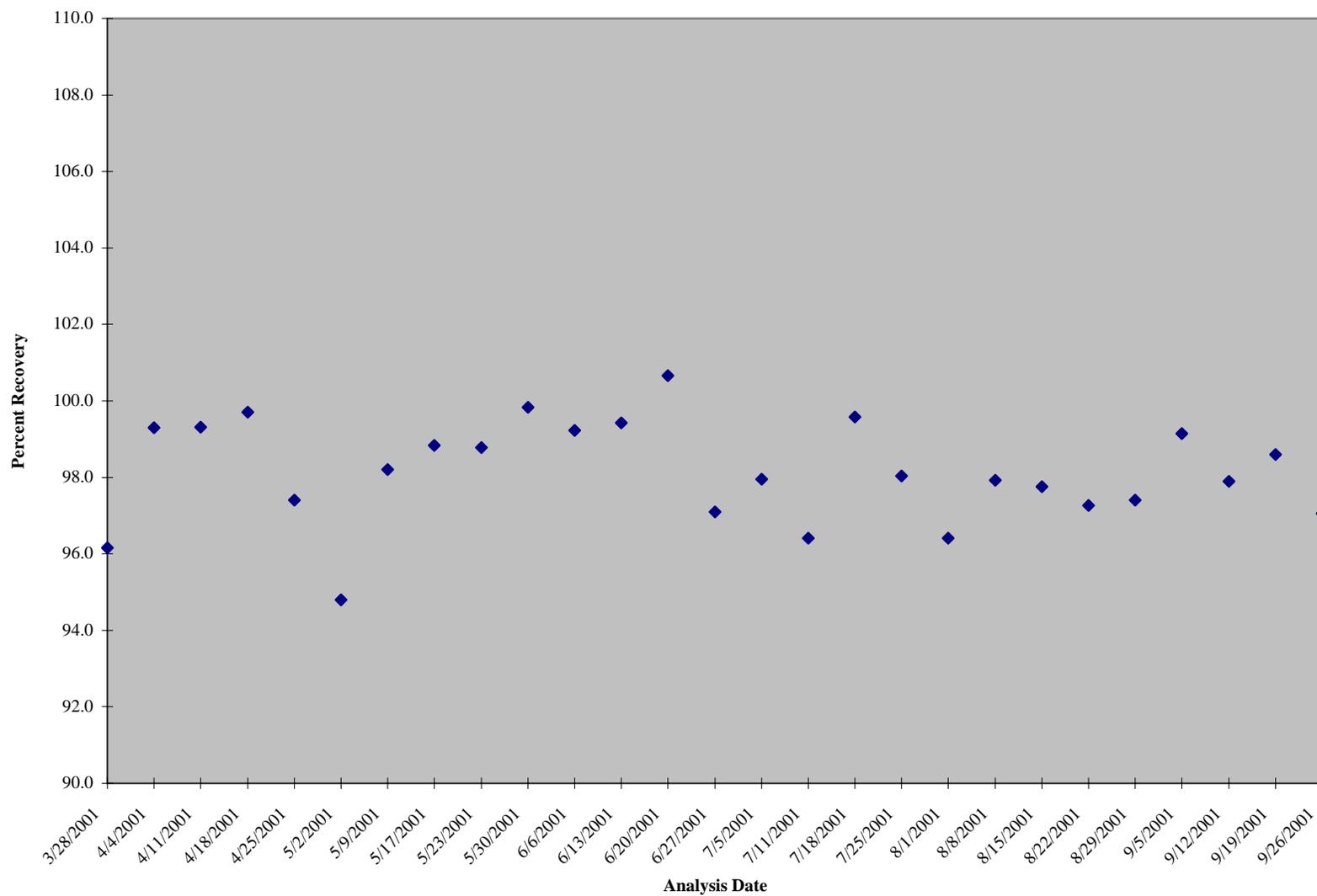
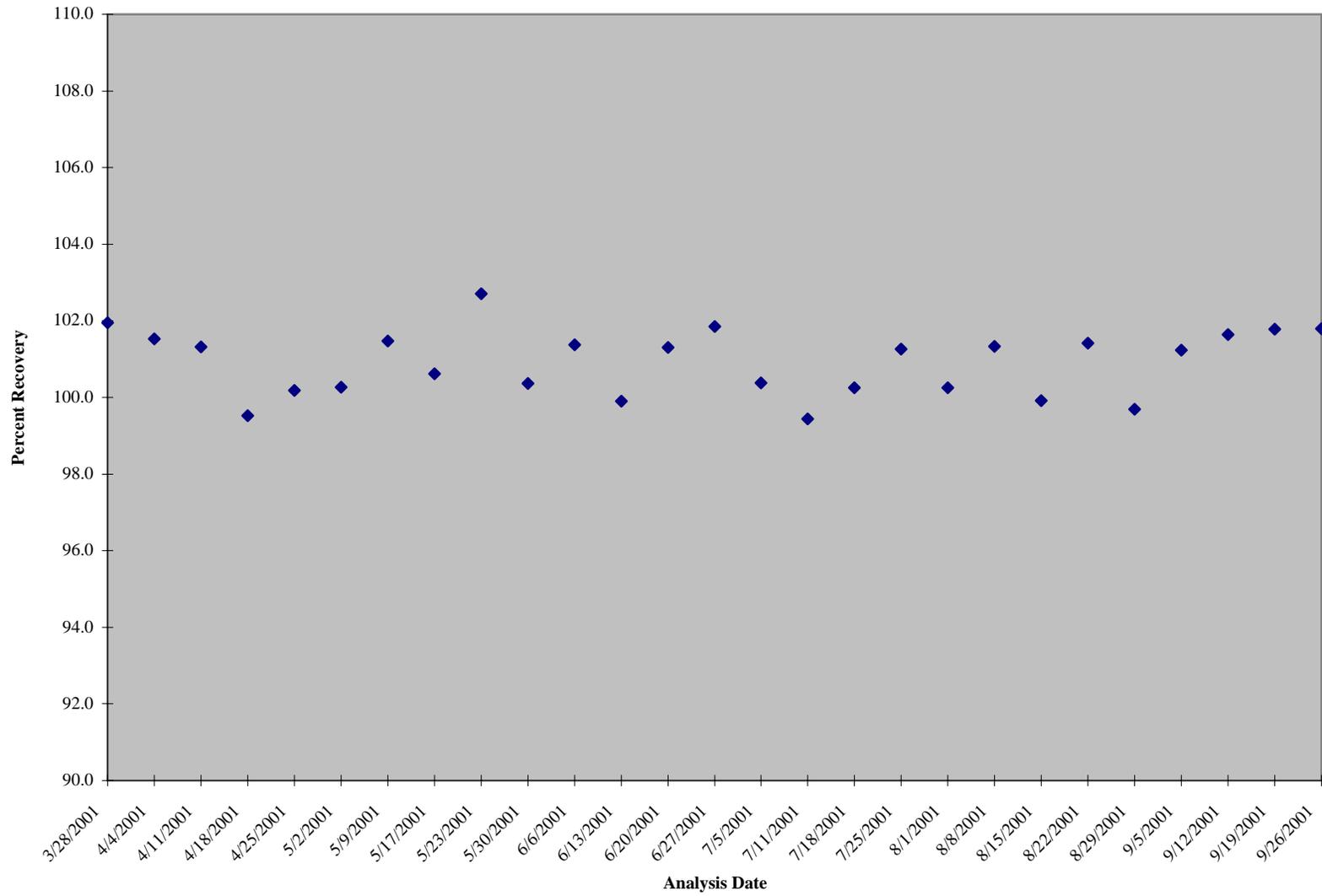


Figure 27. Recovery of Lead (Pb) in NIST SRM 1833



**Figure 28. Results of Replicate Silicon (Si) Analysis
April 1 through September 30, 2001
 $m=1.002, r^2 = 0.9998$**

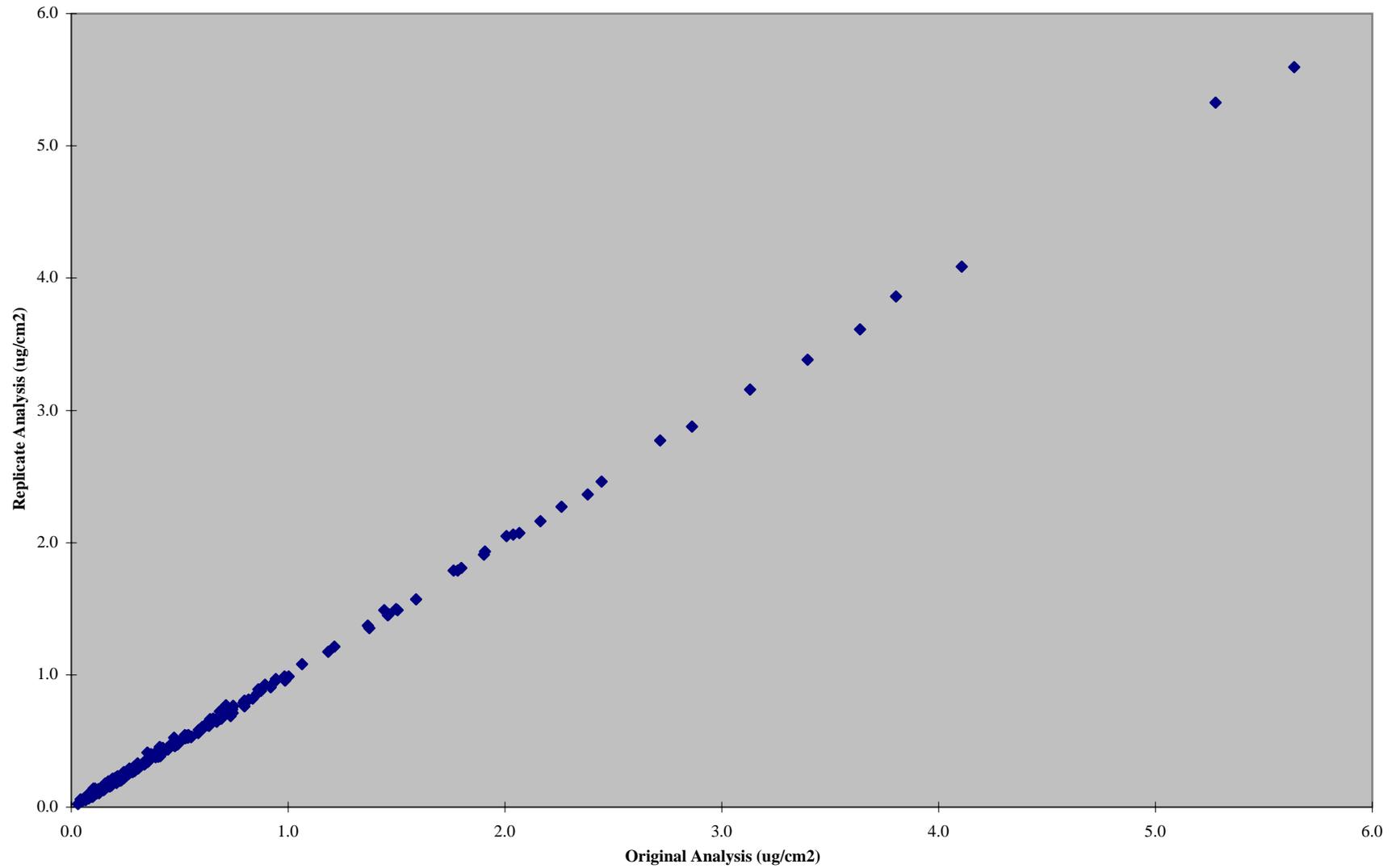


Figure 29. Results of Replicate Sulfur (S) Analysis
April 1 through September 30, 2001
m=0.9991, r2 = 0.9998

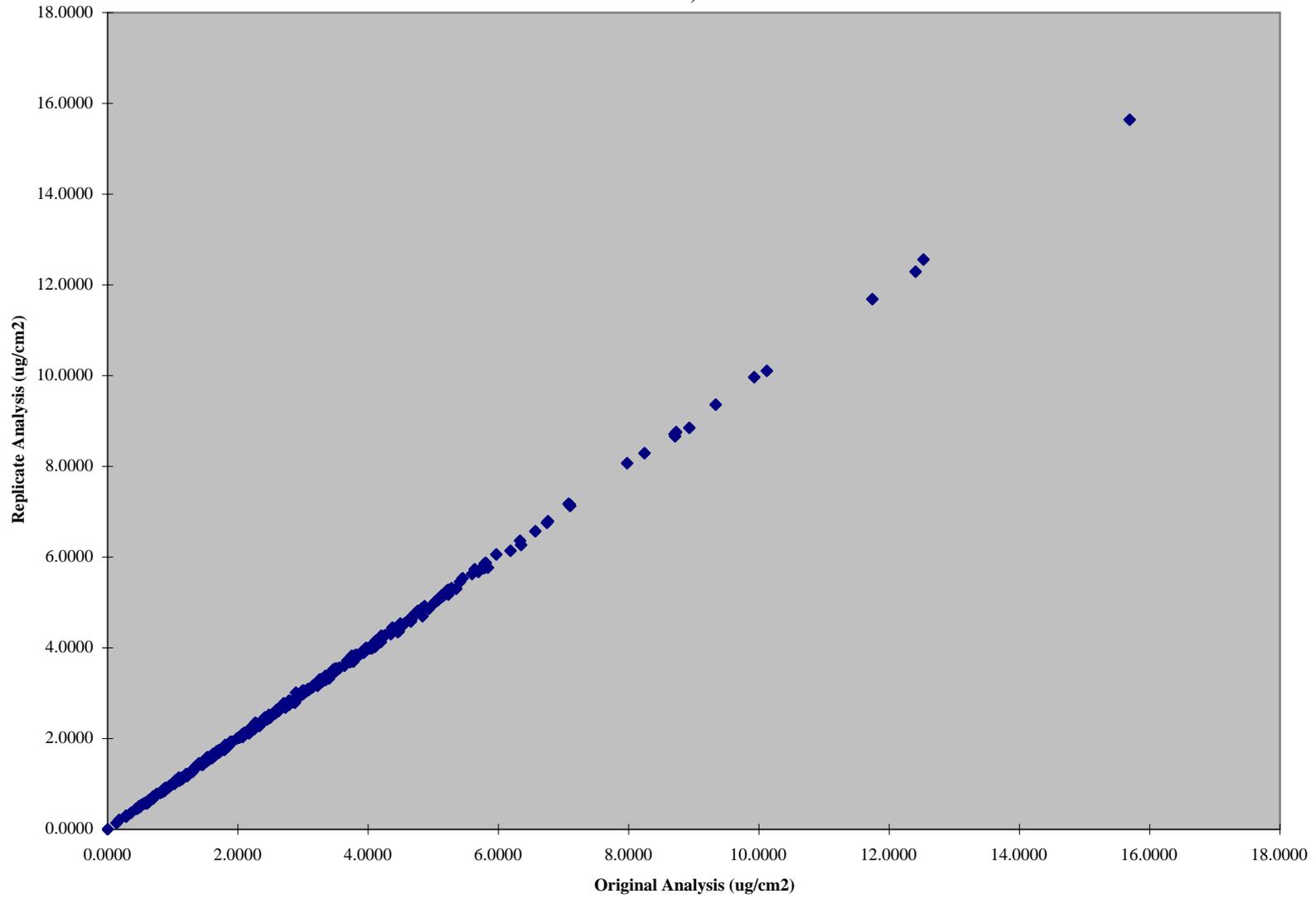


Figure 30. Results of Replicate Potassium (K) Analysis
April 1 through September 30, 2001
 $m=1.007$, $r^2 = 0.9999$

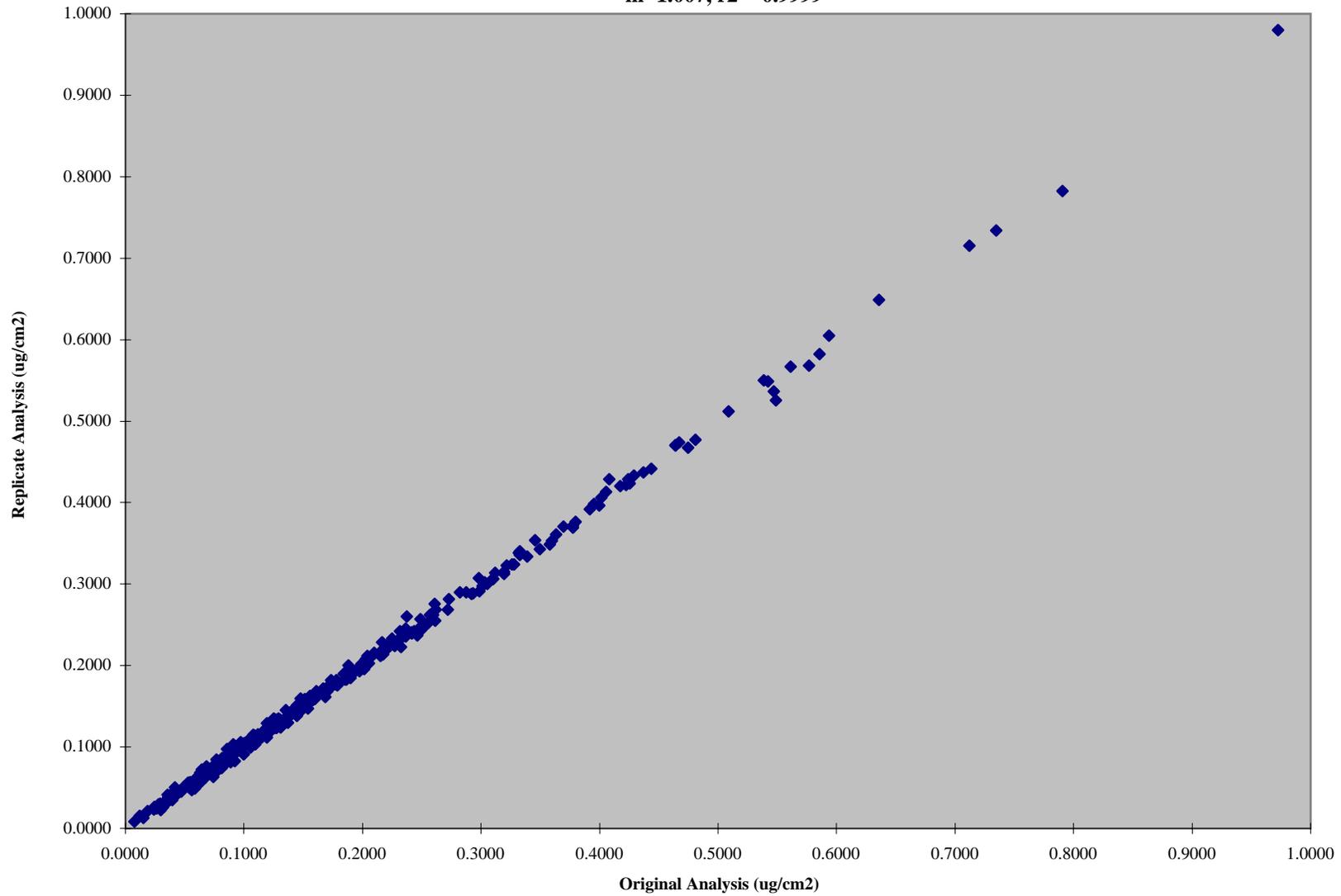


Figure 31. Results of Replicate Calcium (CA) Analysis
April 1 through September 30, 2001
m=1.000, r2 = 0.9999

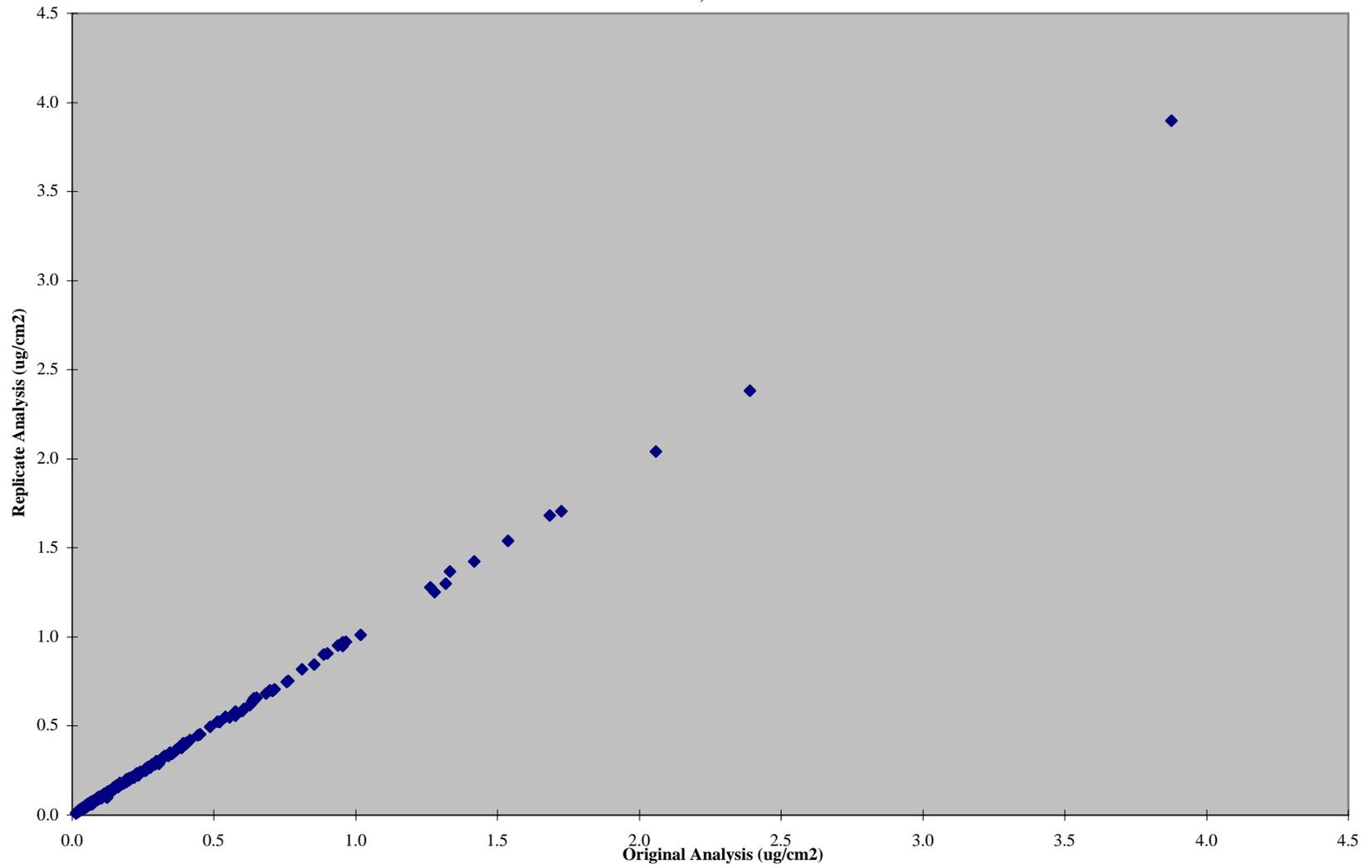


Figure 32. Results of Replicate Iron (Fe) Analysis
April 1 through September 30, 2001
m=1.001, r2 = 0.9998

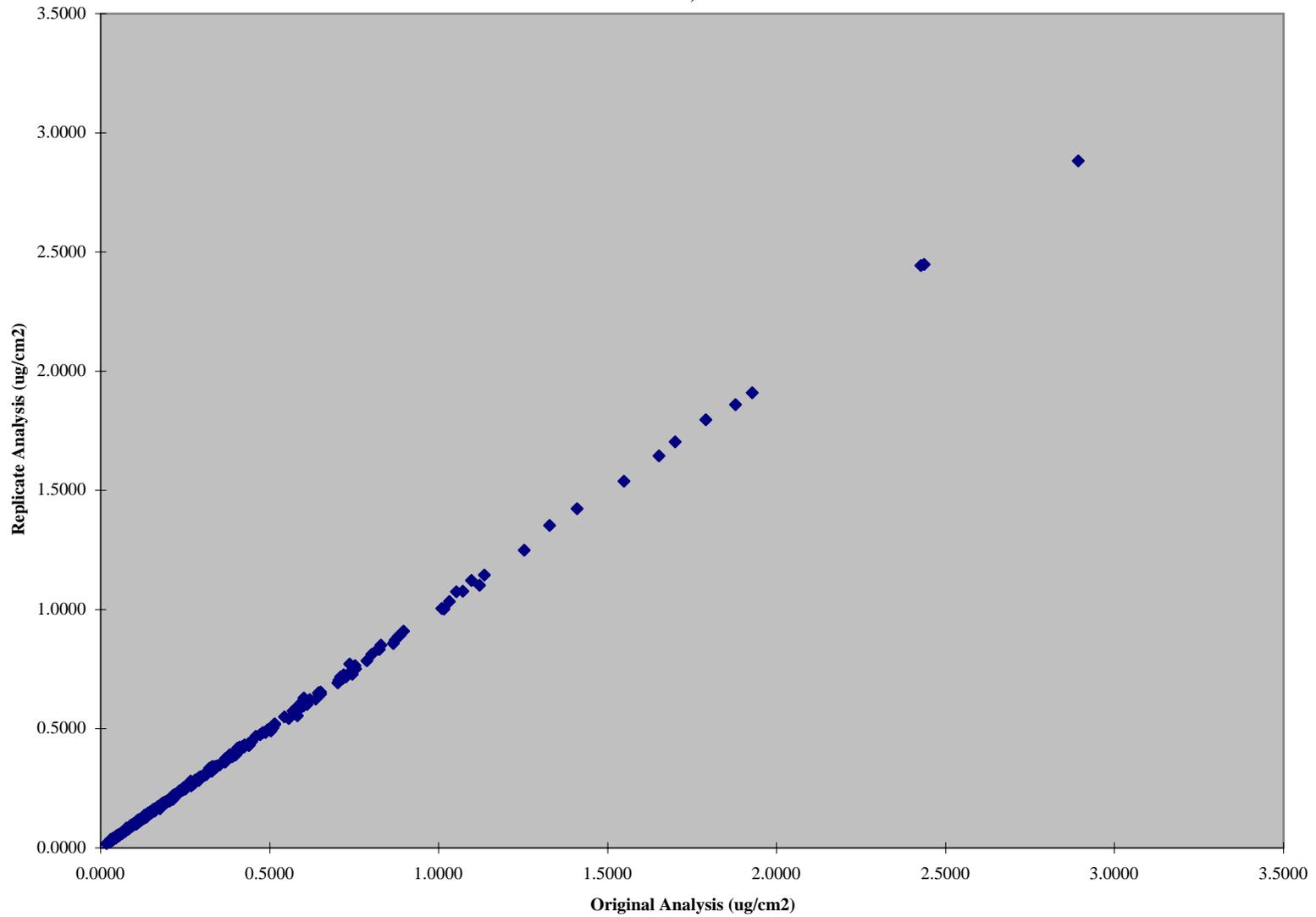
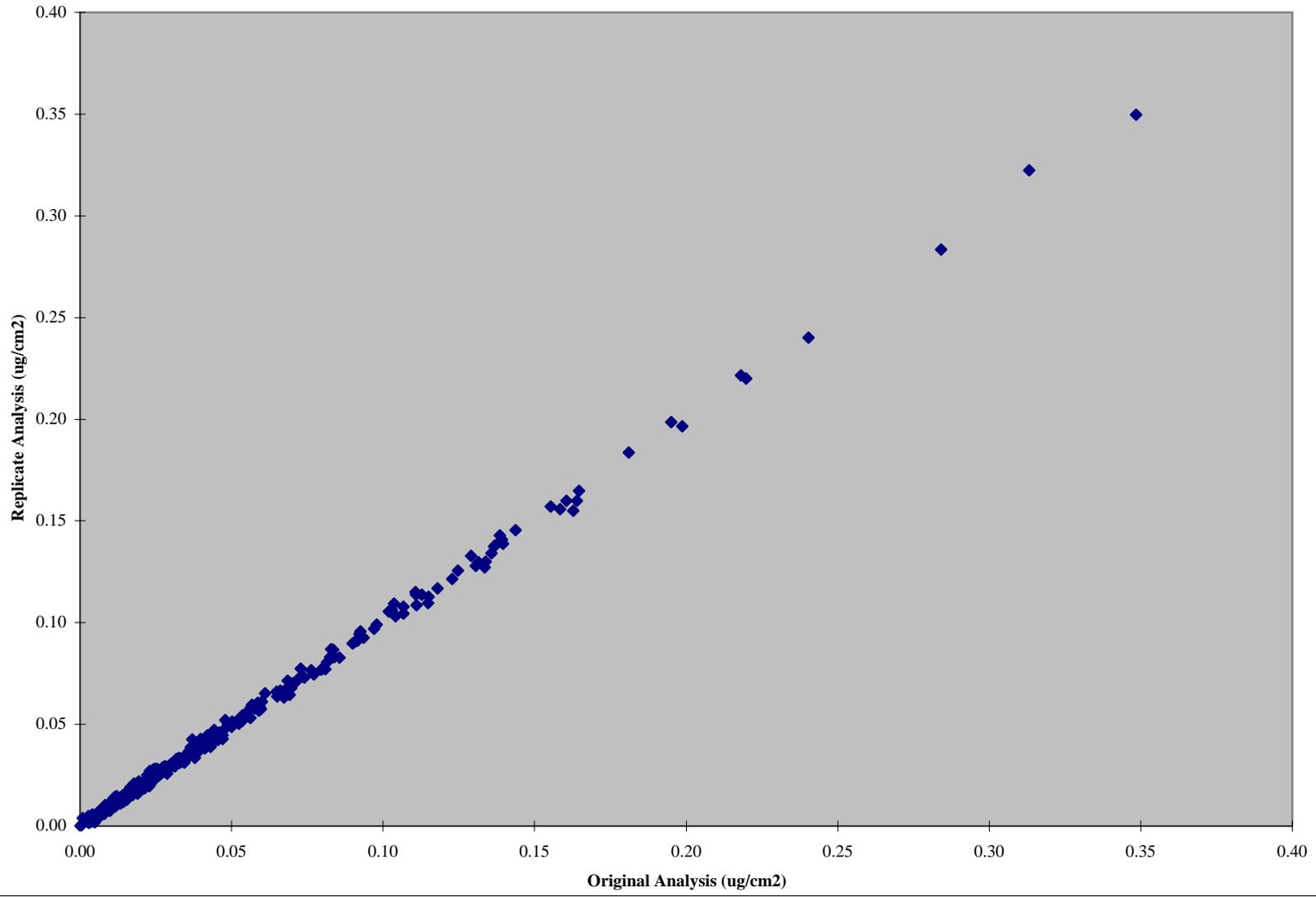


Figure 33. Results of Zinc (Zn) Analysis
April 1 through September 30, 2001
m=1.003, r2 = 0.9992



APPENDIX A

Research to Investigate the Source(s) of High Field Blanks for Teflon® PM2.5 Filters

May 4, 2001

TO: James Flanagan

CC: Robert Perkins
Edward Rickman
Darlene Smith
Stacy Doorn
Diane Haas

FROM: Lisa Greene

SUBJECT: Corrective Action - Chemical Speciation Teflon® Filters 11084814 - 11086332

The laboratory blank for Teflon® filters initially weighed on March 26, 2001, and recorded in spreadsheet 1108481(4)_1108634(3).xls experienced a weight loss well over the acceptable 15 µg between its original (tare) weighing and its subsequent (postsampling) reweighings. Recorded weight loss for duplicate weighings ranged from 31µg to 34µg. The excessive weight change could be due to a number of factors -- the filter may not have conditioned long enough before tare weighing, the filter may be anomalous in some way in terms of outgassing, there may have been some particulate on the filter when it was initially weighed that fell off or was knocked off prior to reweighing (I think this is the most likely cause), the filter may not have been left on the polonium strips long enough to minimize static effects, the balance may not have been zeroed, the balance may not have been leveled, etc. In response to the weight loss, the analyst chose a laboratory blank from a different group of filters to use as the lab blank for this group of filters, and made a note that this was done because none of the other filters in the batch exhibited a negative net mass loading. This is not allowed because the laboratory blank is used to track both contamination and filter handling effects in the Gravimetry Laboratory. The analyst may have been confused because the laboratory has used a blank from a different group of filters on rare occasions in the past when the intended laboratory blank was inadvertently sent to the client for sampling. On those occasions, the analyst was directed to choose a laboratory blank from a group of filters weighed prior to the problematic group. Since that laboratory blank had been in the weighing environment and had been handled even longer than the intended laboratory blank, I do not think we run the risk of underestimating the contamination/filter handling effect on the data. EPA Guidance Document 2.12 does not give a lot of attention to the issue of weight loss. The Gravimetry Laboratory has always just tried to follow good laboratory practices in generating data.

The ID number for the laboratory blank that exceeded specified criteria is 11086343. The filters tared with this laboratory blank should have been flagged with validation flag LBD -- Laboratory Blank duplicate (reweighing) outside limits. This flag will be added to the Gravimetry Laboratory's data spreadsheet (Excel® spreadsheet 1108481(4)_1108634(3).xls), and reported with future data submissions. The filters affected by this problem are as follows:

11084814, 11084825, 11084836, 11084847, 11084858, 11084869, 11084870, 11084881, 11084892, 11084905, 11084916, 11084927, 11084938, 11084949, 11084950, 11084961, 11084972, 11084983, 11084994, 11085000, 11085011, 11085022, 11085033, 11085044, 11085055, 11085066, 11085077, 11085088, 11085099, 11085102, 11085113, 11085124, 11085135, 11085146, 11085157, 11085168, 11085179, 11085180, 11085191, 11085204, 11085215, 11085226, 11085237, 11085248, 11085259, 11085260, 11085271, 11085282, 11085293, 11085306, 11085317, 11085328, 11085339, 11085340, 11085351, 11085362, 11085373, 11085385, 11085408, 11085419, 11085420, 11085431, 11085442, 11085464, 11085475, 11085486, 11085497, 11085500, 11085511, 11085522, 11085533, 11085544, 11085555, 11085566, 11085577, 11085588, 11085599, 11085602, 11085613, 11085624, 11085635, 11085646, 11085657, 11085668, 11085679, 11085680, 11085691, 11085704, 11085715, 11085726, 11085737, 11085748, 11085759, 11085760, 11085771, 11085782, 11085793, 11085806, 11085817, 11085828, 11085839, 11085840, 11085851, 11085862, 11085873, 11085884, 11085895, 11085908, 11085919, 11085920, 11085931, 11085942, 11085953, 11085964, 11085975, 11085988, 11085997, 11086003, 11086025, 11086036, 11086047, 11086058, 11086069, 11086070, 11086081, 11086092, 11086105, 11086116, 11086127, 11086138, 11086149, 11086150, 11086161, 11086172, 11086183, 11086194, 11086207, 11086218, 11086229, 11086230, 11086241, 11086252, 11086263, 11086274, 11086285, 11086296, 11086309, 11086310, 11086321, and 11086332.