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Environmental Monitoring Systems
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Research Triangle Park NC 27711

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National Performance Audit Program Ambient Air Audits of Analytical Proficiency 1983



NATIONAL PERFORMANCE AUDIT PROGRAM
AMBIENT AIR AUDITS OF ANALYTICAL PROFICIENCY
-1983-

by

Robert L. Lampe, Blaine F. Parr, Gregory Pratt,
Oscar L. Dowler and William J. Mitchell
Quality Assurance Division
Environmental Monitoring Systems Laboratory
Research Triangle Park, North Carolina 27711

ENVIRONMENTAL MONITORING SYSTEMS LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
U.S. ENVIRONMENTAL PROTECTION AGENCY
RESEARCH TRIANGLE PARK, NORTH CAROLINA 27711

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ABSTRACT

This report presents the results of the U.S. Environmental Protection Agency's 1983 National Audit Program by pollutant and by analytical method. Semiannual audits were conducted for SO_2 and NO_2 (bubbler methods), Pb, NO_3^- and SO_4^{2-} (filter strips) and CO (continuous monitors). One audit was conducted on high-volume flow rate. Continuous SO_2 monitors were audited throughout the year, such that no monitor was audited more than once. This was the first year that acid rain audits were conducted for U.S. laboratories — approximately 30 laboratories participated in each semiannual acid rain audit. Twenty-four laboratories participated in each SO_2 bubbler audit, 28 in the 0683 NO_2 audit, and 20 in the 1283 audit which represent 20-45% decreases from 1982. Fifty-nine laboratories participated in each of the SO_4^{2-} audits and approximately 50 in each of the NO_3^- audits. The 0183 Pb audit had 103 participants and the 0783 had 92. Three hundred and ninety CO monitors were checked in the 0383 audit and 361 in the 1083 audit. There were 1447 high volume flow devices checked in the 0583 audit. Although slight decreases in participation were noted for the SO_4^{2-} , NO_3^- , Pb, CO and flow audits, the total participation was still not markedly different from 1982 levels.

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SECTION 1

INTRODUCTION

The 1983 ambient air audits of analytical proficiency, which were managed by the Environmental Monitoring Systems Laboratory (EMSL), of the U.S. Environmental Protection Agency (EPA), are a part of a continuing audit program of six ambient air pollutants and high-volume samplers. In 1983, acid rain audits were added to the program. The program, entitled the National Performance Audit Program, allows EPA to monitor the performance of laboratories making air pollution measurements and allows participating agencies to assess their performance with respect to other agencies. The audits are conducted by the Quality Assurance Division (QAD) of EMSL. Inquiries and applications to participate should be directed to: U.S. Environmental Protection Agency, Quality Assurance Division, Environmental Monitoring Systems Laboratory, MD-77B, Research Triangle Park, North Carolina 27711.

Agencies participating in the audits are solicited by the EPA Regional Quality Control Coordinator in each of EPA's 10 regions. Agencies performing ambient air monitoring of criteria pollutants are required by Federal regulation to participate. Once a laboratory enrolls in a particular audit, it is automatically notified of subsequent audits of that pollutant. Participants are assigned a permanent identifying code number. Federal, state, local, industrial and foreign air pollution monitoring agencies participate in the surveys.

Sample materials furnished for the audits are designed to simulate the several types of collected air pollution samples as closely as possible. The materials for the manual methods evaluate only the analytical portion of the total air measurement process; i.e., they do not determine errors in sample collection, transportation, handling, storage, and data processing. For the high volume method for total suspended particulate (TSP), the audit evaluates only the flow measurement portion of the method.

Audits are presently conducted twice a year for carbon monoxide, sulfur dioxide, nitrogen dioxide, lead, sulfate, nitrate and acid rain and once a year for high-volume flow rate. Audits on SO₂ continuous monitors are conducted throughout the year. At the end of the year, a comprehensive report is prepared summarizing the audit results of that year. Each participant is sent a copy of the report.

In addition, each laboratory participating in an audit receives an evaluation of its performance shortly after the audit is completed. When practical, laboratories submitting abnormally high or low results are offered an opportunity to analyze another set of samples. However, the

retest results are not included in this summary report.

There are approximately 400 laboratories registered in the National Performance Audit Program. This report presents the results of those laboratories that participated in the 1983 audits. The category and number of participants in each audit are presented in Table 1. With the exception of the SO₂ monitor audit program which increased by 18%, there was a general decrease in participation in the 1983 audit program compared to the 1982 program: SO₂ bubbler method, 45%; NO₂ bubbler method, 31%; CO, 7%; SO₄⁼, 6%; NO₃⁻, 2%; Pb, 2%, and high volume flow rate, 10%.

Throughout this report, reference is made to "assigned values." These values are the standards against which reported results are evaluated and have been so designated after consideration of the analytical results of the referee laboratory, the QAD/EMSL Standards Laboratory, and the manufacturer of the audit material.

SECTION 2

SUMMARY AND CONCLUSIONS

The 1983 results closely parallel those of last year. With outliers removed and values averaged, the percentage of results within 20 percent of the assigned values ranged from a low of 83.6 (sulfate) to a high of 98.3 (CO). The overall average for all audits is 92.6 percent. This value is slightly less than the 1982 value of 95.4 percent but still above the 90.3 percent average of the previous four years.^{1,2,3}

The following percentage of results were rejected as outliers for each type of audit: SO₂ bubbler (5%), NO₂ bubbler (5.5%), CO (1.3%), SO₄⁼ (3.3%), NO₃⁻ (3.1%), Pb (2.4%), flow rate (4.6%), SO₂ continuous (3.8%) and acid rain (5.1%).

SECTION 3

AUDIT MATERIALS

The audit samples span the wide range of pollutant concentrations experienced in ambient air monitoring. This is achieved directly with the CO samples, which are prepared in cylinders. Dilution is necessary for the acid rain samples, lyophilized SO₂ and aqueous NO₂ samples in order to obtain desired concentrations. Lead, NO₃⁻, and SO₄⁼ filter strip samples require both dissolution and dilution to arrive at the needed range of concentrations. The SO₂ continuous monitor audit samples require dilution of the SO₂ with zero air.

Although many air monitoring sites rarely encounter pollutant concentrations at the higher audit sample levels, these concentrations are included to assure that monitoring methods are verified at the higher levels.

The following paragraphs describe each sample type used in the 1983 audits.

SULFUR DIOXIDE (MANUAL)

Lyophilized samples, composed of sodium sulfite and potassium tetrachloromercurate, simulate ambient air samples collected according to the Pararosaniline Method, the reference method for determining SO₂ in the atmosphere. In the 1983 audits, the concentrations ranged from approximately 21 to 220 µg of sulfur dioxide equivalent per cubic meter when reconstituted properly. A sample set consisted of five different concentrations.

NITROGEN DIOXIDE (MANUAL)

Nitrogen dioxide samples consist of aqueous sodium nitrite solutions that simulate ambient NO₂ samples collected by a 24-hour NO₂ bubbler method. Audit results are expressed in terms of micrograms per milliliter (nitrite concentration). These solutions, when properly diluted according to directions, are equivalent to collected atmospheric NO₂ concentrations of approximately 0.4 to 1.0 µg/ml. A sample set consists of five different concentrations.

CARBON MONOXIDE

These audit materials consist of a mixture of CO, CO₂ and CH₄ and zero air in a pressurized gas cylinder that simulates an ambient air sample. The concentrations of the three CO samples used in the 1983 audits ranged from

6 to 44 ppm. Directions specify that the gas sample be introduced into a continuous analyzer in the "sample" mode, which permits the analyzer to draw the sample in the same fashion and at the same flow rate as during ambient air monitoring.

SULFATE, NITRATE, AND LEAD ON FILTER STRIPS

The filter strip samples used in sulfate, nitrate and lead audits are each 1.9 cm wide by 20 cm long. They are cut from 20- by 24-centimeter glass fiber filters that have been spiked with an aqueous solution of the appropriate solution and then oven dried. After analysis, pollutant concentrations are computed by assuming that the samples were collected on the prescribed high-volume filter with a sample air volume of 2,000 m³. Six sample strips comprise a set.

Sulfate and nitrate audit samples are prepared from sodium sulfate and potassium nitrate. Calculated nitrate concentrations ranged from 0.60 to 14.0 µg/m³ and sulfate from 1.0 to 30.0 µg/m³. Lead samples, which are prepared from lead nitrate ranged in concentration from 0.58 to 8.0 µg/m³ of lead.

HIGH-VOLUME FLOW RATE (ReF DEVICE)

The reference flow (ReF) device used for audits of high-volume flow rates consist of a modified orifice, a wind deflector, a manometer, and a series of resistance plates that simulate particulate loading. A single ReF device is supplied to each participating agency with instructions to check samplers at as many sampling sites as feasible within the allotted time.

Each ReF device is calibrated with a positive displacement meter before use. During use, the device is mounted on top of the sampler, replacing the filter face plate. A wind deflector is used to prevent fluctuations in the measurements due to wind blowing across the orifice.

SULFUR DIOXIDE CONTINUOUS MONITORS

The continuous monitor auditing system is an auditing device for SO₂ continuous ambient air monitors. The device is a porous plug dilution system that provides a mechanism whereby controlled quantities of SO₂ and diluent air are continuously combined in a mixing chamber and passed into the monitor. The flow rate of each gas is controlled by maintaining a predetermined pressure drop across the porous plug flow restrictor. Variable SO₂ concentrations are obtained by switching between four restrictors.

The audit device, which is housed in a compact, lightweight, impact-resistant case, is constructed so that only those controls required for system operation are exposed. By opening and closing different toggle valves, it is possible to generate up to seven preset pollutant concentrations. Five are used for the audit. Two compressed gas cylinders are supplied with each unit, one as the pollutant source and the other for dilution.

Each audit device is calibrated for flow at all the settings used in the audit. Flow calibrations are referenced to laminar flow elements traceable to National Bureau of Standards flow standards. Sulfur dioxide concentrations ranging from 0.00 to 0.864 ppm were used in the 1983 audits.

ACID RAIN

In 1982 an acid rain pilot study was conducted for U.S. participants of the National Performance Audit Program (NPAP). Earlier acid rain audits were generally limited to World Meteorological Organization members. This pilot study proved beneficial and resulted in improvements in sample design, packaging and the data reporting form. For example, replacing the glass vials with polyethylene bottles for the samples markedly improved sample stability.

In April 1983 the first "official" audit for U.S. participants was conducted and in November a second audit was conducted. Approximately 30 laboratories participated in each of these audits. Five samples each in polyethylene bottles were shipped to each of the participating laboratories. Three samples were analyzed for pH, conductivity, acidity and the major cations and anions normally measured in precipitation samples. The other two samples were analyzed for heavy metals. The latter two samples were acid stabilized to prevent loss of metals from the solution.

The chemical composition of these samples was certified by the U.S. National Bureau of Standards. The participants were to analyze the samples using the analytical procedures they normally employ when analyzing their precipitation samples.

SECTION 4

AUDIT RESULTS

The results of the 1983 audit are presented in Tables 2 through 30. The term "audit mean" in these tables denotes the average of all values reported by the participants for that sample after elimination of outliers. Elimination of outliers was accomplished in a two step procedure. First, laboratories or sites reporting values exceeding ± 20 percent of the assigned value, for all samples in a particular audit, have been excluded from this report. These excluded values represent 5.2 percent of the total number of laboratories or sites reporting results. Their values can be largely attributed to malfunctioning equipment and/or inexperienced personnel and would unjustly affect the audit results. Second, rejection of additional individual results as outliers was based on Chauvenet's Criterion.⁴

In addition to the percentages of outliers determined by the two outlier procedures, it is desirable to derive some measures of overall performance of the participants after eliminating the outlier results. At each audit level, the distribution of results from all participants is surprisingly normal in form when the outlier values are eliminated. This normal distribution reflects some state of statistical control of the many variables influencing the results from the participants in the entire nation. Further, the distributions of the percentages of deviations from the assigned values are quite similar across audit levels for each pollutant. How well the participants perform as a whole is reflected by the average and variability of the percentage deviations.

At each audit level, the percent accuracy (% Acc.) and the precision, as measured by the percent coefficient of variation (%CV), were computed as follows:

$$\% \text{ Acc.} = \frac{\text{audit median} - \text{EPA assigned value}}{\text{EPA assigned value}} \times 100$$

$$\% \text{ CV} = \frac{\text{audit standard deviation}}{\text{audit mean}} \times 100$$

The percent accuracy measures how well the average of all participants agrees with EPA's assigned values. The percent coefficient of variation measures the variability among participants.

For each pollutant measurement, it is desired to determine and report a single measurement for "accuracy" and a single measurement for "precision." Because the results across audit levels are somewhat consistent,

average accuracy and average precision values for each audit are computed. These average values are plotted on Figures 1 through 12 to provide a way of tracking trends over the history of the performance audit program. These figures graphically demonstrate the continuing improvement of participant results since the inception of the program. These improvements are indirect measures of the improvement in the quality of air pollutant measurements made in the nation.

SULFUR DIOXIDE (BUBBLER)

Twenty-four laboratories participated in both the April (0483) and the October (1083) audits. The percentage of local agency laboratories decreased during the 1983 audits. This decrease in participation has been evident over the past few years due to the increasing number of laboratories changing to automated analyzers.

The audit mean, percent accuracy and percent CV, with and without outliers, is reported in Tables 2 and 3. In Table 2 with the exception of the third level, the mean value for all levels in the two audits exceeded the assigned value. As usual the lowest precision and accuracy was achieved in level one in both audits. The average percent accuracy appears to have stabilized over the past three audits when compared to audits of previous years (Figure 1). Precision improved in the 1982 audit and continued to show improvement in the 1983 audits (Figure 2).

As shown in Table 3, part A, for the manual method, accuracy ranged from -0.4 to 7.8 for all data and 0.8 to 8.2 after outliers were removed. Accuracy for the automated method ranged from -2.5 to 8.1 with and without the outliers. Concentrations did not appear to affect the precision for the manual methods. However, some improvement can be noticed in the results by the automated method as concentrations increase (Table 3, part B).

Table 4, constructed with the outliers removed, shows the percentage of laboratories that obtained results within ± 10 , 20, 30 and 50 percent of the assigned values. With one exception, better than 87 percent of the measurements fell within 20 percent of the assigned values, a greater percentage than the previous year.

NITROGEN DIOXIDE

Participation decreased from 28 laboratories in the 0683 audit to 20 in the 1283 audit. Overall, total participation in the 1983 audits was 31% less than in 1982. The decrease, which occurred among the state and local participants, likely resulted because an increasing number of laboratories are replacing bubblers with continuous analyzers.

The audit mean, percent accuracy and percent CV with and without outliers is reported in Tables 5 and 6. The accuracy (Figure 3) in the 0683 audit was not as good as those of the 1982 audits. In the 1283 audit accuracy improved. The bias over the past several years seemed to vary from audit to audit and more recently from year to year. The last five audits show improvement and a leveling off in precision (Figure 4). With

few exceptions the precision and accuracy over the years has been good.

Table 7 shows that approximately 95 percent of the laboratories were within $\pm 10\%$ of the assigned values and better than 97% were within ± 20 percent. Although these percentages are above the averages for the past few years, they are not equal to those attained in 1982 when 100% of the values were within $\pm 20\%$ and with two exceptions were within $\pm 10\%$.

CARBON MONOXIDE

The number of monitors being audited increased from 552 in 1977 to a high of 793 in 1982. In 1983 a total of 751 monitors were audited — a 5% decrease from 1982. There has been little change in the number of sites over the past three years. The percent age of state, local and foreign sites being audited has increased slightly since 1982 and the percentage of industrial and federal sites has decreased slightly. The percent accuracy and percent CV are shown in Table 8. Precision and accuracy in the first 1983 audit improved compared to the first 1982 audit; however, the reverse occurred in the second audit in those years.

When the percent accuracy and percent CV are averaged for each audit (see Figures 5 and 6), there is noticeable improvement beginning with the 1980 audits up to the present. Prior to 1980, the variations in precision and accuracy were wider.

As shown in Table 9, the NDIR method continues to show greater accuracy and precision than the GC method. Although a few participants use other methods such as gas filter correlation and electrochemical, but too few to make a meaningful comparison.

With the exception of the lowest level in the 1083 audit the number of measurements falling within 20% of the assigned value closely parallels the 1982 results (Table 10).

SULFATE ON FILTER STRIPS

Approximately 60 laboratories participated in each of the audits. This is about 6 percent fewer than last year. There were less local agencies participating this year than last. In general, participation in $\text{SO}_4^{=}$ audits seems to have reached a plateau over the past several years.

The audit mean percent accuracy and precision are given in Table 11. Accuracy over the years (1976-1983) varied quite a bit usually on the positive side with the best years being 1977 and 1982 (Figure 7). Precision also varied during the period (Figure 8), but showed improvement in the 0282, 0882, and 0283 audits.

In general for the 1983 audits, the percent accuracy and precision for the manual methods (Table 12) improve as sample concentrations increase. With outliers removed the Sulfa-ver method indicates a negative bias in the 0283 audit. A positive bias prevailed in the other audits this year and last where this method was employed. For the automated methods, with excep-

tion of the 0883 audit, both the Thymol Blue and the Ion Chromatograph show a larger negative bias for this year compared to 1982 (Table 13). Sample concentration does not seem to affect the precision and accuracy of the automated methods as it does in the manual methods.

Except for the lowest sample concentration, between 84 and 97 percent of the laboratories reported results within ± 20 percent of the assigned values (Table 14). These results compare favorably with the 1982 audits.

NITRATE ON FILTER STRIPS

There were approximately 50 laboratories taking part in each of the 1983 audits. Participation was down approximately 2 percent from the 1982 audits, mainly because there were fewer industrial participants. Since 1978 the number of participants has been fairly consistent, indicating that a plateau has been reached similar to that in sulfate audits.

In general, accuracy (Figure 9) varied widely from 1976 through 1981. Variation in the last four audits has been small, however, indicating some improvement. The precision chart (Figure 10) shows two periods of improvement--one from August 1978 through August 1979; the other from February 1982 through August 1983. Both periods coincide with those times when accuracy showed some improvement.

A negative bias is apparent in the 0283 audit. Previously, the only negative bias appeared in the 1979 audits.

Results from all methods together (Table 15) show slight improvement over the 1982 audits. For the automated methods tabulated in Table 16, the accuracy for the ion chromatograph method is not as good as the 1982 audits; however, the precision has improved. The cadmium reduction method shows definite improvement for both the accuracy and precision over the 1982 results.

Some other methods used by a few of the participants included the manual cadmium reduction, brucine, hydrazine, 2,4 xylenol, selective ion electrode, and the szechrome NAS methods. The number of results reported was too small to calculate precision and accuracy.

The percentage of values that fell within ± 20 percent of the assigned values was very close to those reported for 1982. When averaged they were almost identical. For the lowest concentration there was noticeable improvement in the percentage of values that fell within the ± 20 percent of the assigned value.

LEAD ON FILTER STRIPS

One hundred and three laboratories participated in the 0183 audit and 92 in the 0783, 2 percent less than in the 1982 audits. The decrease was due to a smaller number of participants among the state and industrial laboratories. Participation has leveled off in the past three years and averages between 95 and 100 laboratories for each of the audits.

The audit mean, percent accuracy and percent CV are shown in Table 18. Accuracy was better in the 0183 than in the 0182 but the reverse is true in the 0782 and 0783 audits. Both of the audits in 1983 show improvement in precision over the 1982 audits. Since 1977, with two exceptions, accuracy has been within 2 percent and usually on the negative side. Precision improved after the first two audits and with one exception has been within ± 8 percent since 1979 (see Figures 11 and 12).

In 1983 the number of measurements within ± 20 percent of the assigned value was slightly less than in the 1982 audits (Table 19). With the exception of two laboratories using the inductively coupled argon plasma optical emission spectrometric method, all others used the atomic absorption method.

SULFUR DIOXIDE (CONTINUOUS MONITORS)

The number of laboratories participating in the 1983 audits totaled 86. The number of individual monitors audited was 187 (Table 20). Compared to 1982 this is an overall increase of approximately 18 percent, mainly because of increased participation among state agencies.

The methods most commonly used were: fluorescence (157), flame photometric (22) and coulometric (6). The accuracy for each of the methods is shown in Table 21. With one exception the accuracy of the fluorescent and the coulometric methods showed improvement over the 1982 results. Overall the mean percent difference has improved each year since 1981. The greatest improvement in 1983 occurred with the coulometric method.

HIGH VOLUME

There were 216 agencies participating in the audit with an average of 6.2 sites per agency. The number of monitors checked this year is 10 percent below the number for 1982. Prior to this year there had been an increase every year in the number of monitors audited beginning with 1977. The decrease is a result of the drop in the number of industrial and federal agencies taking part in the program this year.

The pressure transducer continued to be the most widely used method of measurement (50.9%), the rotometer was next (27.5%), followed by pressure transducer/flow controller (2.8%) and flow controller (2.7%). Other methods accounted for the remaining 16.1 percent of the results and included: orifice manometer, manometer, flow gauge, and pressure transducer/non-continuous. The results (Table 22) were little changed from 1982. For example in 1983, 40% of the rotameters yielded results within 2.4% of the true value, whereas, in 1982 40% of them yielded results within 2.2% of the true values.

ACID RAIN

Twenty-eight laboratories participated in the 0483 audit and thirty-two in the 1183 audit. The greatest percentage of laboratories participating were state operated followed by industrial, federal and local laboratories.

The audit mean, percent accuracy and percent CV for samples 1, 2 and 3 are presented in Tables 23, 24 and 25 for the 0483 audit and Tables 27, 28 and 29 for the 1183 audit. For most of the constituents in these samples the percent accuracy was better in the 1183 audit than in the 0483, but the reverse was true for precision.

The accuracy and precision values are not as reliable for the trace metals in samples 4 and 5 (Tables 26 and 30). The concentrations in these samples are low and a small change in concentration results in a large relative (percentage) change.

In general, for all samples, the percent accuracy and percent CV were better in the 0483 audit than in the 1183 audit.

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TABLE 1. AGENCY PARTICIPATION

Survey	Distribution (%)					No. of Laboratories ^a	No. of Monitors ^a
	States	Local	Industry	Federal	Foreign		
SO ₂ — April 1983	29.2	29.2	37.5	4.2	0.0	24 (0)	—
SO ₂ — October 1983	29.2	29.2	37.5	4.2	0.0	24 (0)	—
NO ₂ — June 1983	32.1	46.4	21.4	0.0	0.0	28 (0)	—
NO ₂ — December 1983	25.0	45.0	30.0	0.0	0.0	20 (0)	—
CO — May 1983	41.4	46.9	7.3	1.3	3.1	—	386 (4)
CO — October 1983	44.2	41.3	8.8	1.7	4.0	—	351 (10)
SO ₄ — February 1983	47.5	18.6	20.3	3.0	5.0	59 (2)	—
SO ₄ — August 1983	42.4	23.7	22.0	3.4	8.5	59 (0)	—
NO ₃ — February 1983	54.5	20.5	13.6	2.0	9.0	44 (7)	—
NO ₃ — August 1983	50.0	23.8	14.3	2.4	9.5	42 (6)	—
Pb — January 1983	41.0	30.0	26.0	2.0	1.0	100 (3)	—
Pb — July 1983	41.3	26.0	26.0	3.2	3.2	92 (0)	—
SO ₂ (continuous)	59.0	26.0	14.0	1.0	0.0	—	187
High-Volume Flow-Rate -- May 1983	34.9	47.5	14.8	0.6	2.2	—	1342 (105)
Acid Rain — April 1983	50.0	7.1	28.6	14.3	NA	28	
Acid Rain -- November 1983	43.8	6.2	37.5	12.5	NA	32	

^aValue in parentheses is the number of laboratories/monitors that reported all values off by more than $\pm 20\%$ from the true value.

TABLE 2. AUDIT RESULTS FOR MANUAL SULFUR DIOXIDE

Audit	Level	n	Assigned value ($\mu\text{g}/\text{m}^3$)	Mean ($\mu\text{g}/\text{m}^3$)	% Acc.	% CV
A. <u>ALL DATA</u>						
0483	1	24	21.60	21.27	6.1	28.2
	2	23	55.60	55.85	1.1	10.3
	3	24	105.2	103.3	-0.4	9.7
	4	24	153.1	151.9	0.8	8.4
	5	24	220.0	224.4	2.8	5.5
1083	1	24	48.80	49.74	2.7	11.1
	2	23	81.90	83.53	2.0	10.6
	3	24	122.0	124.09	3.3	12.4
	4	24	154.50	161.78	5.7	10.8
	5	24	178.50	181.53	1.3	8.9
B. <u>STATISTICAL OUTLIERS REMOVED</u>						
0483	1	22	21.60	22.40	6.2	18.3
	2	22	55.60	56.55	1.2	8.3
	3	23	105.2	104.5	-0.7	7.9
	4	23	153.1	153.5	0.9	6.8
	5	24	220.0	224.7	2.8	5.5
1083	1	22	48.80	50.93	3.1	7.8
	2	22	81.90	84.40	2.1	9.3
	3	23	122.0	126.48	3.4	8.0
	4	22	154.50	162.49	5.7	6.3
	5	23	178.50	179.66	1.3	7.8

TABLE 3. RESULTS FOR THE PARAROSANILINE METHOD

Audit	Level	Assigned value ($\mu\text{g}/\text{m}^3$)	Manual Method (01)				Automated Method (02)			
			n	Mean ($\mu\text{g}/\text{m}^3$)	% Acc.	% CV	n	Mean ($\mu\text{g}/\text{m}^3$)	% Acc.	% CV
A. <u>ALL DATA</u>										
0483	1	21.60	15	20.31	1.9	35.6	8	23.39	8.1	5.3
	2	55.60	14	55.29	0.0	12.0	8	57.43	4.6	6.4
	3	105.20	15	103.16	-0.4	11.5	8	104.90	1.3	5.2
	4	153.10	15	153.76	0.8	9.9	8	154.87	1.3	4.8
	5	220.00	15	224.83	3.4	6.4	8	223.73	2.3	4.0
1083	1	48.80	16	50.49	3.3	11.1	7	48.50	2.0	12.1
	2	81.90	16	85.84	4.0	11.6	7	78.64	-2.5	7.5
	3	122.00	16	125.65	5.5	14.4	7	120.02	-2.0	7.0
	4	154.50	16	164.40	7.8	12.5	7	154.80	1.1	3.8
	5	178.5	16	184.32	3.3	9.6	7	174.90	0.4	7.2
B. <u>STATISTICAL OUTLIERS REMOVED</u>										
0483	1	21.60	15	20.31	1.9	35.6	8	23.39	8.1	5.3
	2	55.60	13	56.47	1.1	9.2	8	57.43	4.6	6.4
	3	105.20	14	105.14	1.4	8.9	8	104.90	1.3	5.2
	4	153.10	14	153.76	0.8	1.1	8	154.87	1.3	4.8
	5	220.00	15	224.83	3.4	6.4	8	223.73	2.3	4.0
1083	1	48.80	15	51.41	3.5	8.9	7	48.50	2.0	12.1
	2	81.90	15	87.45	5.4	8.6	7	78.64	-2.5	7.0
	3	122.00	15	129.42	6.0	7.9	7	120.02	-2.0	7.0
	4	154.50	15	168.30	8.2	8.2	7	154.80	1.1	3.8
	5	178.5	14	184.22	3.3	6.1	6	179.62	0.5	1.1

TABLE 4. PERCENT OF SULFUR DIOXIDE MEASUREMENTS WITHIN INDICATED
PERCENT OF ASSIGNED VALUES (ALL DATA)^a

Audit	Level	Assigned value ($\mu\text{g}/\text{m}^3$)	10%	20%	30%	50%
0483	1	21.60	58.3	75.0	79.2	91.2
	2	55.60	75.0	87.5	95.8	95.8
	3	105.20	83.3	91.7	100.0	100.0
	4	153.10	87.5	95.8	100.0	100.0
	5	220.00	87.5	100.0	100.0	100.0
1083	1	48.80	62.5	87.5	100.0	100.0
	2	81.90	58.3	87.5	95.8	95.8
	3	122.00	70.8	91.2	95.8	100.0
	4	154.50	79.2	87.5	91.7	100.0
	5	178.50	83.3	95.8	100.0	100.0

^aPercentage difference table unchanged after outliers deleted.

TABLE 5. AUDIT RESULTS FOR NITROGEN DIOXIDE

Audit	Level	n	Assigned value ($\mu\text{g/ml}$)	Mean ($\mu\text{g/ml}$)	% Acc.	% CV
A. <u>ALL DATA</u>						
0683	0	28	0.415	0.396	-4.1	4.8
	1	28	0.548	0.543	0.4	5.7
	2	28	0.645	0.616	-4.2	3.9
	5	28	0.553	0.527	-4.5	3.4
	8	27	0.936	0.897	-4.1	2.0
1283	3	19	0.515	0.512	-1.4	3.5
	4	19	0.790	0.791	0.0	2.9
	6	20	0.640	0.656	2.3	3.5
	7	20	0.480	0.483	0.0	4.3
	9	20	1.000	1.046	4.6	2.7
B. <u>STATISTICAL OUTLIERS REMOVED</u>						
0683	0	27	0.415	0.399	-3.9	3.3
	1	26	0.548	0.550	0.5	2.2
	2	27	0.645	0.619	-4.0	2.3
	5	26	0.553	0.527	-4.5	2.3
	8	26	0.936	0.895	-4.3	1.7
1283	3	17	0.515	0.507	-1.6	2.0
	4	18	0.790	0.787	0.0	2.2
	6	19	0.640	0.652	2.2	2.6
	7	19	0.480	0.480	0.0	2.9
	9	19	1.000	1.050	4.8	2.2

TABLE 6. AUDIT RESULTS FOR NITROGEN DIOXIDE BY THE SODIUM ARSENITE METHOD

Audit	Level	Assigned value ($\mu\text{g/mL}$)	Manual Method (05)				Automated Method (06)			
			n	Mean ($\mu\text{g/mL}$)	Z Acc.	Z CV	n	Mean ($\mu\text{g/mL}$)	Z Acc.	Z CV
A. <u>ALL DATA</u>										
0683	0	0.415	18	0.395	-1.7	5.6	7	0.400	-4.1	2.8
	1	0.548	18	0.544	0.5	5.7	7	0.547	-0.7	2.6
	2	0.645	18	0.615	-3.9	4.6	7	0.617	-4.7	1.9
	5	0.553	18	0.528	-4.5	4.0	7	0.528	-4.3	1.8
	8	0.936	17	0.900	-4.1	2.0	7	0.891	-4.8	2.2
1283	3	0.515	11	0.510	-1.6	3.5	5	0.517	-0.2	4.6
	4	0.790	10	0.788	0.0	2.8	6	0.798	-0.3	3.6
	6	0.640	11	0.647	1.4	2.8	6	0.659	2.0	5.3
	7	0.480	11	0.480	0.0	3.5	6	0.491	0.6	6.3
	9	1.000	11	1.042	4.8	3.3	6	1.041	4.1	1.2
B. <u>STATISTICAL OUTLIERS REMOVED</u>										
0683	0	0.415	17	0.399	-3.9	3.5	7	0.400	-4.1	2.8
	1	0.548	17	0.550	0.7	2.1	7	0.547	-0.7	2.6
	2	0.645	17	0.621	-3.7	2.0	7	0.617	-4.7	1.9
	5	0.553	17	0.525	-4.7	3.0	7	0.528	-4.3	1.8
	8	0.936	16	0.897	-4.1	1.6	7	0.891	-4.8	2.2
1283	3	0.515	10	0.506	-2.3	2.4	5	0.517	-0.2	4.6
	4	0.790	10	0.788	0.0	2.8	6	0.798	-0.3	3.6
	6	0.640	10	0.647	0.9	1.7	6	0.659	2.0	5.3
	7	0.480	11	0.480	0.0	3.5	6	0.491	0.6	6.3
	9	1.000	10	1.049	4.9	2.4	6	1.041	4.1	1.2

TABLE 7. PERCENTAGE OF NITROGEN DIOXIDE MEASUREMENTS WITHIN INDICATED PERCENTAGE OF ASSIGNED VALUE (ALL DATA)^a

Audit	Level	Assigned value (µg/mL)	10%	20%	30%	50%
0683	0	0.42	92.9	96.4	100.0	100.0
	1	0.55	92.9	96.4	100.0	100.0
	2	0.65	96.4	96.4	100.0	100.0
	5	0.55	96.4	100.0	100.0	100.0
	8	0.94	96.4	96.4	96.4	96.4
1283	3	0.52	95.0	95.0	95.0	95.0
	4	0.79	95.0	95.0	95.0	95.0
	6	0.64	95.0	100.0	100.0	100.0
	7	0.48	95.0	100.0	100.0	100.0
	9	1.00	100.0	100.0	100.0	100.0

^aPercentage distribution table unchanged after outliers removed.

TABLE 8. AUDIT RESULTS FOR CARBON MONOXIDE

Audit	Level	n	Assigned value (ppm)	Mean (ppm)	% Acc.	% CV
A. <u>ALL DATA</u>						
0583	1	386	6.10	6.00	-1.6	9.2
	2	380	21.50	21.59	0.3	2.1
	3	384	44.00	44.33	0.6	2.6
1083	1	345	8.30	8.36	1.2	8.0
	2	352	15.86	16.14	1.5	6.1
	3	351	36.76	37.33	1.1	5.3
B. <u>STATISTICAL OUTLIERS REMOVED</u>						
0583	1	381	6.10	5.97	-1.6	6.0
	2	375	21.50	21.58	0.3	2.8
	3	380	44.00	44.30	0.6	2.4
1083	1	341	8.30	8.35	1.2	5.5
	2	351	15.86	16.14	1.5	3.7
	3	348	36.76	37.20	1.1	2.8

TABLE 9. AUDIT RESULTS FOR CARBON MONOXIDE BY THE NDIR AND GC METHODS

Audit	Level	Assigned value (ppm)	NDIR (9)				GC (10)			
			n	Mean (ppm)	% Acc.	% CV	n	Mean (ppm)	% Acc.	% CV
A. <u>ALL DATA</u>										
0583	1	6.10	367	6.00	-1.6	8.8	6	5.23	-13.0	11.1
	2	21.50	361	21.58	0.3	3.2	6	20.59	-2.5	6.4
	3	44.00	365	44.30	2.7	2.7	6	43.67	-1.0	1.1
1083	1	8.30	324	8.36	1.2	6.0	3	7.08	-17.0	8.1
	2	15.86	330	16.13	1.8	3.5	3	14.62	-8.8	2.3
	3	36.76	329	37.28	1.2	3.2	3	36.35	0.1	2.5
B. <u>STATISTICAL OUTLIERS REMOVED</u>										
0583	1	6.10	363	5.97	-1.6	5.9	6	5.23	-13.0	11.1
	2	21.50	356	21.59	0.4	2.7	6	20.59	-2.5	6.4
	3	44.00	360	44.31	0.7	2.3	6	43.67	-1.0	1.1
1083	1	8.30	319	8.39	1.2	4.8	3	7.08	-17.0	8.1
	2	15.86	325	16.15	1.8	3.2	3	14.62	-8.8	2.3
	3	36.76	326	37.24	1.2	2.7	3	36.35	0.1	2.5

TABLE 10. PERCENTAGE OF CARBON MONOXIDE MEASUREMENTS WITHIN INDICATED PERCENTAGE OF ASSIGNED VALUE

Audit	Level	Assigned value (ppm)	10%	20%	30%	50%
A. <u>ALL DATA</u>						
0583	1	6.10	88.2	97.9	98.5	99.2
	2	21.50	95.9	98.5	98.5	98.5
	3	44.00	97.7	99.5	99.5	99.5
1083	1	8.30	89.8	93.9	96.7	97.5
	2	15.86	93.9	98.1	98.9	99.4
	3	36.76	95.6	97.8	98.6	98.9
B. <u>STATISTICAL OUTLIERS REMOVED</u>						
0383	1	6.10	89.1	96.7	98.7	99.5
	2	21.50	96.9	98.4	98.4	98.4
	3	44.00	98.7	99.5	99.5	99.5
1083	1	8.30	92.3	96.0	97.4	98.0
	2	15.86	96.6	100.0	100.0	100.0
	3	36.76	98.3	99.1	99.7	99.7

TABLE 11. AUDIT RESULTS FOR SULFATE ON FILTER STRIPS

Audit	Level	n	Assigned value ($\mu\text{g}/\text{m}^3$)	Mean ($\mu\text{g}/\text{m}^3$)	% Acc.	% CV
A. <u>ALL DATA</u>						
0283	1	56	1.20	1.49	1.7	55.7
	2	58	3.64	3.53	-3.8	18.9
	3	59	7.24	7.24	-3.5	14.9
	4	59	12.01	11.72	-3.3	14.8
	5	59	19.30	18.31	-4.2	11.2
	6	58	23.90	22.48	-5.0	10.0
0883	1	55	2.62	2.50	-23.2	88.8
	2	59	4.49	5.04	-0.9	71.2
	3	59	8.96	9.03	-2.9	14.0
	4	58	12.82	12.89	-0.2	10.9
	5	59	21.23	21.06	-0.8	6.6
	6	58	28.51	28.49	-0.3	6.7
B. <u>STATISTICAL OUTLIERS REMOVED</u>						
0283	1	54	1.20	1.37	0.0	41.6
	2	55	3.64	3.53	-3.8	11.8
	3	57	7.24	7.10	-3.6	10.6
	4	57	12.01	11.73	-3.3	8.8
	5	57	19.3	18.40	-4.2	6.3
	6	57	23.90	22.74	-4.6	6.6
0883	1	53	2.62	2.12	23.7	46.2
	2	58	4.49	4.61	-1.1	30.8
	3	57	8.96	8.84	-2.9	8.5
	4	56	12.82	12.93	-0.2	7.5
	5	57	21.23	21.05	-0.8	5.3
	6	56	28.51	28.25	-0.4	5.2

TABLE 12. AUDIT RESULTS FOR SULFATE BY THE MANUAL METHODS

Audit	Level	Assigned value ($\mu\text{g}/\text{m}^3$)	BaCl ₂ (17)				Sulfa-Ver (19)			
			n	Mean ($\mu\text{g}/\text{m}^3$)	% Acc.	% CV	n	Mean ($\mu\text{g}/\text{m}^3$)	% Acc.	% CV
A. <u>ALL DATA</u>										
0283	1	1.20	8	2.38	45.8	61.3	5	1.65	13.3	57.0
	2	3.64	9	3.76	4.4	32.7	5	4.03	6.6	29.0
	3	7.24	9	7.75	6.2	19.6	5	7.08	-7.5	18.6
	4	12.01	9	12.64	3.2	10.2	5	12.01	-9.7	18.8
	5	19.30	9	19.30	-2.6	11.8	5	17.74	-9.1	5.2
	6	23.90	8	22.82	-0.2	4.2	5	21.46	-7.9	7.3
0883	1	2.62	8	3.79	-5.7	97.1	3	2.24	-19.8	23.2
	2	4.49	10	5.48	0.4	51.3	4	5.52	6.4	32.2
	3	8.96	10	9.56	0.4	22.0	4	10.50	8.4	25.4
	4	12.82	10	13.59	3.0	10.7	4	14.10	6.6	12.7
	5	21.23	10	21.78	0.8	7.7	4	20.91	-0.4	6.2
	6	28.51	9	29.74	2.8	7.1	4	28.96	-0.6	15.5
B. <u>STATISTICAL OUTLIERS REMOVED</u>										
0283	1	1.20	8	2.38	45.8	61.3	5	1.65	13.3	57.0
	2	3.64	9	3.76	4.4	32.7	5	4.03	6.6	29.0
	3	7.64	9	7.75	6.2	19.6	5	7.08	-7.5	18.6
	4	12.01	9	12.64	3.2	10.2	5	12.01	-9.7	18.8
	5	19.30	8	18.64	-2.8	6.3	5	17.74	-9.1	5.2
	6	23.90	8	22.82	-0.2	4.2	5	21.46	-7.9	7.3
0883	1	2.62	7	2.66	-6.1	74.1	3	2.24	-19.8	23.2
	2	4.49	9	4.71	0.2	31.2	4	5.52	6.4	32.2
	3	8.96	9	8.99	0.6	12.6	4	10.50	8.4	25.4
	4	12.82	9	13.18	2.7	5.6	4	14.10	6.6	12.7
	5	21.23	9	21.33	0.2	4.3	4	20.91	0.4	6.2
	6	28.51	8	28.51	1.6	2.3	4	28.96	0.6	15.5

TABLE 13. AUDIT RESULTS FOR SULFATE BY THE AUTOMATED METHODS

Audit	Level	Assigned value ($\mu\text{g}/\text{m}^3$)	Methyl Thymol Blue (16)				Ion Chromatograph (34)			
			n	Mean ($\mu\text{g}/\text{m}^3$)	% Acc.	% CV	n	Mean ($\mu\text{g}/\text{m}^3$)	% Acc.	% CV
A. <u>ALL DATA</u>										
0283	1	1.20	25	1.34	0.0	40.3	16	1.14	-0.8	25.4
	2	3.64	25	3.48	-5.5	13.2	17	3.48	-3.6	8.0
	3	7.24	26	7.05	-5.7	10.8	17	7.29	-3.5	16.6
	4	12.01	26	11.28	-4.5	14.6	17	12.07	-2.4	11.6
	5	19.30	26	17.95	-4.4	14.2	17	18.52	-3.8	6.4
	6	23.90	26	22.04	-5.3	14.5	17	23.20	-3.8	7.4
0883	1	2.62	25	2.48	-25.2	100.0	16	1.91	-24.8	21.5
	2	4.49	24	5.46	-1.1	96.0	18	4.19	-1.8	21.7
	3	8.96	25	8.88	-2.9	7.2	17	8.59	-3.7	5.1
	4	12.82	24	12.62	-0.2	12.0	17	12.47	-1.3	5.7
	5	21.23	25	21.09	-0.1	7.0	17	20.82	-1.3	5.3
	6	28.51	25	28.35	-1.1	3.3	17	28.20	-2.8	6.2
B. <u>STATISTICAL OUTLIERS REMOVED</u>										
0283	1	1.20	25	1.34	0.0	40.3	15	1.21	0.0	12.4
	2	3.64	24	3.44	-6.1	11.9	16	3.43	-3.8	6.4
	3	7.24	25	6.97	-5.7	9.6	16	7.00	-3.7	3.9
	4	12.01	25	11.57	-4.2	6.3	16	11.63	-2.7	5.4
	5	19.30	25	18.39	4.2	6.7	16	18.36	-4.0	5.4
	6	23.90	25	22.60	-5.2	6.2	16	23.49	-2.6	3.5
0883	1	2.62	24	2.02	23.3	44.1	15	1.99	-24.8	12.1
	2	4.49	23	4.40	-1.3	10.0	17	4.40	-1.3	5.9
	3	8.96	25	8.88	-2.9	7.2	16	8.67	-3.3	3.8
	4	12.82	23	12.90	-0.2	5.7	16	12.57	-0.9	4.8
	5	21.23	23	21.43	0.0	4.2	17	20.82	-1.3	5.3
	6	28.51	25	28.35	-1.1	3.3	16	28.46	-0.3	5.0

TABLE 14. PERCENTAGE OF SULFATE MEASUREMENTS WITHIN INDICATED PERCENTAGE OF ASSIGNED VALUE

Audit	Level	Assigned value ($\mu\text{g}/\text{m}^3$)	10%	20%	30%	50%
A. <u>ALL DATA</u>						
0283	1	1.20	36.1	54.1	62.3	70.5
	2	3.64	52.5	80.3	88.5	90.2
	3	7.24	63.9	85.2	91.8	93.4
	4	12.01	77.0	90.1	95.1	95.1
	5	19.30	75.4	91.8	96.7	96.7
	6	22.68	77.0	88.5	95.1	95.1
0883	1	2.62	13.6	25.4	54.2	76.3
	2	4.49	67.8	86.4	91.5	91.5
	3	8.96	79.7	93.2	94.9	96.6
	4	12.82	79.7	93.2	94.9	96.6
	5	21.23	89.8	96.6	100.0	100.0
	6	28.51	89.8	94.9	98.3	98.3
B. <u>STATISTICAL OUTLIERS REMOVED</u>						
0283	1	1.20	39.2	58.9	67.9	76.8
	2	3.64	55.1	84.5	93.1	94.8
	3	7.24	66.1	88.1	94.9	96.7
	4	12.01	79.7	91.8	96.7	96.7
	5	19.30	78.0	96.9	98.3	98.3
	6	22.68	81.0	93.1	98.3	98.3
0883	1	2.62	13.6	25.4	54.2	76.3
	2	4.49	67.8	86.4	91.5	91.5
	3	8.96	79.7	93.2	94.9	96.6
	4	12.82	79.7	93.2	94.9	96.6
	5	21.23	89.8	96.6	100.0	100.0
	6	28.51	89.8	94.9	98.3	98.3

TABLE 15. AUDIT RESULTS FOR NITRATE ON FILTER STRIPS

Audit	Level	n	Assigned value ($\mu\text{g}/\text{m}^3$)	Mean ($\mu\text{g}/\text{m}^3$)	% Acc.	% CV
A. <u>ALL DATA</u>						
0283	1	43	0.78	0.81	0.0	39.5
	2	43	2.37	2.46	-0.4	20.7
	3	44	5.69	5.62	-1.9	10.3
	4	44	9.48	9.29	-1.9	8.7
	5	44	11.83	11.59	-2.3	6.6
	6	43	14.00	13.93	-1.4	9.1
0883	1	39	0.60	0.70	3.3	34.3
	2	42	1.81	1.90	1.1	23.7
	3	42	5.06	5.08	-0.8	7.3
	4	42	8.75	8.73	0.6	6.2
	5	42	11.09	11.76	1.0	5.2
	6	42	13.63	13.56	-1.0	6.3
B. <u>STATISTICAL OUTLIERS REMOVED</u>						
0283	1	42	0.78	0.77	-1.3	31.2
	2	42	2.37	2.40	-1.3	14.2
	3	42	5.69	5.61	-1.9	6.8
	4	42	9.48	9.31	-1.9	6.6
	5	43	11.83	11.56	-2.3	5.3
	6	41	14.00	13.72	-1.6	5.7
0883	1	38	0.60	0.67	3.3	25.4
	2	39	1.81	1.80	0.6	13.9
	3	41	5.06	5.05	-1.0	6.7
	4	42	8.75	8.77	0.6	6.2
	5	41	11.09	11.12	0.5	4.7
	6	41	13.63	13.63	-0.9	5.4

TABLE 16. AUDIT RESULTS FOR NITRATE BY THE AUTOMATED METHODS

Audit	Level	Assigned value ($\mu\text{g}/\text{m}^3$)	Ion Chromatograph (34)				Cadium Reduction (12)			
			n	Mean ($\mu\text{g}/\text{m}^3$)	% Acc.	% CV	n	Mean ($\mu\text{g}/\text{m}^3$)	% Acc.	% CV
A. <u>ALL DATA</u>										
0283	1	0.78	14	0.67	-5.1	28.8	16	0.86	0.0	30.2
	2	2.37	14	2.26	-4.2	13.7	16	2.48	0.0	12.1
	3	5.69	14	5.48	-3.3	5.3	17	5.69	-1.6	7.0
	4	9.48	14	9.11	-2.8	7.1	17	9.24	-1.9	9.8
	5	11.83	14	11.50	-3.0	6.1	17	11.55	2.1	4.6
	6	14.00	14	13.6	-1.1	7.4	17	13.85	-1.9	5.1
0883	1	0.60	14	0.81	10.0	42.0	16	0.65	3.3	20.0
	2	1.81	16	1.97	2.2	22.3	16	2.00	1.7	25.0
	3	5.06	15	5.14	1.4	5.8	17	5.06	-1.6	6.1
	4	8.75	15	8.83	1.7	5.8	17	8.68	-0.6	5.5
	5	16.09	15	11.25	0.3	6.0	17	11.33	0.5	3.4
	6	13.63	15	13.70	-0.9	7.7	17	13.50	-2.4	3.6
B. <u>STATISTICAL OUTLIERS REMOVED</u>										
0283	1	0.78	12	0.77	-2.6	15.6	15	0.81	-1.3	21.0
	2	2.37	13	2.33	-3.4	7.3	15	2.43	-0.4	0.1
	3	5.69	13	5.53	-3.0	4.0	16	5.62	-1.7	5.2
	4	9.48	13	9.22	-2.0	5.6	16	9.42	-1.7	6.1
	5	11.83	14	11.50	-3.0	6.1	16	11.63	-1.9	3.8
	6	14.00	13	13.76	-0.8	6.0	16	13.75	-1.9	4.3
0883	1	0.60	13	0.74	10.0	29.7	12	0.62	3.3	16.1
	2	1.81	15	1.87	2.2	11.8	14	1.83	0.6	10.4
	3	5.00	15	5.14	1.4	5.8	16	5.00	-1.8	4.6
	4	8.75	15	8.83	1.7	5.8	17	8.69	-0.6	5.5
	5	11.09	14	11.13	0.0	4.8	17	11.13	0.5	3.4
	6	13.63	14	13.90	0.1	5.2	17	13.56	-2.4	3.6

TABLE 17. PERCENTAGE OF NITRATE MEASUREMENTS WITHIN INDICATED PERCENTAGE OF ASSIGNED VALUE

Audit	Level	Assigned value ($\mu\text{g}/\text{m}^3$)	10%	20%	30%	50%
A. <u>ALL DATA</u>						
0283	1	0.78	39.2	60.7	70.6	74.5
	2	2.37	66.7	74.5	78.4	86.3
	3	5.69	70.6	84.3	86.2	92.2
	4	9.48	74.5	82.4	88.2	94.1
	5	11.83	76.5	84.3	90.2	92.2
	6	14.00	74.5	82.4	84.3	90.2
0883	1	0.60	35.4	56.3	62.5	72.9
	2	1.81	60.4	68.8	81.3	81.3
	3	5.06	75.0	85.4	89.6	91.7
	4	8.75	79.2	87.5	91.7	91.7
	5	11.12	83.3	89.6	93.8	93.8
	6	13.63	77.1	89.6	93.8	93.8
B. <u>STATISTICAL OUTLIERS REMOVED</u>						
0283	1	0.78	46.5	72.0	81.3	86.0
	2	2.37	79.0	88.3	90.7	95.0
	3	5.69	81.8	95.6	95.6	100.0
	4	9.48	86.4	95.5	97.7	100.0
	5	11.83	88.6	97.7	100.0	100.0
	6	14.00	88.4	95.3	97.6	100.0
0883	1	0.60	40.5	64.3	71.4	81.0
	2	1.81	69.0	78.6	90.5	90.5
	3	5.06	85.7	97.6	100.0	100.0
	4	8.75	90.5	100.0	100.0	100.0
	5	11.12	95.2	100.0	100.0	100.0
	6	13.63	88.1	97.6	100.0	100.0

TABLE 18. AUDIT RESULTS FOR LEAD ON FILTER STRIPS

Audit	Level	n	Assigned value ($\mu\text{g}/\text{m}^3$)	Mean ($\mu\text{g}/\text{m}^3$)	% Acc.	% CV
A. <u>ALL DATA</u>						
0183	1	95	0.58	0.58	1.7	8.6
	2	95	1.53	1.51	-0.7	7.9
	3	97	2.91	2.87	-1.4	7.3
	4	97	4.13	3.97	-2.2	12.6
	5	97	5.80	5.80	0.7	7.4
	6	97	7.51	7.53	0.7	5.6
0783	1	92	0.75	0.74	-2.6	16.0
	2	92	1.62	1.57	-3.7	7.6
	3	91	2.67	2.59	-2.6	5.4
	4	91	4.18	4.05	-2.4	6.4
	5	89	6.99	6.71	-3.6	8.0
	6	92	8.01	7.73	-3.2	4.5
B. <u>STATISTICAL OUTLIERS REMOVED</u>						
0183	1	93	0.58	0.58	1.7	8.6
	2	92	1.53	1.52	-0.7	5.9
	3	93	2.91	2.87	-1.4	4.5
	4	96	4.13	4.02	-2.4	7.2
	5	94	5.80	5.78	0.5	5.2
	6	95	7.51	7.52	0.7	4.7
0783	1	90	0.75	0.74	-2.6	8.1
	2	90	1.62	1.57	-3.7	3.8
	3	89	2.67	2.60	-2.6	3.8
	4	89	4.18	4.06	-2.4	4.2
	5	88	6.99	6.76	-3.4	4.3
	6	89	8.01	7.72	-3.2	3.9

TABLE 19. PERCENTAGE OF LEAD MEASUREMENTS WITHIN INDICATED PERCENTAGE OF ASSIGNED VALUE

Audit	Level	Assigned value ($\mu\text{g}/\text{m}^3$)	10%	20%	30%	50%
A. <u>ALL DATA</u>						
0183	1	0.58	74.0	88.0	94.0	96.0
	2	1.53	85.0	91.0	93.0	97.0
	3	2.91	89.0	93.0	96.0	99.0
	4	4.13	89.0	92.0	96.0	98.0
	5	5.80	88.0	44.0	97.0	99.0
	6	7.51	93.0	95.0	97.0	99.0
0783	1	0.75	83.7	92.4	95.7	98.9
	2	1.62	96.7	97.8	97.8	98.9
	3	2.67	94.6	97.8	97.8	98.9
	4	4.18	92.4	97.8	97.8	98.9
	5	6.99	92.4	95.7	95.7	95.7
	6	8.01	89.1	100.0	100.0	100.0
B. <u>STATISTICAL OUTLIERS REMOVED</u>						
0183	1	0.58	76.2	90.7	95.9	96.6
	2	1.53	87.6	93.8	95.9	97.9
	3	2.91	91.8	95.9	97.9	100.0
	4	4.13	91.7	94.8	97.9	99.0
	5	5.80	90.7	96.6	99.0	100.0
	6	7.51	95.9	97.9	100.0	100.0
0783	1	0.75	83.7	92.4	95.7	98.9
	2	1.62	95.7	97.8	97.8	98.9
	3	2.67	94.6	97.8	97.8	98.9
	4	4.18	92.4	97.8	97.8	98.9
	5	6.99	92.4	95.7	95.7	95.7
	6	8.01	89.1	100.0	100.0	100.0

TABLE 20. AUDIT RESULTS FOR SULFUR DIOXIDE CONTINUOUS MONITORS (ALL DATA)

Flow setting	Number of reported values*	Range of values (ppm)	Mean differences		Standard deviation (ppm)
			ppm	% diff.	
1	19	0.632 to 0.864	0.005	0.690	0.076
2	172	0.403 to 0.626	-0.006	-1.188	0.045
3	187	0.208 to 0.326	-0.001	-0.584	0.024
4	187	0.166 to 0.253	-0.002	-0.830	0.018
5	187	0.040 to 0.091	-0.001	-1.039	0.007
6	180	0.000	0.001	—	—

*1983 Audit: Data returned for 187 monitors

TABLE 21. AUDIT RESULTS FOR SULFUR DIOXIDE CONTINUOUS MONITORS
BY VARIOUS INSTRUMENTAL METHODS

Flow setting	Flame photometric			Fluorescent			Coulometric		
	average difference			average difference			average difference		
	n	ppm	%	n	ppm	%	n	ppm	%
1	0	---	---	18	0.006	0.8	1	---	---
2	21	-0.007	-1.1	143	-0.005	-1.1	6	-0.009	-2.3
3	22	-0.000	-0.1	157	-0.001	-0.6	6	-0.001	-0.8
4	22	-0.002	-1.0	157	-0.001	-0.7	6	-0.003	-1.7
5	22	-0.003	-5.0	157	-0.000	-0.4	6	-0.001	-2.5
6	20	0.002	---	152	0.001	---	6	0.000	---

TABLE 22. AUDIT RESULTS FOR HIGH-VOLUME FLOW RATE

Method	No. of results	Results within indicated % of assigned value			
		20%	40%	60%	80%
Rotameter (visifloat)	1313 ¹	1.13	2.38	3.81	5.97
Pressure transducer (continuous)	2467 ²	1.07	2.29	3.69	5.71
Flow controller	136 ³	1.10	2.30	3.91	5.28
Pressure transducer/flow controller	140 ⁴	1.20	2.23	3.49	5.29
All methods	4844 ⁵	1.12	2.33	3.77	5.80

¹1395 measurements reported

²2583 measurements reported

³136 measurements reported

⁴142 measurements reported

⁵5079 measurements reported

TABLE 23. ACID RAIN RESULTS FOR pH, CONDUCTIVITY AND ACIDITY (APRIL 1983)

Audit		Sample	Assigned value (mg/l)	n	Mean (mg/l)	% Acc.	% CV
A. <u>ALL DATA</u>							
0483	pH	1	4.51	26	4.27	-2.00	9.54
		2	3.51	26	3.39	-1.14	9.11
		3	3.92	26	3.77	-0.89	9.18
	Conductivity	1	17.10	25	35.14	5.26	241.89
		2	156.00	25	151.41	0.77	21.16
		3	65.50	25	62.87	-0.61	21.19
	Acidity	1	35.40	16	44.36	23.59	58.46
		2	322.40	16	313.05	6.27	46.73
		3	127.00	16	124.89	4.29	51.10
B. <u>STATISTICAL OUTLIERS REMOVED</u>							
0483	pH	1	4.51	25	4.33	-2.00	6.49
		2	3.51	25	3.45	-1.14	3.31
		3	3.92	25	3.83	-0.76	4.59
	Conductivity	1	17.10	24	18.15	5.26	14.93
		2	156.00	24	157.50	0.86	6.51
		3	65.50	24	65.39	-0.46	6.86
	Acidity	1	35.40	16	44.36	23.59	58.46
		2	322.40	16	313.05	6.27	46.73
		3	127.00	16	124.89	4.29	51.10

TABLE 24. ACID RAIN AUDIT RESULTS FOR ANIONS (APRIL 1983)

Audit		Sample	Assigned value (mg/l)	n	Mean (mg/l)	% Acc.	% CV
A. <u>ALL DATA</u>							
0483	SO ₄ (reported as S)	1	0.600	24	0.599	0.00	40.97
		2	4.270	24	4.595	0.94	32.42
		3	2.110	24	2.202	-1.90	40.60
	NO ₃ (reported as N)	1	0.140	25	0.150	0.00	26.80
		2	2.110	25	2.280	1.90	19.82
		3	0.840	25	0.918	4.76	22.40
	Cl	1	0.400	23	0.376	-5.00	14.25
		2	2.820	24	2.772	1.06	17.27
		3	1.150	24	1.095	-6.52	23.86
	F	1	0.050	17	0.055	0.00	33.30
		2	0.490	19	0.504	2.04	15.66
		3	0.200	19	0.207	-5.00	20.82
B. <u>STATISTICAL OUTLIERS REMOVED</u>							
0483	SO ₄ (reported as S)	1	0.600	22	0.585	0.00	17.14
		2	4.270	23	4.294	0.47	8.38
		3	2.110	23	2.024	-2.37	9.74
	NO ₃ (reported as N)	1	0.140	24	0.140	0.00	13.60
		2	2.110	24	2.203	1.66	11.07
		3	0.840	24	0.879	4.17	7.22
	Cl	1	0.400	23	0.376	-5.00	14.25
		2	2.820	23	2.849	1.42	10.47
		3	1.150	22	1.095	-6.52	12.36
	F	1	0.050	16	0.052	0.00	28.25
		2	0.490	18	0.490	0.00	8.81
		3	0.200	18	0.198	-5.00	9.19

TABLE 25. ACID RAIN AUDIT RESULTS FOR CATIONS (APRIL 1983)

Audit		Sample	Assigned value (mg/l)	n	Mean (mg/l)	% Acc.	% CV
A. <u>ALL DATA</u>							
0483	NH ₄ (reported as N)	1	0.110	19	0.117	0.00	22.33
		2	0.860	20	0.932	0.58	24.23
		3	0.320	20	0.387	6.25	59.81
	Ca	1	0.060	19	0.084	16.67	43.24
		2	0.400	20	0.404	5.00	19.30
		3	0.150	20	0.166	0.00	40.70
	K	1	0.080	21	0.083	0.00	44.47
		2	0.800	22	0.822	0.00	10.40
		3	0.550	22	0.541	-4.54	11.19
	Mg	1	0.020	19	0.019	0.00	49.43
		2	0.080	20	0.079	0.00	14.41
		3	0.060	20	0.062	0.00	14.57
	Na	1	0.250	22	0.254	-2.00	23.91
		2	1.830	22	1.782	0.00	21.00
		3	1.360	22	1.240	-5.51	21.01
B. <u>STATISTICAL OUTLIERS REMOVED</u>							
0483	NH ₄ (reported as N)	1	0.110	18	0.114	0.00	19.32
		2	0.860	19	0.889	0.00	13.63
		3	0.320	19	0.339	6.25	26.36
	Ca	1	0.060	18	0.078	16.67	30.73
		2	0.400	19	0.418	5.00	11.58
		3	0.150	19	0.154	0.00	24.17
	K	1	0.080	20	0.079	0.00	40.64
		2	0.800	21	0.812	0.00	9.06
		3	0.550	21	0.532	-5.46	8.75
	Mg	1	0.020	17	0.016	0.00	36.81
		2	0.080	19	0.081	0.00	11.56
		3	0.060	19	0.061	0.00	10.78
	Na	1	0.250	21	0.242	-4.00	8.73
		2	1.830	21	1.859	0.55	6.05
		3	1.360	21	1.293	-4.41	5.77

TABLE 26. ACID RAIN AUDIT RESULTS FOR TRACE METALS (APRIL 1983)

Audit		Sample	Assigned value (mg/l)	n	Mean (mg/l)	% Acc.	% CV
A. <u>ALL DATA</u>							
0483	Mn	4	0.120	15	0.125	0.00	9.99
		5	0.030	16	0.037	0.00	41.88
	Fe	4	0.090	15	0.092	0.00	14.93
		5	0.030	14	0.033	0.00	36.66
	Cd	4	0.140	14	0.144	3.57	21.62
		5	0.020	14	0.025	0.00	48.99
	Cu	4	0.210	16	0.334	2.38	138.92
		5	0.060	16	0.058	0.00	21.04
	Ni	4	0.130	15	0.132	-7.69	30.06
		5	0.060	15	0.052	-16.67	14.90
	Pb	4	0.400	13	0.401	0.00	7.59
		5	0.120	13	0.113	0.00	15.05
	Zn	4	0.870	14	0.803	-2.30	26.59
		5	0.160	15	0.161	0.00	7.61
B. <u>STATISTICAL OUTLIERS REMOVED</u>							
0483	Mn	4	0.120	14	0.122	0.00	6.56
		5	0.030	15	0.034	0.00	21.67
	Fe	4	0.090	15	0.092	0.00	14.93
		5	0.030	13	0.031	0.00	31.01
	Cd	4	0.140	12	0.143	3.57	7.49
		5	0.020	13	0.022	0.00	32.50
	Cu	4	0.210	15	0.218	0.00	11.66
		5	0.060	15	0.055	0.00	9.33
	Ni	4	0.130	14	0.122	-7.69	9.18
		5	0.060	14	0.054	-16.67	9.28
	Pb	4	0.400	12	0.408	1.25	3.44
		5	0.120	12	0.117	0.00	5.29
	Zn	4	0.870	13	0.858	-2.30	7.14
		5	0.160	14	0.159	0.00	5.99

TABLE 27. ACID RAIN RESULTS FOR pH, CONDUCTIVITY AND ACIDITY (NOVEMBER 1983)

Audit		Sample	Assigned value (mg/l)	n	Mean (mg/l)	% Acc.	% CV
A. <u>ALL DATA</u>							
1183	pH	1	4.45	29	4.42	0.00	2.97
		2	3.72	28	3.69	-0.40	2.13
		3	3.49	30	3.45	-0.29	2.74
	Conductivity	1	19.00	26	18.00	-5.79	27.46
		2	135.00	25	125.59	-3.11	19.90
		3	165.80	27	152.52	-4.22	19.91
	Acidity	1	35.80	14	52.71	22.91	53.10
		2	202.50	15	233.24	9.14	22.64
		3	339.40	15	371.07	4.27	13.64
B. <u>STATISTICAL OUTLIERS REMOVED</u>							
1183	pH	1	4.45	27	4.44	0.45	2.34
		2	3.72	27	3.69	-0.27	1.92
		3	3.49	29	3.46	-0.29	1.98
	Conductivity	1	19.00	24	18.07	-5.79	13.88
		2	135.00	24	130.24	-2.96	7.18
		3	165.80	26	157.73	-4.07	8.87
	Acidity	1	35.80	13	45.85	17.32	25.18
		2	202.50	14	221.69	8.40	13.13
		3	339.40	15	371.07	4.27	13.64

TABLE 28. ACID RAIN RESULTS FOR ANIONS (NOVEMBER 1983)

Audit		Sample	Assigned value (mg/l)	n	Mean (mg/l)	% Acc.	% CV
A. <u>ALL DATA</u>							
1183	SO ₄ (reported as S)	1	0.570	26	0.616	0.00	42.49
		2	3.720	26	3.932	-0.13	43.74
		3	5.920	28	5.971	-1.10	42.27
	NO ₃ (reported as N)	1	0.030	24	0.045	0.00	107.68
		2	1.380	24	1.360	-1.09	5.67
		3	1.020	26	1.006	-1.96	6.80
	Cl	1	1.010	26	0.996	-1.48	31.52
		2	10.330	25	9.772	-2.23	19.98
		3	4.170	27	4.165	-3.12	12.30
	F	1	0.050	17	0.054	0.00	41.35
		2	0.130	16	0.132	-3.85	25.48
		3	0.200	18	0.213	5.00	11.49
B. <u>STATISTICAL OUTLIERS REMOVED</u>							
1183	SO ₄ (reported as S)	1	0.570	25	0.570	0.00	19.79
		2	3.720	25	3.621	-0.54	18.82
		3	5.920	27	5.570	-1.35	25.01
	NO ₃ (reported as N)	1	0.030	22	0.031	0.00	28.08
		2	1.380	23	1.352	-1.45	4.97
		3	1.020	25	0.999	-1.96	5.98
	Cl	1	1.010	25	0.956	-1.98	25.40
		2	10.330	24	10.067	-2.23	13.01
		3	4.170	25	4.046	-4.08	7.24
	F	1	0.050	16	0.051	0.00	34.94
		2	0.130	15	0.125	-7.69	14.73
		3	0.200	17	0.209	5.00	8.78

TABLE 29. ACID RAIN AUDIT RESULTS FOR CATIONS (NOVEMBER 1983)

Audit		Sample	Assigned value (mg/l)	n	Mean (mg/l)	% Acc.	% CV
A. <u>ALL DATA</u>							
1183	NH ₄ (reported as N)	1	0.330	21	0.334	0.00	15.02
		2	1.790	20	1.724	-2.51	13.72
		3	0.340	22	0.371	0.00	37.03
	Ca	1	0.110	24	0.193	0.00	125.76
		2	3.630	23	3.251	-9.09	10.41
		3	2.060	25	1.892	-8.74	9.78
	K	1	0.050	25	0.084	0.00	151.64
		2	1.470	24	1.525	3.74	10.78
		3	2.680	26	2.744	3.17	7.79
	Mg	1	0.010	23	0.021	0.00	135.23
		2	0.370	23	0.379	2.70	7.65
		3	0.250	25	0.257	4.00	6.50
	Na	1	0.080	25	0.094	-12.50	98.93
		2	1.440	24	1.536	4.17	8.92
		3	0.260	26	0.368	3.85	118.35
B. <u>STATISTICAL OUTLIERS REMOVED</u>							
1183	NH ₄ (reported as N)	1	0.330	19	0.320	-3.03	8.00
		2	1.790	18	1.722	-2.51	7.30
		3	0.340	21	0.344	0.00	17.02
	Ca	1	0.110	22	0.125	0.00	63.65
		2	3.630	21	3.254	-9.09	6.18
		3	2.060	24	1.864	-8.73	6.67
	K	1	0.050	23	0.048	0.00	51.20
		2	1.470	23	1.550	4.08	7.40
		3	2.680	24	2.745	3.17	5.33
	Mg	1	0.010	22	0.017	0.00	116.61
		2	0.370	23	0.379	2.70	7.65
		3	0.250	25	0.257	4.00	6.50
	Na	1	0.080	24	0.077	-12.50	49.95
		2	1.440	23	1.520	4.17	7.59
		3	0.260	25	0.284	3.85	24.56

TABLE 30. ACID RAIN AUDIT RESULTS FOR TRACE METALS (NOVEMBER 1983)

Audit		Sample	Assigned value (mg/l)	n	Mean (mg/l)	% Acc.	% CV
A. <u>ALL DATA</u>							
1183	Mn	4	0.020	14	0.041	0.00	183.66
		5	0.040	15	0.065	25.00	101.72
	Fe	4	0.020	13	0.026	0.00	70.74
		5	0.070	15	0.077	14.29	35.74
	Cd	4	0.020	15	0.028	0.00	111.48
		5	0.060	16	0.064	0.00	16.01
	Cu	4	0.020	16	0.024	0.00	95.86
		5	0.460	16	0.442	-1.09	22.08
	Ni	4	0.230	13	0.248	8.70	8.51
		5	0.020	12	0.026	50.00	25.88
	Pb	4	0.680	16	0.539	-9.56	35.37
		5	0.420	15	0.381	-7.14	18.24
	Zn	4	0.050	14	0.052	10.00	21.51
		5	0.480	14	0.476	0.00	5.58
B. <u>STATISTICAL OUTLIERS REMOVED</u>							
1183	Mn	4	0.020	13	0.021	0.00	23.76
		5	0.040	14	0.048	25.00	20.37
	Fe	4	0.020	12	0.022	0.00	43.27
		5	0.070	14	0.072	7.14	27.28
	Cd	4	0.020	14	0.020	0.00	19.61
		5	0.060	15	0.062	0.00	6.68
	Cu	4	0.020	15	0.019	0.00	56.79
		5	0.460	15	0.464	0.00	9.17
	Ni	4	0.230	13	0.248	8.70	8.51
		5	0.020	11	0.027	50.00	17.13
	Pb	4	0.680	15	0.571	-8.82	25.66
		5	0.420	14	0.395	-5.95	10.96
	Zn	4	0.050	13	0.055	20.00	12.09
		5	0.480	14	0.476	0.00	5.56

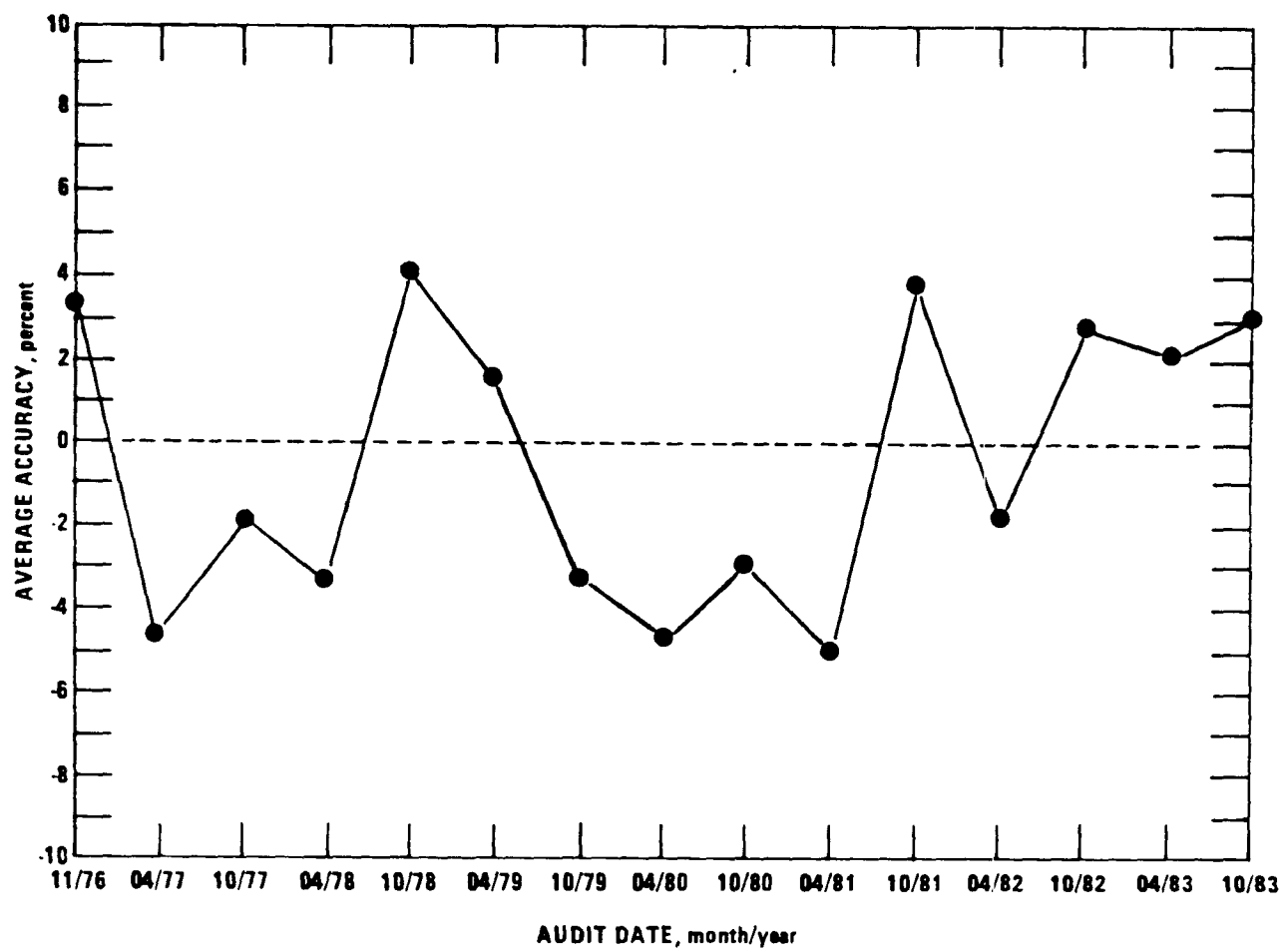


Figure 1. SO₂ bubbler audits accuracy.

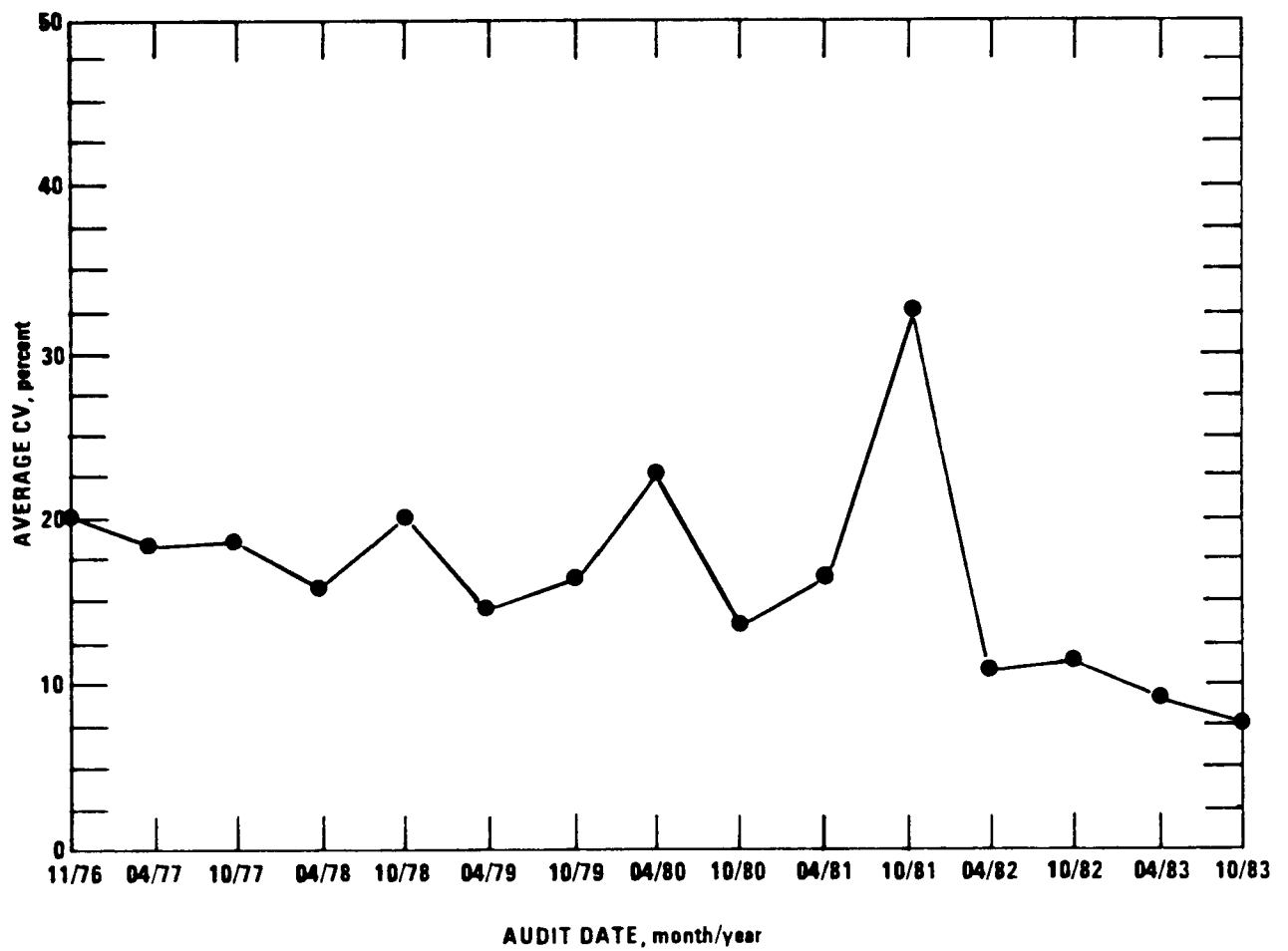


Figure 2. SO₂ bubbler audits precision.

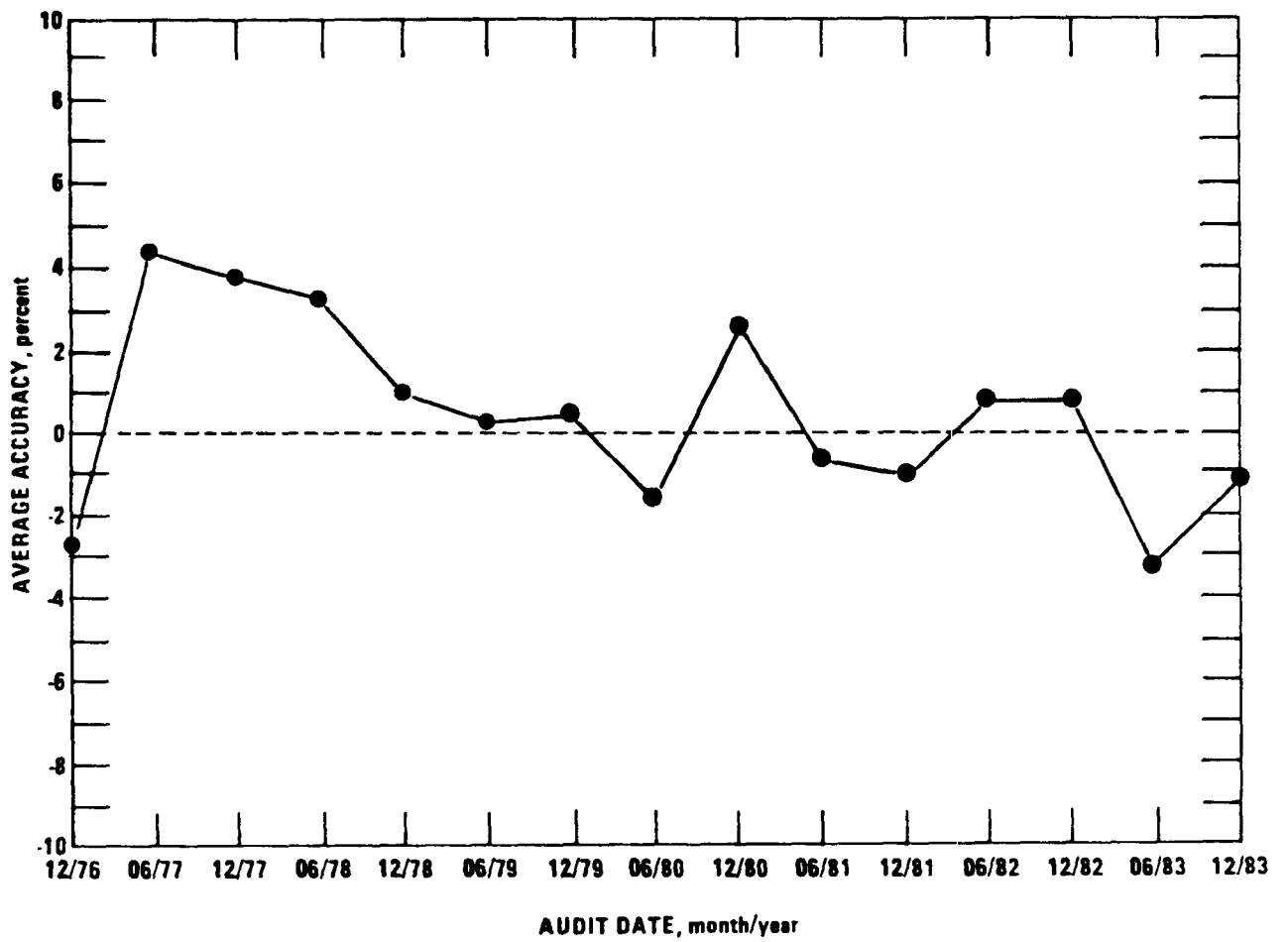


Figure 3. NO₂ bubbler audits accuracy.

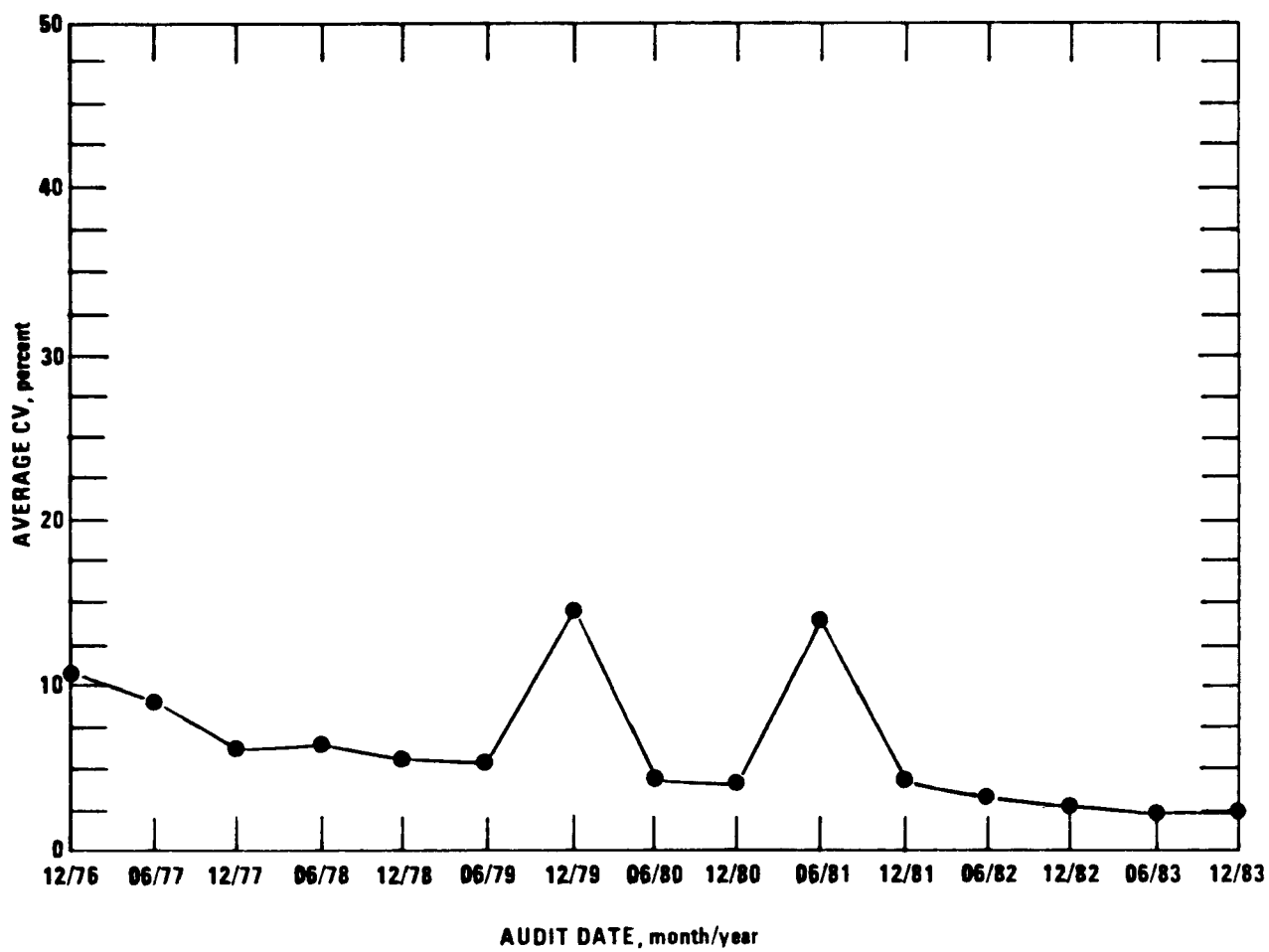


Figure 4. NO₂ bubbler audits precision.

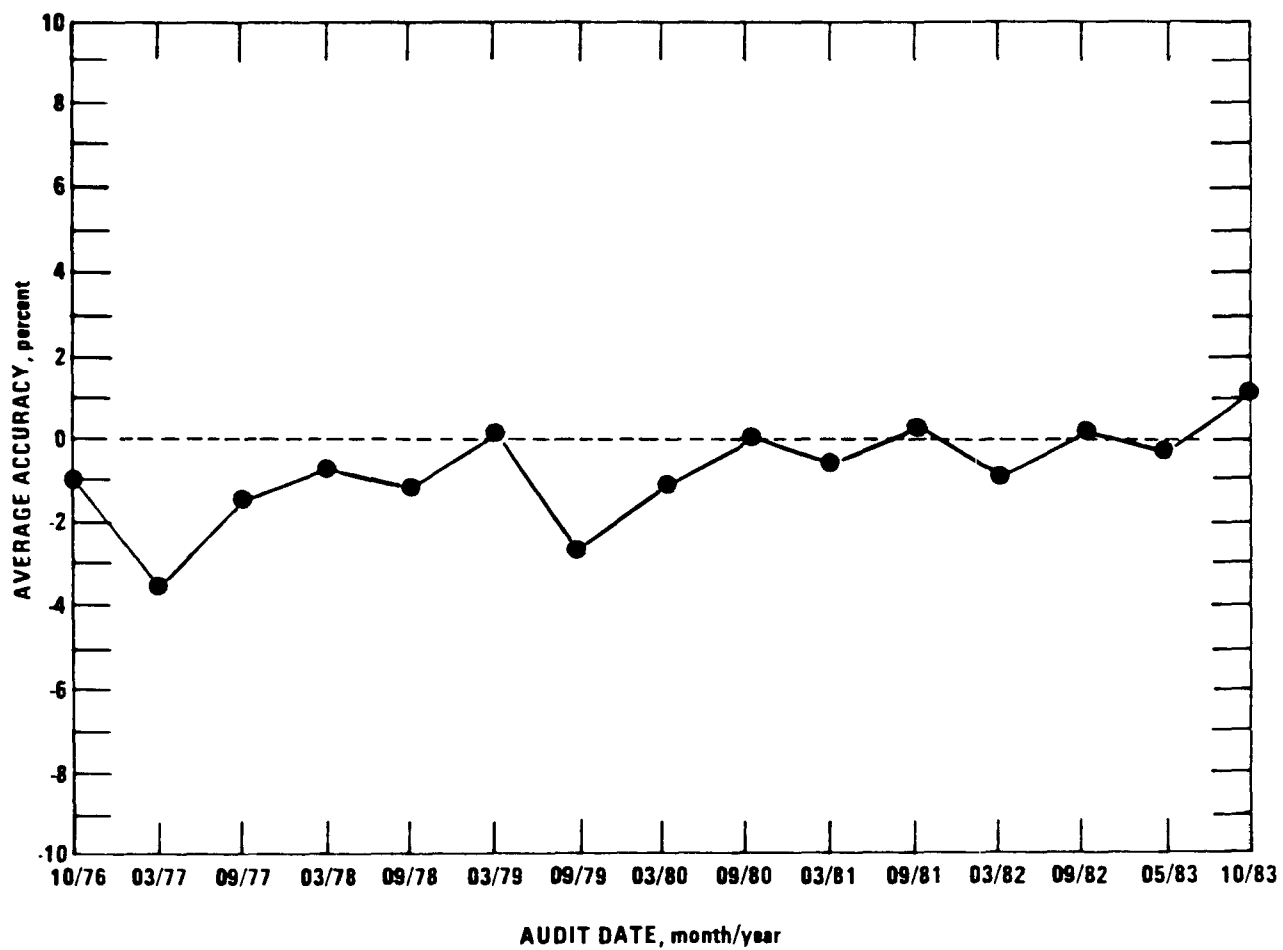


Figure 5. Carbon monoxide audits accuracy.

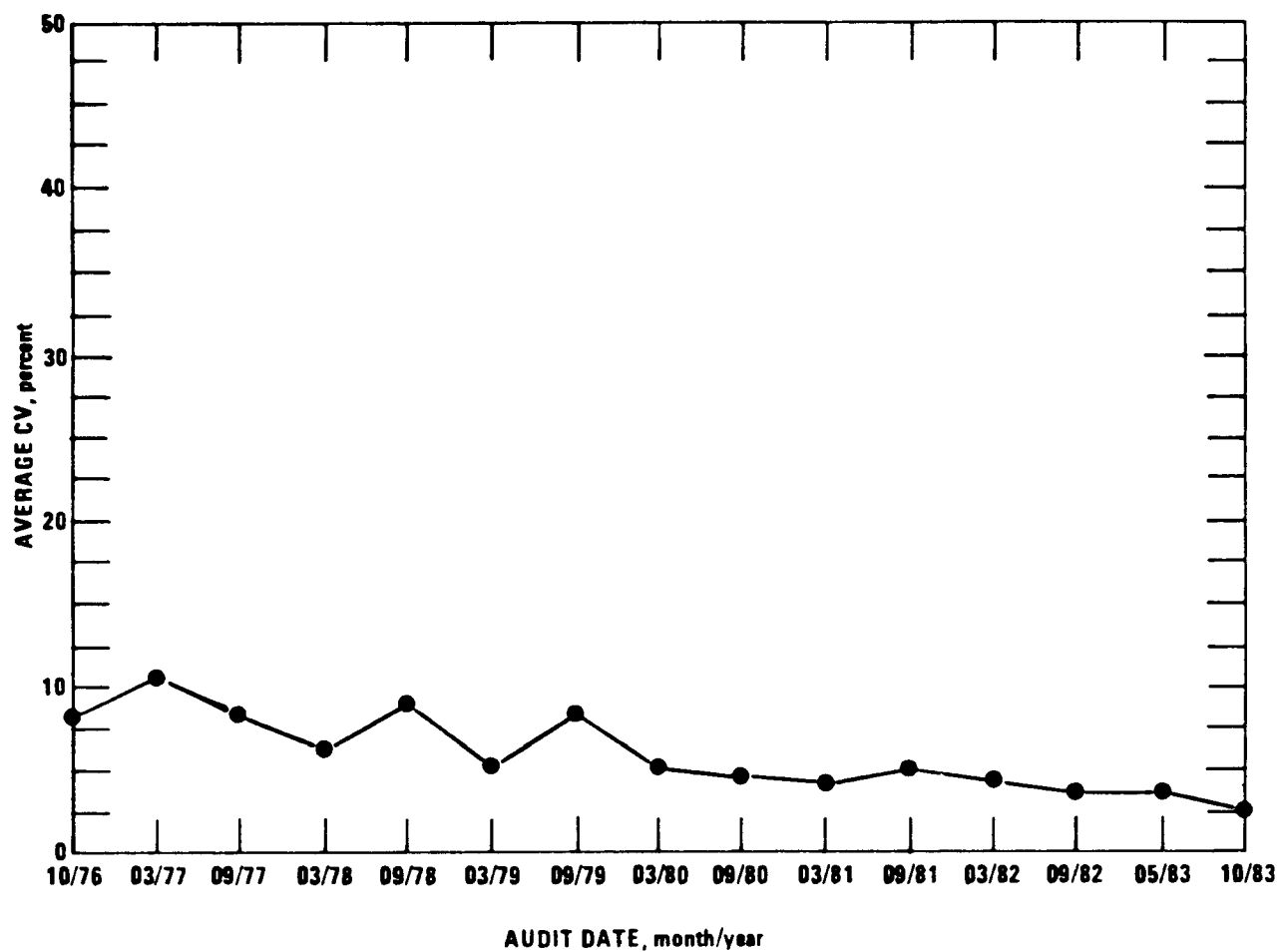


Figure 6. Carbon monoxide audits precision.

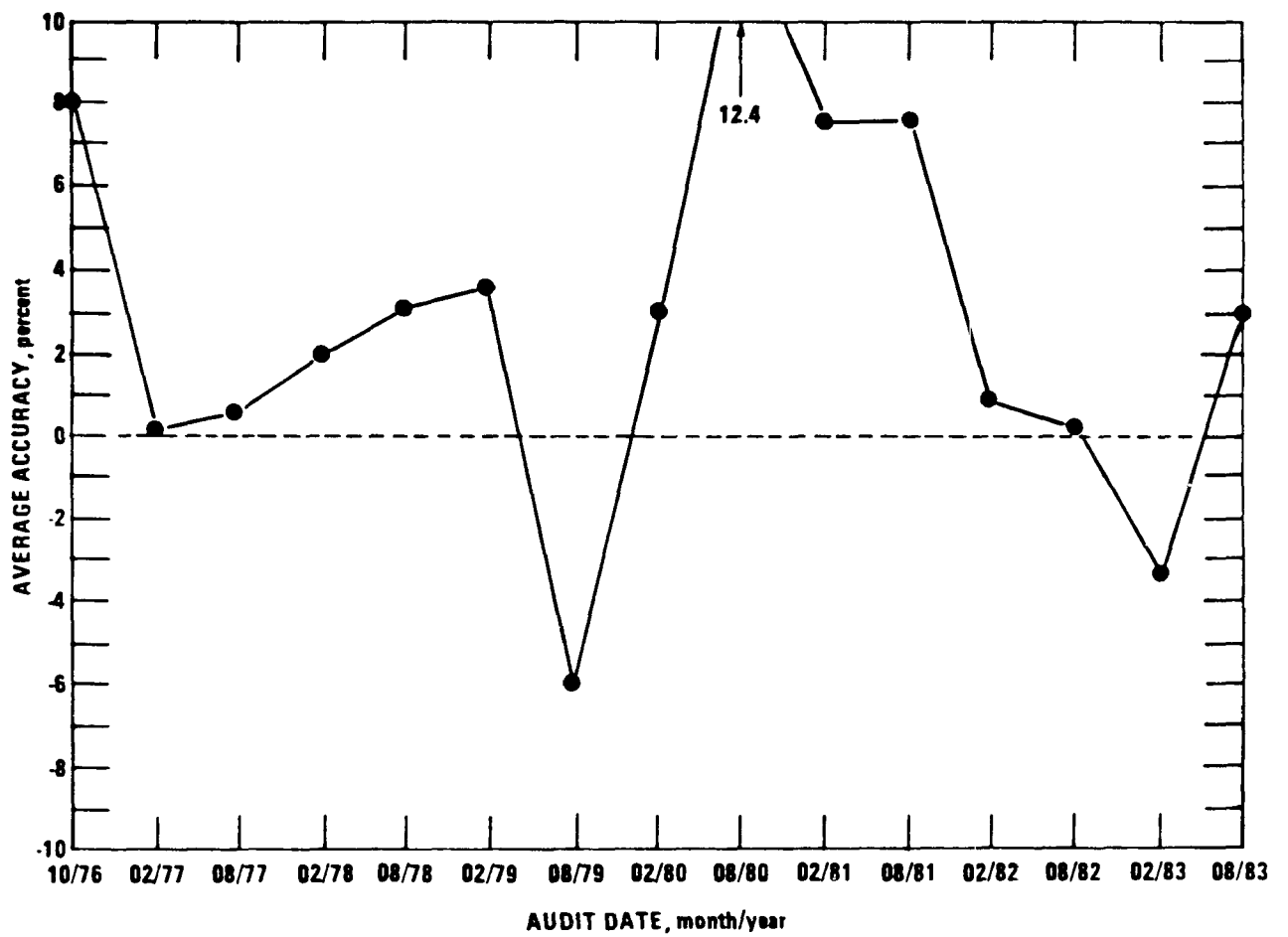


Figure 7. Sulfate audits accuracy.

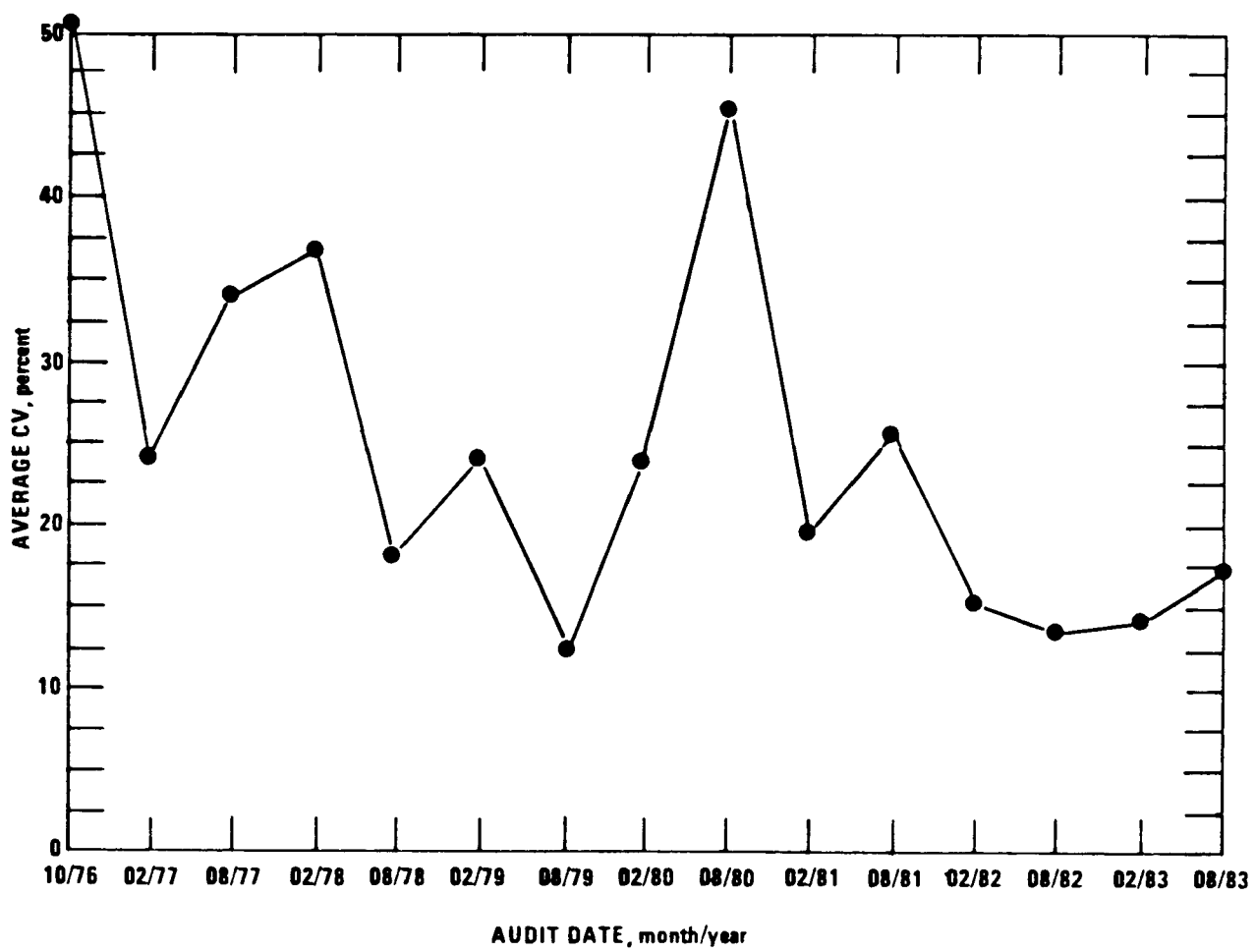


Figure 8. Sulfate audits precision.

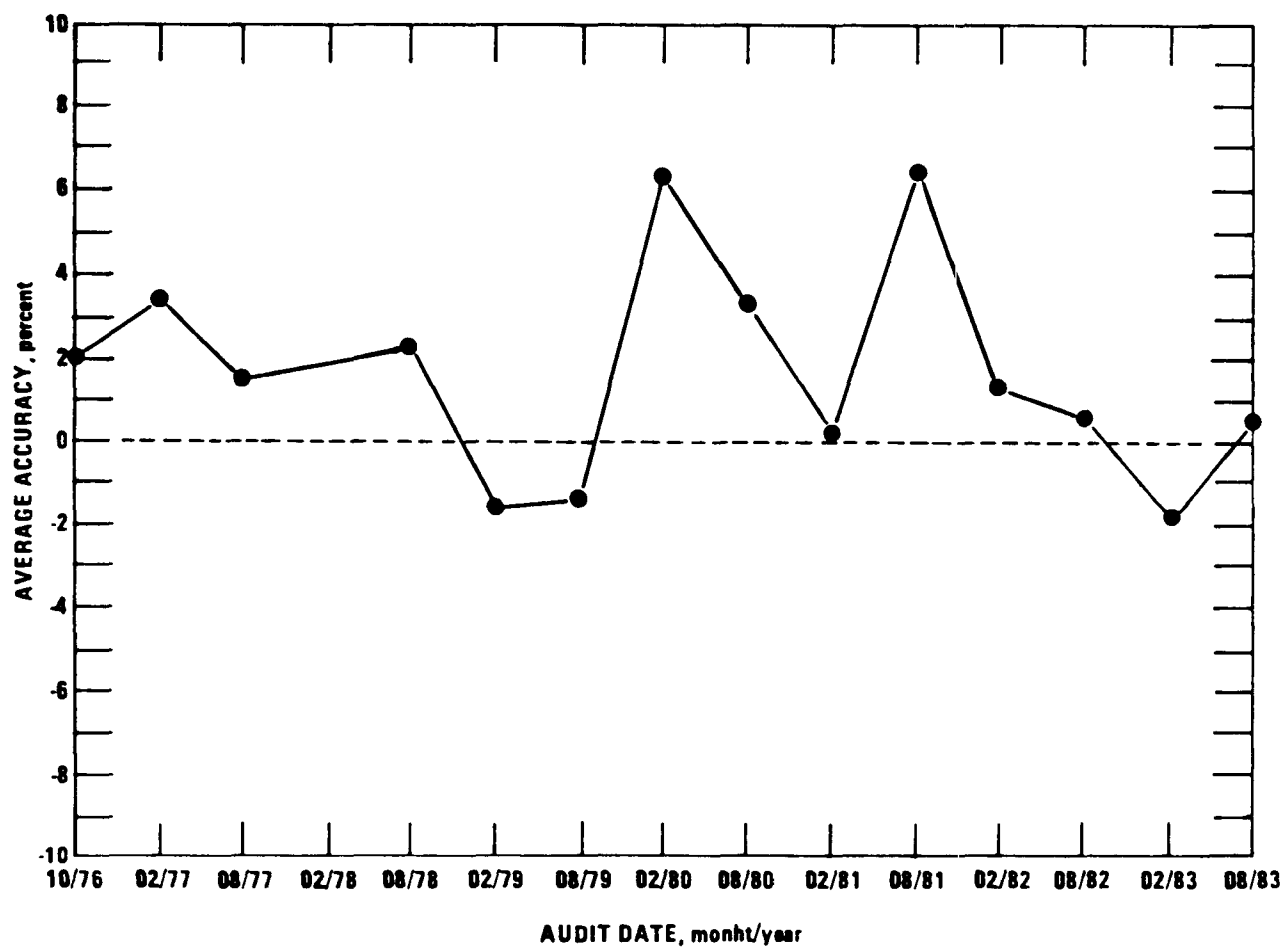


Figure 9. Nitrate audits accuracy.

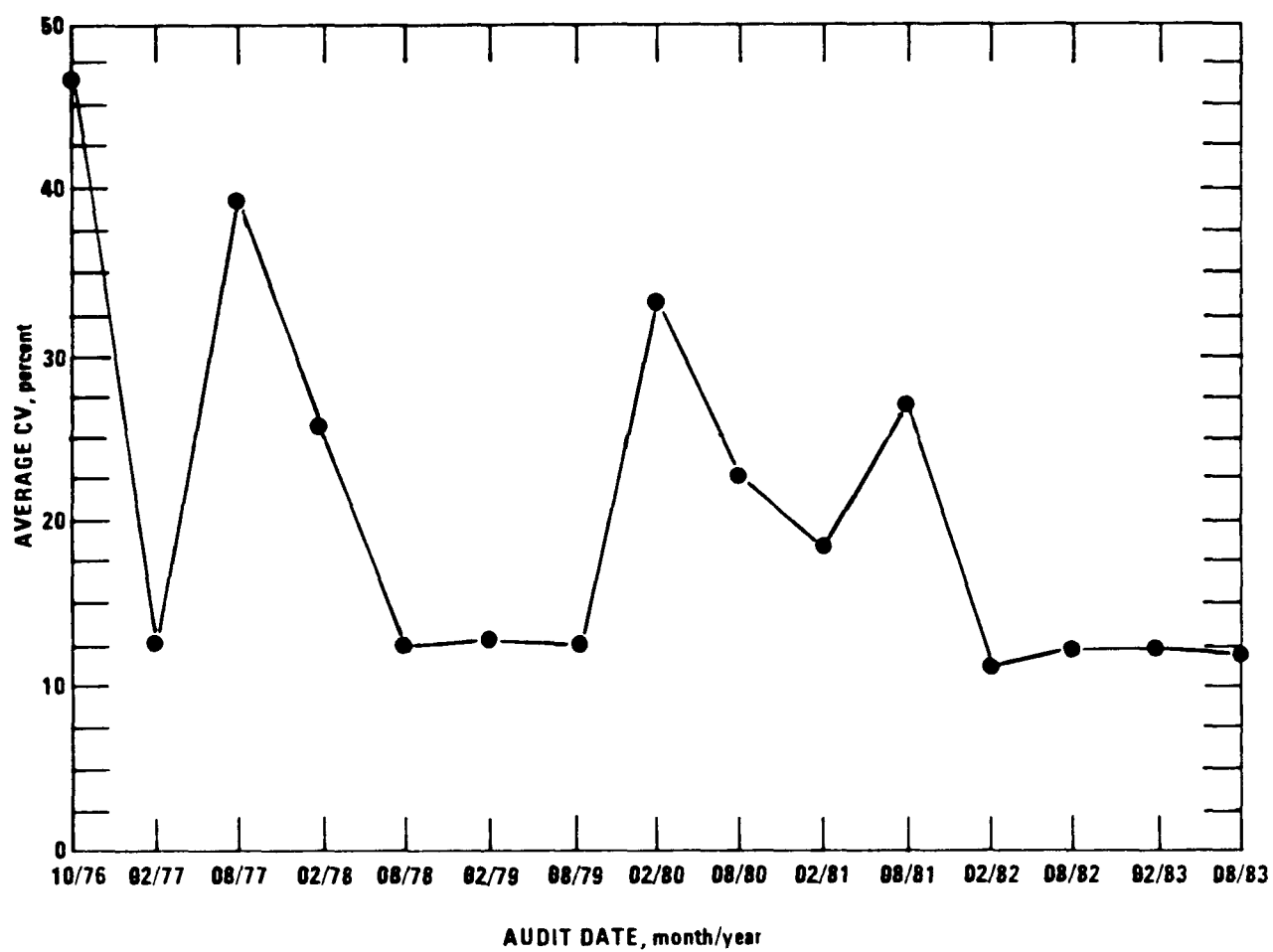


Figure 10. Nitrate audits precision.

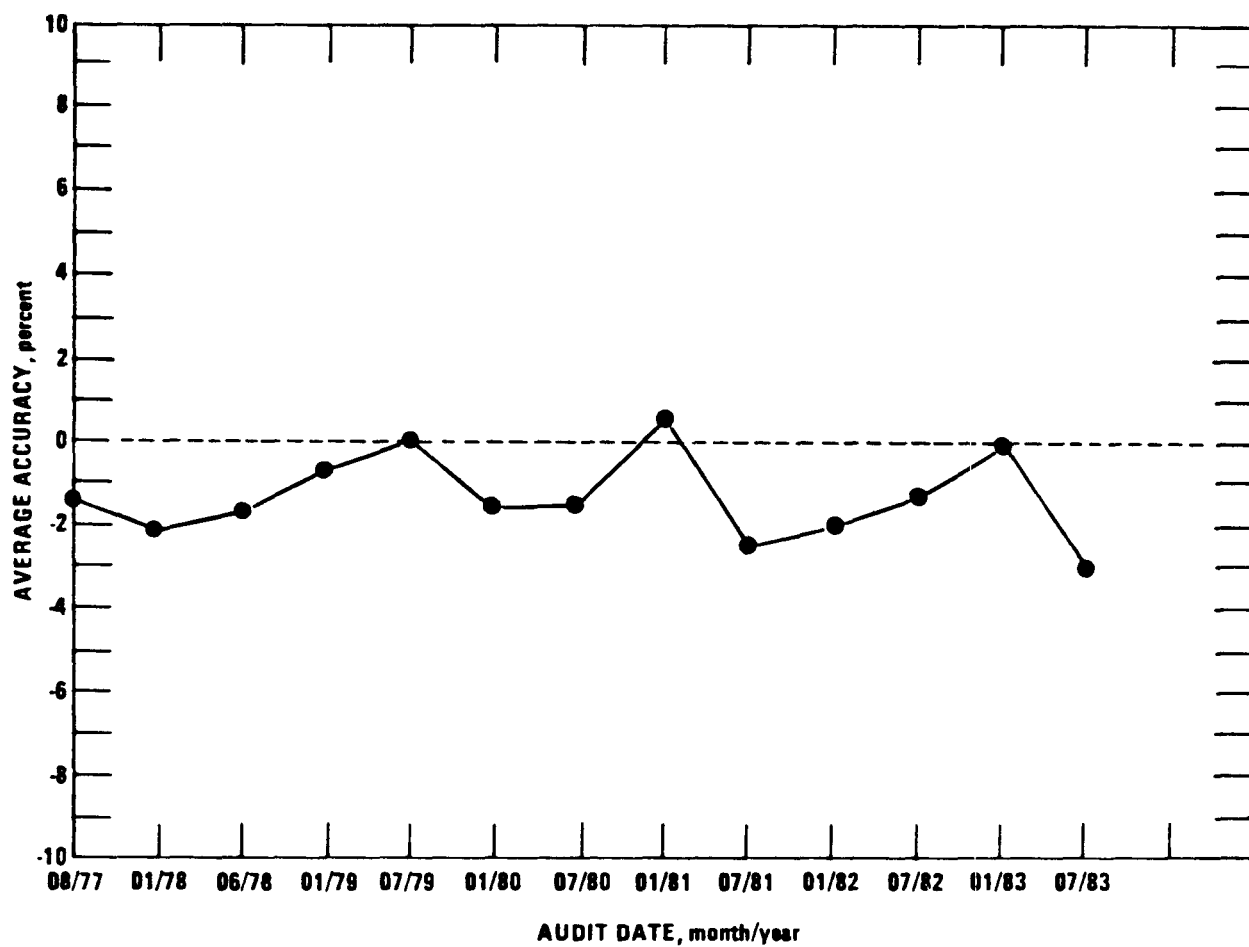


Figure 11. Lead audits accuracy.

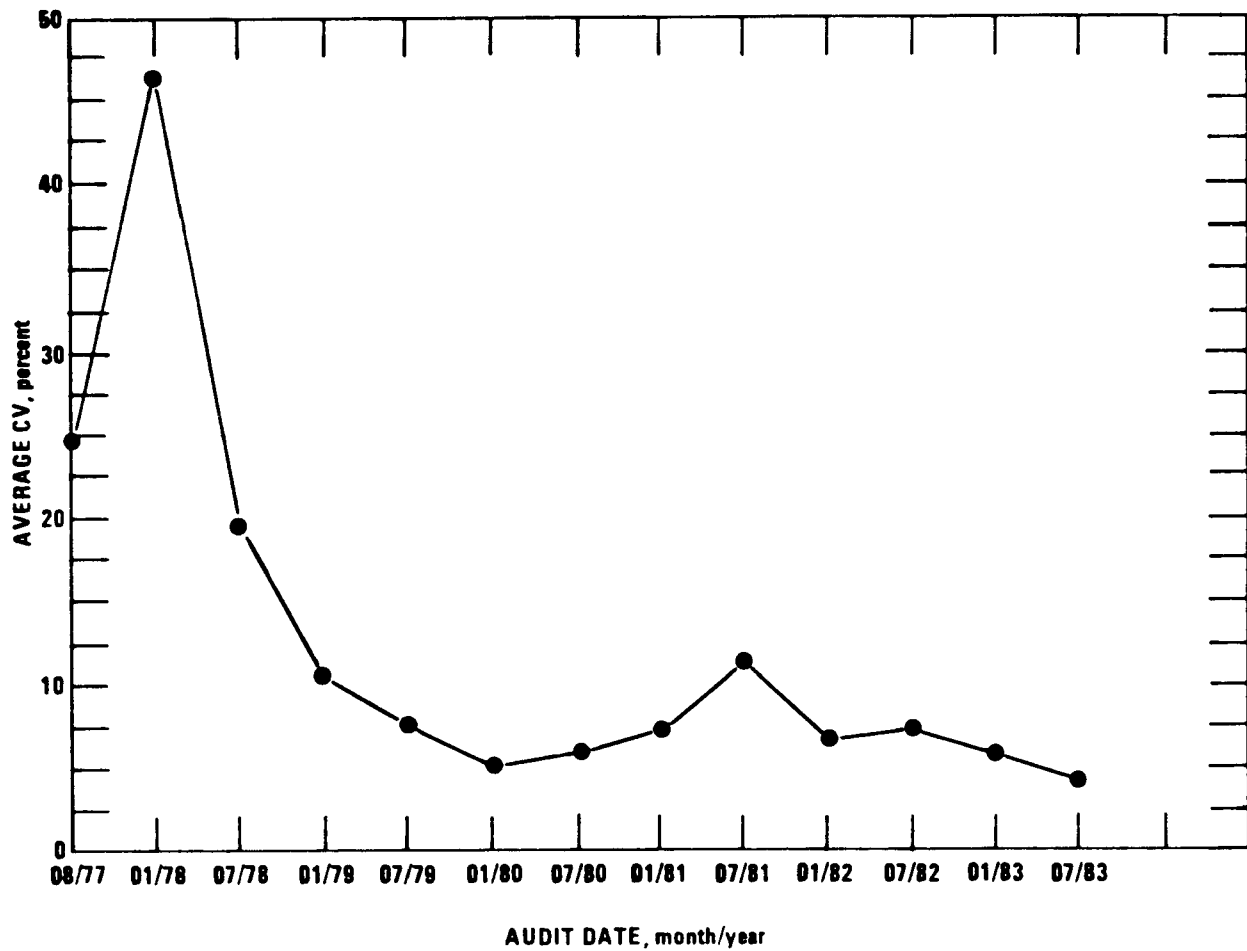


Figure 12. Lead audits precision.