EXTERNAL QUALITY-ASSURANCE RESULTS FOR THE NATIONAL ATMOSPHERIC DEPOSITION PROGRAM AND THE NATIONAL TRENDS NETWORK DURING 1986

By Randolph B. See and Leroy J. Schroder,
U.S. Geological Survey, and
Timothy C. Willoughby,
Goodson and Associates

U.S. GEOLOGICAL SURVEY

Water-Resources Investigations Report 88-4007

Denver, Colorado
1988

U.S. DEPARTMENT OF THE INTERIOR
March 3, 1849

DEPARTMENT OF THE INTERIOR

DONALD PAUL HODEL, Secretary

U.S. GEOLOGICAL SURVEY

Dallas L. Peck, Director

For additional information
write to:

Randolph B. See
U.S. Geological Survey
5293 Ward Road
Arvada, Colorado 80002

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CONVERSION FACTORS

The metric units (International system) used in this report may be converted to inch-pound units by the use of the following conversion factors:

Multiply metric unit	*By*	*To obtain inch-pound unit*
liter (L)	1.0567	quart, liquid
milliliter (mL)	0.03381	ounce, fluid

The following term and abbreviation were also used in this report:

microsiemens per centimeter at 25 degrees Celsius (μS/cm).

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ABSTRACT

During 1986, the U.S. Geological Survey operated three programs to provide external quality-assurance monitoring of the National Atmospheric Deposition Program and National Trends Network. An intersite-comparison program was used to assess the accuracy of onsite pH and specific-conductance determinations at quarterly intervals. The blind-audit program was used to assess the effect of routine sample handling on the precision and bias of program and network wet-deposition data. Analytical results from four laboratories, which routinely analyze wet-deposition samples, were examined to determine if differences existed between laboratory analytical results and to provide estimates of the analytical precision of each laboratory.

An average of 78 and 89 percent of the site operators participating in the intersite-comparison met the network goals for pH and specific conductance. A comparison of analytical values versus actual values for samples submitted as part of the blind-audit program indicated that analytical values were slightly but significantly ($\alpha = 0.01$) larger than actual values for pH, magnesium, sodium, and sulfate; analytical values for specific conductance were slightly less than actual values. The decreased precision in the analyses of blind-audit samples when compared to interlaboratory studies indicates that a large amount of uncertainty in network deposition data may be a result of routine field operations. The results of the interlaboratory comparison study indicated that the magnitude of the difference between laboratory analyses was small for all analytes. Analyses of deionized water blanks by participating laboratories indicated that the laboratories had difficulty measuring analyte concentrations near their reported detection limits.

INTRODUCTION

The National Atmospheric Deposition Program (NADP) and the National Trends Network (NTN) were established to monitor spatial and temporal trends in the chemical composition of natural wet deposition. During 1986, wet-deposition samples were collected at about 200 sites in the United States and Canada. The purpose and scope of this report is to describe the results of the 1986 external quality-assurance programs operated by the U.S. Geological Survey in an effort to detect problems, to decrease uncertainties, and to provide a quality assessment of the data base generated by the NADP/NTN. Sample-site selection and sample-handling procedures have been described previously (Schroder and Malo, 1984). Previous reports (Schroder and Brennan, 1984; Brooks and others, 1985; Schroder and others, 1985; Schroder and others, 1986a,b; Brooks and others, 1987a,b,c) have documented the NADP/NTN external quality-assurance program of the U.S. Geological Survey for 1980 through 1985.

EXTERNAL QUALITY-ASSURANCE RESULTS

Three programs provided external quality-assurance for NADP/NTN data collected during 1986. The intersite-comparison program was used to evaluate the precision and accuracy of onsite pH and specific-conductance measurements made by NADP/NTN site operators. The blind-audit program was used to assess the variations of analyte determinations caused by routine onsite and laboratory sample-handling procedures. The interlaboratory comparison program was used to evaluate four laboratories by comparing the analytical results from the laboratories, by determining the analytical bias for each of the laboratories, and by estimating the analytical precision of each laboratory.

Intersite-Comparison Program

The intersite-comparison program was used to estimate the accuracy and precision of the onsite pH and specific-conductance measurements determined by each NADP/NTN site operator. NADP/NTN site operators were requested to participate in the study; however, their participation was voluntary. Detailed descriptions of the experimental design and protocols of the intersite-comparison program and assessments of onsite pH and specific-conductance measurements of previous years have been discussed in earlier reports (Schroder and Brennan, 1984; Schroder and others, 1986a,b).

A 125-mL bottle of reference solution was mailed to each active network site in January, April, July, and October of 1986. The solution mailed in the first quarter of the year was a reference solution prepared by the National Performance Audit Program, Environmental Systems Laboratory[1]. Subsequent bottles mailed during the last three quarters of 1986 contained a dilute solution of nitric acid prepared by the U.S. Geological Survey. The site operators were requested to use routine procedures (Bigelow, 1982) to determine the pH and specific conductance of the solutions. Although site operators were aware that they were participating in an external quality-assurance program, the actual pH and specific-conductance values of the solutions were not available to them. Any unused solution remaining in the bottle was returned to the U.S. Geological Survey with the results of the site operator's measurements. Reports summarizing the measurements for the network were mailed to each of the participating site operators at the end of each quarter.

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[1] Use of firm names in this report is for identification purposes only and does not constitute endorsement by the U.S. Geological Survey.

When reported values of pH or specific conductance were more than ± 1.5 F-pseudosigma of the median (Hoaglin and others, 1983), the U.S. Geological Survey re-analyzed the contents of the returned sample bottle. The F-pseudosigma is analogous to the standard deviation; however, it is resistant to the effects of outlying data values. Re-analysis of samples outside the preselected limits was made to determine whether a value was different because of site-operator error, instrument error, or sample contamination. The U.S. Geological Survey re-analyzed 15 percent of the intersite samples for pH and specific conductance. All U.S. Geologic Survey measurements for pH and specific conductance were closer to the median values calculated for all sites than the individual onsite measurements, indicating that sample-bottle contamination was not a source of onsite measurement errors.

A summary of the four intersite comparisons done during 1986 is listed in table 1. Although participation in the intersite-comparison study was voluntary, 87 to 90 percent of the operators sent samples in 1986, analyzed them, and returned results. A maximum of 25 out of 194 (first quarter of 1986) site operators failed to respond in any way during the 1986 studies.

The program and network goals for accuracy of onsite measurements were the actual pH value, ± 0.1 unit, and the actual specific-conductance value, ± 4 µS/cm (National Atmospheric Deposition Program Quality Assurance Steering Committee, 1984). The percentage of participating site operators achieving the above goals for the four comparison solutions ranged from 64 to 88 percent for pH and from 74 to 95 percent for specific conductance. The smallest percentage of pH results that were within the network goal was obtained during April 1986. The April solution had the largest pH value and, therefore, the smallest hydrogen-ion concentration. Some site operators may have had difficulty accurately measuring comparison solutions as the pH became closer to 7.0. The goal for specific conductance was not distribution dependent; as a result, the percentage of site operators achieving the goal for accuracy was affected by the magnitude of the specific-conductance value for each comparison solution. The comparison solution mailed in July 1986 had the largest median specific-conductance value and had the smallest percentage of site operators that achieved the goal for accuracy, whereas the comparison solution mailed in April 1986 had the smallest median specific-conductance value and the largest percentage of site operators that achieved the goal for accuracy.

Median values (50th percentile) were used to estimate the actual pH and specific-conductance values of the comparison solutions. The median is a resistant statistic that is affected only slightly by a small number of outlying data points (Hoaglin and others, 1983). A Wilcoxon-Mann test (Steel and Torrie, 1980) on the ranked differences between the 10th and 90th percentiles for pH indicates that the differences were significantly ($\alpha = 0.05$) smaller in 1986 as compared to 1985. These percentile rankings may represent an improvement in measurement techniques since the 1985 onsite measurements were made. No significant ($\alpha = 0.05$) difference was noted between the range of specific-conductance values for 1986 when they were compared to values for 1985, using the Wilcoxon-Mann test.

Table 1.--*Summary statistics for the intersite-comparison program*

[pH, in units; specific conductance, in microsiemens per centimeter at 25 degrees Celsius]

Date	Number of site operators responding	Analyte	Percentage of site operators achieving accuracy goals[1]	Percentile						
				Minimum	10th	25th	50th	75th	90th	Maximum
January 1986	168	pH	79	3.33	4.50	4.56	4.60	4.66	4.72	7.25
	169	Specific conductance	93	1.0	8.5	9.7	10.3	11.0	12.0	655
April 1986	174	pH	64	3.87	4.82	4.88	4.96	5.02	5.09	5.90
	172	Specific conductance	95	2.8	3.7	4.1	4.4	4.8	6.0	98.3
July 1986	177	pH	82	3.29	3.82	3.89	3.92	3.95	4.01	5.91
	178	Specific conductance	74	4.0	45.8	48.6	51.4	53.1	55.5	163.5
October 1986	175	pH	88	3.64	4.23	4.28	4.32	4.35	4.39	5.60
	179	Specific conductance	93	1.1	19.0	19.9	21.0	21.7	22.3	30.0

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[1] Accuracy goal for pH is ± 0.1 unit; accuracy goal for specific conductance is ± 4 microsiemens per centimeter at 25 degrees Celsius.

Blind-Audit Program

The blind-audit program was used to provide an estimate of the analyte bias and precision that resulted from routine sample handling, processing, and shipping. In the blind-audit program, reference samples were mailed to site operators who disguised them as actual wet-deposition samples and submitted them to the Illinois State Water Survey, Central Analytical Laboratory (CAL). The CAL staff receiving and analyzing the blind-audit samples were not aware that the blind-audit samples were part of an external quality-assurance program and had no information concerning the chemical composition of the samples. Previous reports have detailed the experimental design and summarized results for previous years (Schroder and others, 1985; Brooks and others, 1987a; Brooks and others, 1987c).

Sample solutions were prepared from several sources for the 1986 blind-audit program. Seven of the solutions used were diluted standards from the U.S. Environmental Protection Agency's performance audit solutions. Three of the solutions used were prepared from standard reference water solutions from the U.S. Geological Survey (Janzer, 1985; 1986). Two solutions were used as blanks in the 1986 blind-audit program. Ultrapure, deionized water was prepared by the U.S. Geological Survey and a dilute, pH 4.3, nitric-acid solution was prepared by CAL. The dilute nitric-acid solution was selected to determine if any neutralization processes were occurring as a result of sample handling or shipping.

During the 1986 blind-audit program, 100 samples were submitted from randomly selected NADP/NTN sites. Sites were distributed evenly among four geographic areas of the United States. The site operator poured two-thirds of the blind-audit sample into a clean network sampling container (a 13-L polyethylene bucket and lid). Hereafter, this portion of the blind-audit sample is referred to as the bucket sample. Routine onsite measurements were done on the bucket samples, after which the bucket was sealed and shipped to the CAL for analysis. Fictitious site-operator information was recorded on the field-observer report form that accompanied the blind-audit sample to CAL. When the sample containers arrived at CAL, the samples appeared to be normal wet-deposition samples. Thus, bucket samples analyzed in the blind-audit program were treated as routine samples by the CAL staff.

The site operators left about one-third of the blind-audit sample in the original bottles and mailed the bottles to CAL separately from the bucket samples. Hereafter, the portion of the blind-audit sample remaining in the bottle is referred to as the bottle sample. Analyses of the bucket and bottle portions of the blind-audit sample provided paired analyses that were compared to determine whether hydrogen ions had been neutralized or if other contamination had occurred in the bucket samples.

Results of the 1985 NADP/NTN blind-audit program (Brooks and others, 1987a) indicate that analyte concentrations in the bottle samples were consistently larger than the known or expected analyte concentrations. Because these results indicated possible contamination during the preparation of the solutions, a detailed comparison of the expected analyte concentrations and the concentrations determined by CAL was not made during the 1986 blind-audit program. A comparison between the bucket and bottle analyses (both analyzed by the same laboratory) provides the best estimate of analyte variability in the NADP/NTN samples due to routine onsite handling and shipping procedures.

Of the 100 site operators that were sent blind-audit samples by the U.S. Geological Survey, 6 site operators did not participate in the program. Of the remaining 94 bucket samples, 29 samples or 31 percent were flagged by CAL staff as contaminated by debris or not handled according to standard operating procedures. Most of the 25 samples flagged as contaminated by debris contained 1 or more of an assortment of fibers. A fiber packaging material used by the NADP/NTN network may be a source of some of these fibers. Further investigation is needed to determine the actual source of the sample contamination and the effects on sample analysis. All 29 flagged samples were removed from the data set and were not included in the statistical summary for the 1986 blind-audit program.

A paired T test was used to determine if a significant difference existed between the bucket- and bottle-sample analyses. The comparison indicated sample pH, specific conductance, magnesium, and sodium were significantly different at the 99-percent probability level. The differences of the mean bottle minus the mean bucket analyte concentrations are listed with T-test statistics in table 2. In all but one sample, the pH of the bucket sample was larger than that of the bottle sample. The larger pH of the bucket samples indicates that a neutralization process may be occurring during sample-handling or shipping. Increased pH in the bucket samples may be caused by residues left in the bucket after the cleaning process. Buckets are cleaned at CAL by wiping the buckets free of particulates and then washing the buckets in a commercial dishwasher using four cycles of distilled water; no detergents are used in the cleaning process (Lockard, 1987).

Table 2.--*Paired T analyses for the blind-audit program*

[All units are in milligrams per liter, except pH, in units, and specific conductance, in microsiemens per centimeter at 25 degrees Celsius]

Analyte	Sample type	Mean	Mean difference	T value	Probability of larger T
pH	Bucket	5.02	-0.33	-7.69	0
	Bottle	4.69			
Specific conductance	Bucket	13.8	2.4	8.77	0
	Bottle	16.2			
Calcium	Bucket	0.20	-0.02	-1.30	0.199
	Bottle	0.18			
Magnesium	Bucket	0.061	-0.013	-6.73	0
	Bottle	0.048			
Sodium	Bucket	0.20	-0.06	-3.45	0.001
	Bottle	0.14			
Potassium	Bucket	0.051	-0.004	-1.46	0.149
	Bottle	0.047			
Ammonium	Bucket	0.04	-0.01	-1.37	0.175
	Bottle	0.03			
Chloride	Bucket	0.18	0.00	-0.45	0.652
	Bottle	0.18			
Nitrate	Bucket	0.66	0.06	1.14	0.261
	Bottle	0.72			
Sulfate	Bucket	1.25	-0.020	-1.72	0.090
	Bottle	1.23			

An additional summary of analyte percentiles is included in table 3. Although the paired T analyses indicated few significant differences between bucket- and bottle-sample concentrations, percentile concentrations seem to indicate a trend of increased analyte concentrations in the bucket samples compared to those in the bottle samples.

Table 3.--*Percentile rankings for measured bucket- and bottle-sample concentrations in the blind-audit samples*

[All units are in milligrams per liter except pH, in units, and specific conductance, in microsiemens per centimeter at 25 degrees Celsius; *, indicates a significant difference at the 99-percent probability level between the bucket- and bottle-sample analyses]

Analyte	Sample type	Percentile 25th	50th	75th
pH*	Bucket	4.42	4.80	5.68
	Bottle	4.33	4.61	4.99
Specific conductance*	Bucket	7.8	14.4	19.9
	Bottle	9.8	18.3	24.1
Calcium	Bucket	0.06	0.13	0.28
	Bottle	0.02	0.07	0.27
Magnesium*	Bucket	0.021	0.040	0.076
	Bottle	0.009	0.022	0.059
Sodium*	Bucket	0.09	0.21	0.25
	Bottle	0.05	0.13	0.20
Potassium	Bucket	0.009	0.044	0.077
	Bottle	0.005	0.038	0.070
Ammonium	Bucket	0.01	0.01	0.06
	Bottle	0.01	0.01	0.03
Chloride	Bucket	0.05	0.15	0.30
	Bottle	0.05	0.12	0.31
Nitrate	Bucket	0.01	0.16	0.53
	Bottle	0.01	0.14	0.52
Sulfate	Bucket	0.09	0.89	2.62
	Bottle	0.07	0.90	2.53

Precision of analyte data was estimated for the 1986 blind-audit samples by pooling the variance of replicate samples (Dixon and Massey, 1969, p.113). The pooled standard deviations estimated from nine groups of samples, which had 3 to 10 replicates per group, are listed in table 4. The pooled standard deviations for the blind-audit program in 1986 are comparable to the standard deviations determined in the program in 1985 (Brooks and others, 1987a). The pooled standard deviations for 1985 and 1986 were larger than the precision values reported by CAL (Peden, 1986) or the precision estimates obtained through the interlaboratory-comparison programs for 1980 through 1985 (Brooks and others, 1985; Schroder and others, 1986a; Brooks and others, 1987a,c).

The decreased precision in the analyses of blind-audit samples when compared to the interlaboratory studies and single-operator studies at CAL, indicate that a large proportion of the uncertainty in wet-deposition data may be a result of routine onsite operations rather than a result of laboratory analyses.

Table 4.--*Estimated precision of analyte data based on replicate analyses of blind-audit samples*

[All units in milligrams per liter except pH, in units, and specific conductance, in microsiemens per centimeter at 25 degrees Celsius]

Analyte	Minimum	Maximum	Estimated standard deviation
pH	4.33	6.36	0.21
Specific conductance	1.6	24.5	1.4
Calcium	0.01	0.68	0.04
Magnesium	0.002	0.216	0.013
Sodium	0.01	0.59	0.11
Potassium	0.002	0.102	0.013
Ammonium	0.01	0.18	0.04
Chloride	0.015	0.47	0.05
Nitrate	0.015	3.38	0.36
Sulfate	0.015	2.89	0.06

Interlaboratory-Comparison Program

The interlaboratory-comparison program was used to determine if differences existed between the analytical results of participating laboratories and to estimate analytical precision of the participating laboratories. Program results from 1982 through 1985 have been detailed in previous reports (Brooks and others, 1985; Brooks and others, 1987a,b,c).

Four laboratories participated in the program during 1986: (1) Illinois State Water Survey, Central Analytical Laboratory (CAL); (2) Inland Waters Directorate, National Water Quality Laboratory (IWD); (3) Combustion Engineering Inc., Environmental Monitoring and Services (EMS); (4) U.S. Geological Survey, National Water Quality Laboratory (DEN). Four types of samples were prepared for the interlaboratory comparison program. Ultrapure, deionized water was prepared by the U.S. Geological Survey; and dilute, pH 4.3, nitric acid was prepared by Illinois State Water Survey for use as blank samples. The blank solutions were prepared by individuals who were not associated with the analytical divisions of the participating laboratories, to avoid any chance of biasing the results. Natural wet-deposition samples that had a volume of 750 mL or greater were selected randomly by CAL for use in the interlaboratory comparison program. The natural samples were split into

10 aliquots using a decasplitter and shipped to the U.S. Geological Survey in insulated containers. The U.S. Geological Survey relabeled and shipped two aliquots of each sample to each of the four participating laboratories. Standard reference samples from the U.S. Environmental Protection Agency, the National Bureau of Standards, and the U.S. Geological Survey also were used as comparison samples.

The laboratories were mailed duplicate natural wet-deposition samples for analysis and, to provide a measure of precision, triplicate standard reference water samples were mailed. Single aliquots of the ultrapure, deionized water and dilute, pH 4.3, nitric acid were submitted. The laboratory staffs were unaware of the actual analyte concentrations in the samples or whether the samples were blanks, natural wet-deposition samples, or standard reference samples, because the U.S. Geological Survey relabeled all sample bottles.

Laboratory precision in determining analytes was estimated by calculating a pooled standard deviation (Dixon and Massey, 1969, p. 113) from the results of analyses of the natural wet-deposition and standard reference samples submitted to each laboratory. The estimated precision in determining analytes for the interlaboratory comparison in 1986 were similar to estimates from previous years (Brooks and others, 1985; 1987a,c). The calculated precision estimates for each laboratory are listed in table 5.

Table 5.--*Estimated analyte precision for four laboratories measuring constituents in natural wet-deposition samples*

[CAL, Illinois State Water Survey, Central Analytical Laboratory, Champaign, Ill.; IWD, Inland Waters Directorate, National Water Quality Laboratory, Ontario, Canada; EMS, Combustion Engineering Inc., Environmental Monitoring and Services, Camarillo, Calif.; DEN, U.S. Geological Survey, National Water Quality Laboratory, Denver, Colo.; Nat, analyses of natural wet-deposition samples; Sim, analyses of simulated wet-deposition samples; all units in milligrams per liter except pH, in units, and specific conductance, in microsiemens per centimeter at 25 degrees Celsius]

	CAL		IWD		EMS		DEN	
Analyte	Nat	Sim	Nat	Sim	Nat	Sim	Nat	Sim
pH	0.03	0.03	0.03	0.03	0.04	0.03	0.10	0.14
Specific conductance	0.25	0.43	0.38	0.20	0.42	2.06	0.59	3.10
Calcium	0.004	0.003	0.003	0.008	0.007	0.006	0.059	0.021
Magnesium	0.001	0.001	0.002	0.002	0.001	0.001	0.007	0.008
Sodium	0.003	0.009	0.006	0.006	0.101	0.004	0.043	0.068
Potassium	0.018	0.002	0.007	0.004	0.091	0.108	0.041	0.023
Ammonium	0.031	0.004	0.006	0.002	0.005	0.007	0.008	0.284
Chloride	0.08	0.01	0.03	0.07	0.09	0.10	0.08	0.03
Nitrate	0.01	0.07	0.05	0.11	0.01	0.17	0.03	0.10
Sulfate	0.02	0.04	0.04	0.11	0.01	0.34	0.41	0.35

Statistical analyses of the differences between laboratory results were performed using a Friedman's test (Steel and Torrie, 1980). The Friedman's test is an analysis of variance that is performed on the ranks of the observations rather than on the actual data values. Results of each analyte determination were ranked from smallest to largest for each laboratory. For every analyte, analysis of variance of the ranked data indicated differences between each of the laboratories at the 99.9-percent level. Summary of the percentiles for each of the laboratories is listed in table 6.

Although the Friedman's test (Steel and Torrie, 1980) indicated that statistically significant differences existed between the mean analyte determinations for the laboratories, many of the actual differences seem to be small. Using the precision as a range around the median values and concentrations listed in table 6, the magnitude of the differences seems minimal.

Analyte bias for laboratories participating in the interlaboratory comparison study was evaluated using certified values and concentrations for the National Bureau of Standards' standard reference material 2694, level I and level II. Laboratory-reported analyte values were compared against the certified values and concentrations using a Students t test. Bias was indicated by a significant ($\alpha = 0.01$) difference between a laboratory's mean analyte value and the certified value. A summary of each laboratory's mean analyte analyses and the certified value is presented in table 7. Analyses by CAL had the fewest number of biased mean analyte values with pH at level II and sulfate at both levels appearing to be significantly greater than the certified value. IWD had the greatest number of biased analytes with pH at both levels, specific conductance at level I, sodium and nitrate at level II, and sulfate at both levels appearing to have significant difference from the certified value. Mean analyte concentrations determined by EMS appeared to be significantly different from the certified value for magnesium at level II, sodium and potassium at both levels, and sulfate at level II. DEN appeared to have significant differences from the certified value for magnesium, sodium, and potassium at level I and nitrate at level II.

The estimates of bias were limited to analyses of the National Bureau of Standards' standard reference material 2694, levels I and II. Analyte values in this solution generally are within the range of values present in natural wet-deposition samples collected by the NADP/NTN. However, these estimates of bias are considered to be valid only for the analyte values in the standard reference solutions and probably cannot be extrapolated to the full range of analyte values present in natural wet-deposition samples.

Ultrapure, deionized water samples were included among the samples submitted in the interlaboratry comparison to determine the percentage of times that each laboratory reported a false positive concentration and the median concentration of the false positive concentrations. A summary of the laboratory analyses of ultrapure, deionized water is presented in table 8. IWD did not report any false positives for any analyte except ammonium.

Table 6.--*Percentile ranking for individual laboratory analyses of interlaboratory-comparison samples shipped to each of four laboratories*

[CAL, Illinois State Water Survey, Central Analytical Laboratory, Champaign, Ill.; IWD, Inland Waters Directorate, National Water Quality Laboratory, Ontario, Canada; EMS, Combustion Engineering Inc., Environmental Monitoring and Services, Camarillo, Calif.; DEN, U.S. Geological Survey, National Water Quality Laboratory, Denver, Colo.; all units are in milligrams per liter except pH, in units, and specific conductance, in microsiemens per centimeter at 25 degrees Celsius]

	Pecentiles											
	CAL			IWD			EMS			DEN		
Analyte	25th	50th	75th	25th	50th	75th	25th	50th	75th	25th	50th	75th
pH	4.36	4.90	5.34	4.28	4.79	5.15	4.40	4.92	5.35	4.30	4.80	5.20
Specific conductance	6.70	12.10	23.50	7.36	11.70	22.03	6.25	11.00	23.50	6.00	11.00	21.00
Calcium	0.020	0.060	0.150	0.030	0.060	0.155	0.020	0.057	0.158	0.010	0.050	0.110
Magnesium	0.010	0.022	0.038	0.005	0.020	0.040	0.010	0.022	0.038	0.020	0.030	0.050
Sodium	0.022	0.060	0.156	0.020	0.055	0.150	0.016	0.052	0.160	0.020	0.050	0.170
Potassium	0.009	0.020	0.049	0.005	0.020	0.050	0.008	0.022	0.045	0.005	0.010	0.030
Ammonium	0.015	0.110	0.410	0.010	0.093	0.372	0.030	0.112	0.395	0.006	0.013	0.193
Chloride	0.060	0.110	0.245	0.050	0.105	0.230	0.055	0.119	0.260	0.120	0.180	0.297
Nitrate	0.200	0.590	1.150	0.133	0.531	1.107	0.178	0.525	1.150	0.186	0.558	1.195
Sulfate	0.525	1.100	2.330	0.430	1.020	2.220	0.464	1.004	2.149	0.620	1.149	2.575

CAL reported the greatest percentage of false positive concentrations for sodium. EMS reported false positive concentrations for every analyte and reported the greatest percentage of false positive concentrations for magnesium, potassium, ammonium, nitrate, and sulfate. DEN reported the greatest percentage of false positive concentrations for calcium and chloride. The median concentrations of the false positive values are similar to the analytical limits of detection reported by the laboratories. These false positive concentrations may represent an inability of the laboratories to measure analyte concentrations that are near their reported detection limits.

Table 7.--*Mean analysis estimates for National Bureau of Standards' standard reference solution 2694*

[NBS, National Bureau of Standards; CAL, Illinois State Water Survey, Central Analytical Laboratory, Champaigne, Ill.; IWD, Inland Waters Directorate, National Water Quality Laboratory, Ontario, Canada; EMS, Combustion Engineering Inc., Environmental Monitoring and Services, Camarillo, Calif.; DEN, U.S. Geological Survey, National Water Quality Laboratory, Denver, Colo.; all units in milligrams per liter except pH, in units, and specific conductance, in microsiemens per centimeter at 25 degrees Celsius; *, indicates a significant difference from the certified values at $\alpha = 0.01$ level]

Analyte	NBS standard	NBS certified values	Laboratory analyses			
			CAL	IWD	EMS	DEN
pH	2694-I	4.27 ± 0.03	4.28	4.18*	4.29	4.26
	2694-II	3.59 ± 0.02	3.56*	3.49*	3.58	3.72
Specific conductance	2694-I	26 ± 2	26	29*	26	26
	2694-II	130 ± 2	130	--	134	132
Calcium	2694-I	0.014 ± 0.003	0.01	0.02	0.02	0.02
	2694-II	0.049 ± 0.011	0.05	0.05	0.04	0.04
Magnesium	2694-I	0.024 ± 0.002	0.024	0.03	0.025	0.03*
	2694-II	0.051 ± 0.003	0.050	0.05	0.049*	0.05
Sodium	2694-I	0.205 ± 0.009	0.20	0.20	0.196*	0.22*
	2694-II	0.419 ± 0.015	0.42	0.40*	0.404*	0.54
Potassium	2694-I	0.052 ± 0.007	0.050	0.05	0.047*	0.03*
	2694-II	0.106 ± 0.008	0.104	0.10	0.101*	0.16
Nitrate	2694-I	--	0.20	0.23	0.25	0.26
	2694-II	7.06 ± 0.15	7.23	6.89*	7.14	7.53*
Sulfate	2694-I	2.75 ± 0.005	2.86*	2.62*	2.61*	2.73
	2694-II	10.9 ± 0.2	11.19*	9.77*	10.11	11.00

Table 8.--*Summary of laboratory analyses of ultrapure, deionized water samples*

[CAL, Illinois State Water Survey, Central Analytical Laboratory, Champaign, Ill.; IWD, Inland Waters Directorate, National Water Quality Laboratory, Ontario, Canada; EMS, Combustion Engineering, Inc., Environmental Monitoring and Services, Camarillo, Calif.; DEN, U.S. Geological Survey, National Water Quality Laboratory, Denver, Colo.; percent, percentage of analyses resulting in a false positive concentration; median, median concentration of reported false positive concentrations; mg/L, milligrams per liter]

	CAL		IWD		EMS		DEN	
Analyte	Percent	Median (mg/L)	Percent	Median (mg/L)	Percent	Median (mg/L)	Percent	Median (mg/L)
Calcium	0	(1)	0	(1)	18	0.02	50	0.02
Magnesium	0	(1)	0	(1)	73	0.00	58	0.02
Sodium	92	0.01	0	(1)	64	0.00	42	0.02
Potassium	0	(1)	0	(1)	91	0.00	0	(1)
Ammonium	0	(1)	50	0.00	55	0.02	8	0.04
Chloride	8	0.09	0	(1)	55	0.00	67	0.08
Nitrate	0	(1)	0	(1)	64	0.02	8	0.04
Sulfate	25	0.09	0	(1)	55	0.02	50	0.05

[1] Median concentration not applicable.

SUMMARY AND CONCLUSIONS

The U.S. Geological Survey used three programs in 1986 to provide external quality-assurance for the NADP/NTN network. Onsite pH and specific-conductance determinations were evaluated in the intersite-comparison program. The effects of routine sample-handling on analyte determinations and an estimated precision of analyte values and concentrations in the onsite samples were evaluated by the blind-audit program. Differences between analytical results and an estimate of the analytical precision of four participating laboratories were determined by the interlaboratory-comparison program.

Results of the intersite-comparison program indicated that 78 percent of the onsite pH measurements and 89 percent of the onsite specific-conductance measurements were within NADP/NTN goals during 1986. The effect of routine sample-handling, processing, and shipping, as determined in the blind-audit program, seems to introduce a large proportion of uncertainty in the natural wet-deposition data. Additionally, a large percentage of blind-audit samples were contaminated by fibers or other foreign materials. The most common cause of the contamination was the presence of fibers similar to the fiber used in the packaging materials surrounding the sample bucket. These fibers also are assumed to be in some of the natural wet-deposition sample buckets. Although a Friedman's test indicated a statistically significant difference between the laboratories participating in the interlaboratory-comparison program, estimates of laboratory precision and differences between median values indicated that the magnitude of the differences between laboratories was small for all analytes.

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U.S. GOVERNMENT PRINTING OFFICE: 1988—574-901 85,116 REGION NO. 8