

INTERLABORATORY COMPARABILITY, BIAS, AND PRECISION FOR FOUR
LABORATORIES MEASURING CONSTITUENTS IN PRECIPITATION,

NOVEMBER 1982-AUGUST 1983

By Myron H. Brooks, LeRoy J. Schroder, and Bernard A. Malo

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METRIC CONVERSION TABLE

For the reader who may prefer to use inch-pound units, conversion factors for terms used in this report are listed below:

<i>Multiply SI units</i>	<i>By</i>	<i>To obtain inch-pound units</i>
milliliter (mL)	0.03382	ounce, fluid (oz)
milligram (mg)	3.527 x 10	ounce, avoirdupois (oz)

Degree Celsius (°C) may be converted to degree Fahrenheit (°F) by using the following equation:

$$^{\circ}\text{F} = 9/5^{\circ}\text{C} + 32$$

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ABSTRACT

Four laboratories have been evaluated in their analysis of identical natural and simulated precipitation samples. Interlaboratory comparability was evaluated using analysis of variance coupled with Duncan's multiple range test, and linear-regression models describing the relations between individual laboratory analytical results for natural precipitation samples. Results of the statistical analyses indicate that certain pairs of laboratories produce different results when analyzing identical samples. Analyte bias for each laboratory was examined using analysis of variance coupled with Duncan's multiple range test on data produced by the laboratories from the analysis of identical simulated precipitation samples. Bias for a given analyte produced by a single laboratory has been indicated when the laboratory mean for that analyte is shown to be significantly different from the mean of the most-probable analyte concentrations in the simulated precipitation samples. Ion-chromatographic methods for the determination of chloride and sulfate have been compared with the colorimetric methods that were also in use during the study period. Comparisons were made using analysis of variance coupled with Duncan's multiple range test for means produced by the two methods. Analyte precision for each laboratory has been estimated by calculating a pooled variance for each analyte. Analyte estimated precisions have been compared using F-tests and differences in analyte precisions for laboratory pairs have been reported.

INTRODUCTION

Four laboratories are currently participating in a continuous inter-laboratory comparison study examining laboratory analysis of major chemical constituents found in precipitation. Laboratories participating in the study are: (1) Inland Waters Directorate, Ontario, Canada (IWD); (2) Illinois State Water Survey, Champaign, Illinois (CAL); (3) U.S. Geological Survey National Water Quality Laboratory, Atlanta, Georgia (ATL); and (4) U.S. Geological Survey National Water Quality Laboratory, Denver, Colorado (DEN).

IWD analyzes precipitation samples collected by the Canadian Air and Precipitation Monitoring Network (CAPMoN); CAL analyzes precipitation samples collected by the National Atmospheric Deposition Program (NADP) and the National Acid Precipitation Assessment Program's National Trends Network (NTN). ATL and DEN routinely analyze precipitation samples collected by the U.S. Geological Survey and are prepared to serve as contingency laboratories for the NADP or NTN. The interlaboratory comparison began in November 1982 with ATL, CAL, and DEN participating. IWD joined the study in February 1983. Each laboratory received both natural and simulated precipitation samples to be analyzed for calcium, magnesium, potassium, sodium, ammonia, chloride, nitrate, sulfate, ortho-phosphate, pH, and specific conductance. Analytical results for calcium, magnesium, potassium, sodium, chloride, nitrate, sulfate, pH, and specific conductance were compared in the study.

The principal goals of the study were to: (1) Determine if the four laboratories are producing comparable results for the nine constituents; (2) document any analytical bias for each of the four laboratories; and (3) estimate the analytical precision of each laboratory. This report documents the performance of the laboratories for the period from November 1982 through August 1983.

EXPERIMENTAL DESIGN

Sample Selection and Distribution

Analytical results for both natural and simulated precipitation samples were compared. Natural precipitation samples were selected from those received each week at CAL from the NADP/NTN nationwide network of sampling sites. CAL personnel selected samples using a random number table (Dixon and Massey, 1969). Selected samples with volumes less than 750 mL were rejected for use as interlaboratory-study samples, and the next suitable sample in sequence was evaluated. This selection process continued until three or four samples with volumes greater than 750 mL were obtained. The chosen samples then were filtered, using a 0.45 micrometer pore-size organic-membrane filter, and a subsample was retained by CAL and analyzed as required by the NADP/NTN network. The remaining sample was split into 10 aliquots using a sample splitter developed by the U.S. Geological Survey. Each aliquot was stored in a de-ionized water-rinsed 125-mL high-density polyethylene bottle. All aliquots were stored at 4°C until they were shipped in insulated containers to the U.S. Geological Survey acid-rain quality-assurance project in Arvada, Colorado. The U.S. Geological Survey project relabeled the samples, and then distributed them among the participating laboratories.

Simulated precipitation samples were prepared by the U.S. Geological Survey project. These samples were primarily dilutions of Standard Reference Water Samples (SRWS) for which most-probable analyte concentrations had been previously established (Malo and others, 1978; and Schroder and others, 1980). Dilutions were made with 2.5 megohm de-ionized water, and the hydrogen-ion concentration was increased with perchloric acid to a pH between 4.0 and 6.5. Dilution factors were chosen to approximate the levels of various analytes normally found in precipitation. Concentrations of analytes in the dilutions were checked by atomic-absorption spectrophotometry and compared with the

values calculated for each dilution factor. Prepared dilutions having analyte relative errors greater than + or - 10 percent were rejected for use as simulated precipitation samples. Each simulated-precipitation sample was split into 12 identical aliquots and distributed in triplicate to the participating laboratories.

Periodically a de-ionized water blank was prepared at CAL by passing de-ionized water through the U.S. Geological Survey sample splitter. The purposes of this blank were to: (1) Determine if the samples were being contaminated by handling and bottling at CAL; and (2) monitor the laboratories for reporting of false positive values. One aliquot of each blank sample was analyzed at a U.S. Geological Survey research project laboratory using atomic-absorption spectroscopy and ion-chromatography. The remaining aliquots were distributed to the participating laboratories for analysis.

Laboratory Analysis and Reporting

Since the natural precipitation samples were filtered prior to splitting at CAL, and the simulated precipitation and de-ionized water samples required no filtration, the participating laboratories were asked not to filter the samples upon receipt. With this exception, all laboratories were requested to receive, process, and analyze the intercomparison samples using their routine precipitation-analysis procedures. The laboratories were aware that the samples received were not normal precipitation samples, but did not know which type of intercomparison sample they were receiving. The laboratories determined calcium, magnesium, potassium, and sodium by atomic-absorption spectrophotometry, except IWD, which determined potassium and sodium using flame-photometric procedures. All laboratories used colorimetric methods to determine chloride, nitrate, ammonia, sulfate, and phosphate. ATL and DEN switched to a turbidimetric method for determining sulfate during the study period. All laboratories determined pH and specific conductance electrometrically. Documentation of the analytical methods and quality assurance practices used by the laboratories are covered in the following references: (1) ATL and DEN; Skougstad and others, 1979; (2) CAL; Peden and others, 1979; and (3) IWD; Environment Canada, 1979.

During the study, ion-chromatographic methods for the determination of chloride, sulfate, and nitrate were being developed at ATL, DEN, and IWD. Data generated by these methods were reported, in addition to that generated by the colorimetric methods in use during this time.

All analyte concentrations were reported in accordance with the individual laboratory's procedures. Individual analyte detection limits and number of significant figures reported varied from laboratory to laboratory. Values below the limit of detection were not used in the determination of comparability, bias, and estimated precision. Analyte concentrations reported as below analytical detection limits were treated as missing data.

RESULTS AND DISCUSSION

Results from the analyses of de-ionized water blanks prepared at CAL are listed in table 1. ATL, DEN, and CAL analyzed duplicates of four blank samples while IWD analyzed duplicates of two of the four blanks. IWD reported the least number of false positives, reporting values for chloride twice and sulfate once. CAL reported values for potassium, sodium, sulfate, and nitrate. ATL reported values for calcium, magnesium, potassium, sodium, chloride, sulfate, and nitrate. ATL reported a false positive value for calcium each of the eight times a blank sample was analyzed. DEN reported a value, at least once, for every analyte checked, and reported a false positive value for chloride each of the eight times a blank sample was analyzed. With few exceptions all reported values were at or near the limit of detection for the laboratory generating the false positive values. For example, the detection limit for calcium at ATL was 0.01 mg/L. Of the eight values that ATL reported for the eight blank samples, six values were 0.01 mg/L and two values were 0.20 mg/L. As another example, ATL reported five values of 0.01 mg/L for sodium. The ATL detection limit for sodium was also 0.01 mg/L.

Table 1.--Percentage of false positives reported by laboratories
for the analysis of de-ionized water blanks

[ATL=U.S. Geological Survey National Water Quality Laboratory, Atlanta, Georgia; CAL=Illinois State Water Survey, Champaign, Illinois; DEN=U.S. Geological Survey National Water Quality Laboratory, Denver, Colorado; IWD=Inland Waters Directorate, Ontario, Canada; n=number of analyses performed]

Analyte	Percentage of analyses of de-ionized water resulting in a report of a false positive value			
	ATL n=8	CAL n=8	DEN n=8	IWD n=4
Calcium	100	0	62.5	0
Magnesium	75	0	37.5	0
Potassium	75	87.5	50	0
Sodium	62.5	75	25	0
Chloride	75	0	100	50
Sulfate	25	25	12.5	25
Nitrate	0	12.5	50	0

Comparability of results from each of the four laboratories was examined using data from natural precipitation samples. To facilitate the statistical analysis of these data, only samples for which all four laboratories reported a value for a given analyte were used for comparison of laboratory measurements of that analyte. Laboratories were compared by a two-way analysis of variance, with laboratory and sample identification number designated as treatments or classification variables. Relations between laboratory results were described by formulating linear-regression models for all possible laboratory pairs for each analyte. The analysis of variance results and linear-regression model parameters were generated using SAS (SAS Institute Inc., 1982), a statistical analysis package available on the U.S. Geological Survey AMDAHL computer. Analysis of variance results indicated that laboratory treatment resulted in significantly different means for every analyte examined. To further investigate these differences, Duncan's multiple range test for means was employed. Results from this test are presented in table 2. Laboratories whose analyte means are significantly different at $\alpha=0.05$ have different letters in the column labeled "group." According to the test results all six possible laboratory pairs produced significantly different results for calcium, sodium, chloride, sulfate, and nitrate. Test results for magnesium indicated the following pairs of laboratories produced significantly different results for this analyte; DEN and ATL, DEN and IWD, and CAL and IWD. Test results for potassium indicated that DEN and IWD, and ATL and IWD produced significantly different results for this analyte. Test results for pH indicated that only CAL and DEN results were not significantly different for this analyte. Test results for specific conductance indicated that ATL and IWD produced significantly different results for this analyte. Linear-regression model parameters for all possible analyte and laboratory pair combinations are presented in table 3. The laboratory listed first in the table is modeled as the dependent variable in the regression equation. For example, under the heading DEN-ATL, and in the row calcium, the following relation is described;

$$Y = X \times 0.799 + 0.038$$

where

Y = DEN calcium results, and

X = ATL calcium results.

Data users interested in data from two or more precipitation sampling networks, generated by different laboratories that are compared in this report, must decide whether or not to employ the linear-regression model parameters as correction factors between the two different data sets.

Table 2.--Duncan's multiple range test results for laboratory means from the analysis of natural precipitation samples

[ATL=U.S. Geological Survey National Water Quality Laboratory, Atlanta, Georgia; CAL=Illinois State Water Survey, Champaign, Illinois; DEN=U.S. Geological Survey National Water Quality Laboratory, Denver, Colorado; IWD=Inland Waters Directorate, Ontario, Canada; group=Duncan's multiple range test grouping laboratories having different group values, such as A and B, have significantly different means at alpha=0.05; mean=mean of all analyses; n=number of analyses performed; lab=laboratory performing the analyses; $\mu\text{S}/\text{cm}$ =microsiemens per centimeter; mg/L=milligrams per liter]

Calcium				Magnesium				Sodium			
group	mean (mg/L)	n	lab	group	mean (mg/L)	n	lab	group	mean (mg/L)	n	lab
A	0.328	28	CAL	A	0.054	47	DEN	A	0.264	49	ATL
B	.302	28	ATL	BA	.051	47	CAL	B	.254	49	CAL
C	.291	28	IWD	BC	.050	47	ATL	C	.241	49	IWD
D	.279	28	DEN	C	.047	47	IWD	D	.187	49	DEN

Potassium				Chloride				Sulfate			
group	mean (mg/L)	n	lab	group	mean (mg/L)	n	lab	group	mean (mg/L)	n	lab
A	.059	34	DEN	A	.470	49	DEN	A	1.64	54	IWD
A	.057	34	ATL	B	.435	49	ATL	B	1.60	54	ATL
BA	.054	34	CAL	C	.410	49	CAL	C	1.53	54	DEN
B	.051	34	IWD	D	.390	49	IWD	D	1.46	54	CAL

Nitrate				pH				Specific conductance			
group	mean (mg/L)	n	lab	group	mean	n	lab	group	mean ($\mu\text{S}/\text{cm}$)	n	lab
A	.254	54	CAL	A	5.38	55	ATL	A	14.3	54	ATL
B	.197	54	DEN	B	5.06	55	CAL	BA	13.9	54	DEN
C	.195	54	ATL	B	5.05	55	DEN	BA	13.7	54	CAL
D	.175	54	IWD	C	4.98	55	IWD	B	13.2	54	IWD

Table 3.--Linear-regression model coefficients for analytes and laboratory pairs
analyzing natural and simulated precipitation samples

[ATL=U.S. Geological Survey National Water Quality Laboratory, Atlanta, Georgia; CAL=Illinois State Water Survey, Champaign, Illinois; DEN=U.S. Geological Survey National Water Quality Laboratory, Denver, Colorado; IWD=Inland Waters Directorate, Ontario, Canada; a=slope of regression line; b=intercept of regression line; laboratory listed first has results modeled as dependent variable]

Analyte	Linear-regression model parameters for laboratory pairs											
	DEN-ATL		DEN-CAL		DEN-IWD		ATL-CAL		ATL-IWD		IWD-CAL	
	a	b	a	b	a	b	a	b	a	b	a	b
Calcium	0.799	0.038	0.894	-0.013	0.918	0.012	1.029	-0.035	1.049	-0.003	0.968	-0.027
Magnesium	.789	.014	.850	.010	.869	.013	1.006	-.002	1.030	.002	.959	-.003
Potassium	1.026	.001	1.096	.000	1.171	-.001	1.070	.000	1.121	.000	.914	.002
Sodium	.834	-.034	.858	-.031	.851	.019	1.026	.004	1.021	.018	.997	-.012
Chloride	.993	.039	1.004	.059	.979	.088	1.001	.024	.980	.052	.995	-.017
Nitrate	.888	.024	.749	.007	1.032	.016	.820	-.013	1.141	-.004	.712	-.006
Sulfate	.941	.020	1.000	.069	.945	-.024	1.060	.055	.993	-.028	1.007	.173
pH	.453	2.612	1.026	-.146	1.016	-.017	.652	2.080	.805	1.367	.961	.120
Specific conductance	.864	1.571	1.047	-.429	1.026	.336	.773	3.692	.729	4.627	1.023	-.769

Analyte bias for each laboratory was evaluated using data from laboratory analysis of simulated precipitation samples only. Laboratory-reported analyte concentrations were compared against most probable analyte concentrations in the simulated precipitation samples. The pH and specific conductance of the simulated precipitation samples were measured only once after the addition of perchloric acid; thus, a most probable analyte concentration for pH and specific conductance was not available. Nitrate was not stable in the simulated precipitation samples. Only samples for which all four laboratories reported values for a given analyte were used for comparison of laboratory measurements of that analyte. Comparison was by two-way analysis of variance, with laboratory and sample identification number as treatments or classification variables. Analysis of variance results indicated that the laboratory means for all analytes considered were significantly different. Duncan's multiple range test was used to further investigate these differences. Results of these tests are presented in table 4. A fifth sample treatment designation (laboratory), MPV, represents the most-probable analyte concentrations in the simulated precipitation samples. Laboratory analyte means that are significantly different from the MPV mean are judged biased. Using this criterion, DEN analyses of simulated precipitation displayed bias for calcium, magnesium, sodium, chloride, and sulfate. ATL analyses of simulated precipitation displayed bias for calcium, magnesium, and potassium. CAL analyses of simulated precipitation displayed bias for sodium. IWD analyses of simulated precipitation displayed bias for calcium, magnesium, and sodium. These bias estimates must be interpreted with caution because analyte concentrations were considerably higher in the simulated precipitation samples than the levels normally encountered in natural precipitation (Peden, Mark, Illinois State Water Survey, written commun., 1984). The bias estimates presented in table 4 are only valid for samples whose analyte concentrations closely match the concentrations of the simulated precipitation samples. The bias estimates may or may not reflect laboratory analyte bias at the lower concentrations often encountered in natural precipitation samples. This weakness in study design will be addressed in future work.

Ion-chromatographic methods were in development at ATL, DEN, and IWD during the study period. Consequently, data for chloride and sulfate from these three laboratories were produced by two different methods, ion-chromatography and colorimetry. Comparison of the two methods employed by each of the three laboratories used data from both natural and simulated precipitation samples. Two-way analysis of variance using laboratory method and sample identification number was coupled with Duncan's multiple range test to produced the desired comparisons. Duncan's multiple range test results are presented in table 5. Laboratory means resulting from ion-chromatographic analyses have their associated laboratory name suffixed with the letters "IC." The test results indicate significant differences between colorimetric and ion-chromatographic results for DEN analyses of sulfate, ATL analyses of chloride, and IWD analyses of chloride.

Table 4.--Duncan's multiple range test results for laboratory means from the analysis of simulated precipitation samples

[ATL=U.S. Geological Survey National Water Quality Laboratory, Atlanta, Georgia; CAL=Illinois State Water Survey, Champaign, Illinois; DEN=U.S. Geological Survey National Water Quality Laboratory, Denver, Colorado; IWD=Inland Waters Directorate, Ontario, Canada; group=Duncan's multiple range test grouping laboratories having different group values, such as A and B, have significantly different means at alpha=0.05; MPV=most-probable analyte concentrations in the simulated precipitation samples; mean=mean of all analyses; n=number of analyses performed; lab=laboratory performing the analyses; mg/L=milligrams per liter]

Calcium				Magnesium				Sodium			
group	mean (mg/L)	n	lab	group	mean (mg/L)	n	lab	group	mean (mg/L)	n	lab
A	1.82	37	CAL	A	0.707	37	MPV	A	1.48	44	MPV
A	1.81	37	MPV	A	.705	37	CAL	A	1.48	44	ATL
B	1.78	37	IWD	B	.694	37	ATL	B	1.45	44	IWD
B	1.76	37	ATL	B	.686	37	DEN	C	1.43	44	CAL
C	1.58	37	DEN	C	.594	37	IWD	D	1.23	44	DEN

Potassium				Chloride				Sulfate			
group	mean (mg/L)	n	lab	group	mean (mg/L)	n	lab	group	mean (mg/L)	n	lab
A	.224	45	ATL	A	.918	48	DEN	A	4.76	50	DEN
B	.213	45	MPV	BA	.841	48	ATL	B	4.49	50	IWD
B	.207	45	CAL	B	.828	48	MPV	B	4.48	50	CAL
B	.207	45	IWD	B	.824	48	CAL	B	4.44	50	ATL
B	.203	45	DEN	B	.781	48	IWD	B	4.40	50	MPV

Table 5.--*Duncan's multiple range test results for laboratory means from the analysis of anions in natural and simulated precipitation samples by colorimetry and ion-chromatography*

[ATL=U.S. Geological Survey National Water Quality Laboratory, Atlanta, Georgia, analyses performed by colorimetry; DEN=U.S. Geological Survey National Water Quality Laboratory, Denver, Colorado, analyses performed by colorimetry; IWD=Inland Waters Directorate, Ontario, Canada, analyses performed by colorimetry; ATLIC=analyses performed by ion-chromatography; DENIC=analyses performed by ion-chromatography; IWDIC=analyses performed by ion-chromatography; group=Duncan's multiple range test grouping laboratories having different group values, such as A and B, have significantly different means at $\alpha=0.05$; mean=mean of all analyses; n=number of analyses performed; lab=laboratory performing the analyses; mg/L=milligrams per liter]

Chloride				Sulfate			
group	mean (mg/L)	n	lab and analytical method	group	mean (mg/L)	n	lab and analytical method
A	.793	82	DEN	A	2.47	116	DEN
A	.791	82	ATL	BA	2.44	116	IWD
A	.778	82	DENIC	BA	2.41	116	ATL
B	.747	82	ATLIC	BAC	2.37	116	IWDIC
B	.746	82	IWDIC	BC	2.35	116	ATLIC
C	.705	82	IWD	C	2.30	116	DENIC

Analyte precisions for each laboratory and analyte were estimated by calculating a pooled variance for each laboratory and analyte. Pooled variances were calculated according to the equation of Dixon and Massey (1969). Data used for the calculations were tested for relations between concentration level and standard deviation prior to use. Linear-regression models for the mean values of replicate measurements versus the standard deviations of those measurements were formulated. Regression-model parameters indicated that no significant relations between concentration level and standard deviation existed for any analyte reported by any of the four participating laboratories, thus pooling was justified. Pooled variances are listed in table 6. As shown in table 6, CAL results were the least disperse of the four laboratories. In general, IWD results were more disperse than CAL results, and DEN and ATL dispersions were roughly equal and greater than IWD dispersion. Pooled variances for each analyte were compared for all possible laboratory pairs using the F-test at the 5-percent confidence level. The F-test evaluates a null hypothesis that no significant difference exists between the variances of two sets of laboratory measurements of identical samples. Results of the F-test analyses are found in table 7. No significant difference at the 5-percent confidence level was demonstrated for DEN and ATL variances for calcium and potassium; DEN and CAL variances for pH; DEN and IWD variances for specific conductance; and ATL and IWD variances for sodium and chloride. At the 5-percent confidence level, the remaining differences in analyte variances were shown not to arise from random error, but from actual differences in the variances reported by the individual laboratories.

Table 6.--Laboratory-pooled variances for analytes in precipitation

[ATL=U.S. Geological Survey National Water Quality Laboratory, Atlanta, Georgia; CAL=Illinois State Water Survey, Champaign, Illinois; DEN=U.S. Geological Survey National Water Quality Laboratory, Denver, Colorado; IWD=Inland Waters Directorate, Ontario, Canada; mg²/L²=milligrams squared per liter squared]

Analyte	Number of determinations	Laboratory-pooled variance (mg ² /L ²)				Concentration range
		ATL	CAL	DEN	IWD	
Calcium	60	0.087	0.016	0.075	0.032	0.31-5.4
Magnesium	60	.027	.008	.054	.019	.096-2.93
Potassium	60	.051	.003	.054	.007	.048-0.92
Sodium	60	.045	.021	.098	.045	.14-5.80
Chloride	60	.049	.025	.089	.049	.09-8.80
Sulfate	60	.132	.062	.58	.34	.67-23
pH	60	.084	.007	.011	.044	4.7-7.7
Specific conductance	60	2.15	.28	1.03	.89	5.4-98

Table 7.--F-test analyses of pooled variances for laboratory pairs

[ATL=U.S. Geological Survey National Water Quality Laboratory, Atlanta, Georgia; CAL=Illinois State Water Survey, Champaign, Illinois; DEN=U.S. Geological Survey National Water Quality Laboratory, Denver, Colorado; IWD=Inland Waters Directorate, Ontario, Canada; F=F-test value; null=accept or reject null hypothesis]

Analyte	F-test results for pairs of laboratory variances											
	DEN-ATL		DEN-CAL		DEN-IWD		ATL-CAL		ATL-IWD		IWD-CAL	
	F	null	F	null	F	null	F	null	F	null	F	null
Calcium	1.16	accept	4.69	reject	2.34	reject	5.44	reject	2.72	reject	2.00	reject
Magnesium	2.00	reject	6.75	reject	2.84	reject	3.38	reject	1.42	accept	2.38	reject
Potassium	1.06	accept	18.0	reject	7.71	reject	17.0	reject	7.29	reject	2.33	reject
Sodium	2.18	reject	4.67	reject	2.18	reject	2.14	reject	1.00	accept	2.14	reject
Chloride	1.82	reject	3.56	reject	1.82	reject	1.96	reject	1.00	accept	1.96	reject
Nitrate	1.18	accept	5.50	reject	5.50	reject	4.67	reject	4.67	reject	1.00	accept
Sulfate	4.39	reject	9.36	reject	1.71	reject	2.13	reject	2.58	reject	5.48	reject
pH	7.63	reject	1.58	accept	4.00	reject	12.0	reject	1.91	reject	6.29	reject
Specific conductance	2.09	reject	3.68	reject	1.16	accept	7.68	reject	2.42	reject	3.18	reject

SUMMARY

Four laboratories analyzed identical natural and simulated precipitation samples from November 1982 through August 1983. Analyte results compared were those for calcium, magnesium, potassium, sodium, chloride, sulfate, nitrate, pH, and specific conductance. Analytical results were interpreted to provide measures of interlaboratory comparability, possible analyte bias, and estimated precision for each laboratory. Interlaboratory comparability was evaluated using results of laboratory analyses of natural precipitation samples. Analysis of variance, Duncan's multiple range test for means, and linear-regression model parameters were used to test for significant differences between laboratory means, and to mathematically describe those differences. Thirty-one of the 54 possible analyte and laboratory-pair combinations were significantly different at $\alpha=0.05$. Analyte bias for each laboratory was evaluated using results of laboratory analyses of known value simulated precipitation samples. Analysis of variance and Duncan's multiple range test were used to compare laboratory analyte means versus most-probable analyte concentration means. Test results for the simulated precipitation analyses indicated bias for CAL analyses of sodium, IWD analyses of calcium, magnesium, and sodium, ATL analyses of calcium, magnesium, and potassium, and DEN analyses of calcium, magnesium, sodium, chloride, and sulfate. Bias estimates were valid only for the analyte concentration ranges that were present in the simulated precipitation samples, and may not reflect bias introduced by the laboratories when they analyze natural precipitation samples. Ion-chromatographic methods being developed at ATL, DEN, and IWD for the measurement of chloride, nitrate, and sulfate were compared with colorimetric methods in use at these laboratories during the same time. Four of the nine possible sets of ion-chromatographic versus colorimetric data pairings were significantly different at $\alpha=0.05$. Analyte precision was estimated using pooled variances. In general CAL achieved greater precision than IWD which achieved greater precision than ATL and DEN.

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