USGS
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Techniques of Water-Resources Investigations
of the United States Geological Survey

Chapter A6

QUALITY ASSURANCE PRACTICES FOR THE CHEMICAL AND BIOLOGICAL ANALYSES OF WATER AND FLUVIAL SEDIMENTS

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Book 5

Laboratory Analysis

Initial Evaluation of Cooperator and Contractor Laboratories

1. Application or scope

1.1 This practice describes procedures to follow in order to evaluate a laboratory.

1.2 Laboratory analytical data used by the Geological Survey are provided by numerous cooperator and contractor laboratories in addition to Geological Survey laboratories. The quality of all data must be comparable since data must be able to be used without qualifications.

2. Practice

2.1 The facility

2.1.1 In order to evaluate data to be provided by a cooperator or contractor laboratory, an initial assessment of the facility should be obtained from a visit to it. An 8-page form (fig. 21), has been designed to aid in this initial evaluation.

2.1.2 Prepare documentation on the laboratory's interior. Include information on bench space, safety standards, temperature regulation, air quality, hood space, and so forth.

2.1.3 Summarize education and experience of laboratory director and analysts.

2.1.4 Examine sample receipt and inventory (log-in) procedures, storage space (including refrigeration) and time of storage of samples (before and after analyses).

2.2 Analyses

2.2.1 Obtain a list of the number and type of determinations, both those which are routinely done by the laboratory and those which are planned as part of the contract or cooperation agreement.

2.2.2 Obtain a description of the instruments and analytical methods to be used and submit samples to test analytical proficiency prior to the award or initiation of the contract.

2.2.3 Update all information as changes occur.

2.3 Quality control

2.3.1 Examine quality control procedures.

2.3.2 Since experience has shown that some analyses will be in error and need to be remade when a properly functioning quality control program exists, obtain acceptability criteria and estimates of the percentages of analyses which are rerun.

2.3.3 Record the percentage of standards, blanks, spiked samples, laboratory duplicates, and unknown reference material which are analyzed for each constituent.

2.3.4 Obtain any quality control summaries which a laboratory may have. Also tabulate any data from analysis of proficiency testing samples or from analysis obtained in "round-robin" studies.

2.4 Quality assurance

2.4.1 Prepare or obtain a quality assurance plan for each laboratory, using the practice "Reference material submitted to cooperator and contractor laboratories" in section "Quality Assurance Monitoring," as a guide.

2.4.2 Prepare (or obtain from Geological Survey quality assurance project) a summary and evaluation of quality assurance data semiannually. Use examples outlined in this section as guides.

References

U.S. Environmental Protection Agency, 1978, Manual for the interim certification of laboratories involved in analyzing public drinking water supplies, criteria and procedures: U.S. Environmental Protection Agency EPA–600/8–78–008, Washington, D.C., 92 p.

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District _____ District liaison _____ Phone No. (FTS) _____

Laboratory name _____

Location _____

Director _____ Phone No. _____

Staff: Professionals _____ Technicians _____ Clerical _____

Computer _____ Other _____

(Organizational chart should be attached to this form, if available. Identify those sections and personnel routinely providing data for USGS.)

1. SAMPLE LOADS:

Approximate annual sample load for USGS and total analytical work for all agencies (USGS plus state, county, city, etc.) by category:

USGS: Major ions _____ Metals _____ Nutrients _____ Radiochemical _____

Total: _____ _____ _____ _____

USGS: Pesticides _____ Biological _____ Other[1/] _____

Total: _____ _____ _____

[1/] Identification of other _____

2. LABORATORY FACILITIES:

Approximate lab size _____ (ft^2) Linear bench space _____ (ft)

Hoods (number or linear feet) _____

Hoods (face velocity)	Adequate _____	Inadequate _____
Sinks	Adequate _____	Inadequate _____
Lighting	Adequate _____	Inadequate _____
Heating	Adequate _____	Inadequate _____

Figure 21.—Sample evaluation form for laboratories providing analytical data for the U.S. Geological Survey.

Cooling	Adequate _____	Inadequate _____
Humidity control	Adequate _____	Inadequate _____
Air quality-detectable fumes	Yes _____	No _____
Air quality-visible dust	Yes _____	No _____

Other _____

Apparent conformance to OSHA safety standards: _____

3. MAJOR LABORATORY EQUIPMENT:

Item	Model	No.	Age

Figure 21.—Continued

Major instrumentation:

Service contracts for: Most _____ Some _____ Few _____

Comments _____

Calibration procedures detailed: Most _____ Some _____ Few _____

Comments _____

Records kept:

Repairs Yes _____ No _____ Inspection Yes _____ No _____

Calibration Yes _____ No _____

4. CHEMICALS AND REAGENTS:

Date of receipt or preparation shown Yes _____ No _____

Analyst preparing reagents identified Yes _____ No _____

Proper storage:

Light-sensitive reagents Yes _____ No _____

Heat-sensitive reagents Yes _____ No _____

Flammable materials Yes _____ No _____

Carcinogenic compounds Yes _____ No _____

Other _____

5. SAMPLE COLLECTION:

Sampling for USGS analyses:

Personnel collecting samples: USGS _____ Cooperator _____

Other _____

Sample collection procedure reference(s) _____

_____

_____

Figure 21.—Continued

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Location indicated by (name, number, etc.) _____

_____

Sample identification includes:

Water type (surface water, ground water, etc.)	Yes _____	No _____
Analyses required	Yes _____	No _____
Name of collector	Yes _____	No _____
Date	Yes _____	No _____
Time	Yes _____	No _____
Treatment (filtered, raw, acidified, etc.)	Yes _____	No _____

Collection procedures (in brief) _____

_____

_____

_____

Preservation methods _____

_____

_____

_____

6. SAMPLE HANDLING:

Mode of shipment _____

Average elapsed time for shipment _____

Sample identification in laboratory: Program _____

Station location _____ Lab number _____

Other _____

Storage: Ambient _____ Refrigerated at _____ ^{o}C

_____

Figure 21.—Continued

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7. ANALYSES:

Generally begun within _____ days of receipt.

Average sample backlog (days, weeks, etc.) for following types of samples:

Major ions _____ Trace constituents _____ Nutrients _____

Pesticides _____ Biological _____ Other _____

Form of Analytical Data Report (letter, computer output, etc.)

_____

Analysts identified _____ Date of completion shown _____

Data review procedures (in brief) _____

_____

_____

_____

_____

_____

8. LABORATORY DATA RECORDS:

Raw data: Retention period _____ Form _____

Final data: Retention period _____ Form _____

Comments: _____

_____

_____

9. METHODS:

Analytical references available in laboratory Yes _____ No _____

Written procedures available at bench Yes _____ No _____

Figure 21.—Continued

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Source of methods other than USGS _____

_____

_____

_____

_____

_____

(Attach list of method references for each constituent.)

10. QUALITY CONTROL:

Summaries prepared:

Quarterly _____ Semiannually _____ Annually _____ Other _____

Obtained Yes _____ No _____

Analytical acceptability criteria obtained: Yes _____ No _____

Estimate percent of analyses passed on "first run": _____

Rerun criteria available to laboratory personnel: Yes _____ No _____

Obtained Yes _____ No _____

Approximate percent of total sample load: Standards _____ Blanks _____

Lab duplicates _____ Spiked standard additions _____

Blind reference samples _____ Other _____

_____

_____

Control charts:

Used Yes _____ No _____

Frequency Yes _____ No _____

Checked by (other analyst, lab chief, etc.) _____

Figure 21.—Continued

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11. QUALITY ASSURANCE PROGRAM PARTICIPATION:

Agency or organization (USGS, EPA, ASTM, etc.)	Sample type (major ions, nutrients, etc.)	Participation dates Initial	Last	Last performance Excellent	Average	Poor

Comments: _____

_____

_____

Report copies available: Yes _____ No _____

Obtained Yes _____ No _____

Laboratory certified by:

EPA Yes _____ No _____

State Yes _____ No _____

Other Yes _____ No _____

Copies of certificates available: Yes _____ No _____

Obtained Yes _____ No _____

Comments: _____

_____

_____

_____

Figure 21.—Continued

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12. SUMMARY:

General overall evaluation: _____

Suggestions for improvement: _____

Evaluator(s): _____ Date of visit: _____

Figure 21.—Continued

Methods for Data Summation and Evaluations: Tabular Presentations

1. Application or scope

1.1 This practice gives examples of tabular summaries and provides a guide for the type of information that should be included in a semiannual quality assurance report.

1.2 Often quality control and (or) quality assurance data are found in notebooks and charts throughout a laboratory as well as in laboratory computer files. Although, to be effective, laboratory quality control data must be examined as soon after an analysis as possible so that necessary corrections can be made, a periodic summary of quality control and quality assurance data will give the data user information on the quality of his data. Such a summary should be made at least semiannually.

1.3 In order to evaluate the quality of data so summarized, the precision and bias of the data should be calculated, reported, and compared to expected values when possible. As can be seen in the examples, the precision and bias can also be indicated in the tabular summation.

1.4 Quality control charts may also be included as visual summaries in the report and the precision and bias can be indicated graphically. The practice "Quality control charts" in the section "Laboratory Quality Control" and the practice "Methods for data evaluation: graphical presentation" in this section should be referred to.

1.5 Other practices in this section which describe techniques to evaluate the data should also be referred to.

2. Practice

2.1 Summary of data from analysis of reference materials

2.1.1 Present the value of the theoretical or most probable concentration along with the value or the mean value obtained by each laboratory. Indicate the total number of determinations used in the computations.

2.1.2 Tables 11 through 15 are examples of su uality control data summaries. Table 11 sum rizes 6 months of quality control data for flu le analyses made by the Geological Survey entral Laboratories on Standard Reference ater Samples (SRWS); table 12 summarize out 2 months of quality control data for nu nt analyses made by the Geological Survey entral Laboratories on solutions prepared m U.S. Environmental Protection Agenc PA) ampouled concentrates; table 13 summa s a year of Geological Survey Central Labora y radiochemical results obtained by analyz EPA "round- robin" samples; table 14 summa s data obtained in an evaluation of pH me rements made in the field; and table 15 sho a summary of results obtained by using SAS computer program (Barr and others, 76) to get a frequency distribution for the re s from the measurement of pH and specifi nductance.

2.2 mmary of data from replicate sample analys

2.2 Summarize results from analyses of sample hich are "split" by field personnel and submit to the laboratory as duplicates or replicate lso summarize results from individual sample alyzed two or more times by the laboratory

2.2 Tables 16 through 19 are summaries of resu from repeated analyses of samples. Table hows results from duplicates split by field p nnel and submitted to the laboratory and gi published (in Skougstad and others, 1979) p ision data; table 17 lists results from "duplic polychlorinated biphenyl analyses made the laboratory on bottom sediment sample able 18 gives the mean concentrations and pe nt relative standard deviation for replicate lyses made on samples and standards for rad -226; and table 19 lists results from replica radiochemical analyses submitted periodically to the laboratory by the laboratory.

Table 11.—Summary of standard reference water sample results for fluoride analyses

Constituent	Most probable values			Combined laboratory values			Laboratory 1			Laboratory 2			SRWS number
	Mean	Standard deviation	N[a]	Mean	Standard deviation	N[b]	Mean	Standard deviation	N[b]	Mean	Standard deviation	N[b]	
Fluoride, dissolved (mg/L)	.78	± .08	19	.77	± .10	44	.69	± .05	21	.84	± .06	23	55
	.80	± .06	25	.78	± .09	12	.72	± .08	6	.83	± .05	6	62
	.84	± .10	27	.84	± .14	73	.75	± .05	33	.92	± .13	40	60
	.92	± .07	17	.92	± .10	99	.83	± .06	44	.99	± .06	55	58
	1.03	± .14	19	.99	± .10	30	.89	± .05	13	1.06	± .05	17	54

[a] N = number of laboratories in interlaboratory test.
[b] N = number of determinations.

Table 12.—Summary of nutrient quality control data: 11/77–12/77

Determination	Theoretical value (mg/L)	Combined laboratory data				Laboratory 1				Laboratory 2			
		Mean (mg/L)	Relative deviation (percent)	Bias (percent)	No. of determinations	Mean (mg/L)	Relative deviation (percent)	Bias (percent)	No. of determinations	Mean (mg/L)	Relative deviation (percent)	Bias (percent)	No. of determinations
Nitrogen, ammonia dissolved	0.23	0.227	± 22	- 1	75	0.236	± 6	+ 3	28	0.221	± 28	- 4	47
	1.59	1.518	± 7	- 5	79	1.572	± 7	- 1	28	1.488	± 8	- 6	51
Nitrogen, ammonia plus organic, dissolved	0.41	0.371	± 19	- 10	96	0.420	± 8	+ 2	38	0.338	± 20	- 18	58
	3.51	3.297	± 6	- 6	98	3.468	± 3	- 1	38	3.189	± 5	- 9	60
Nitrogen, nitrite plus nitrate, dissolved	0.11	0.121	± 16	+ 10	75	0.119	± 10	+ 8	27	0.122	± 18	+ 11	48
	0.38	0.407	± 8	+ 7	80	0.380	± 3	0	27	0.421	± 7	+ 11	53
Phosphorus, dissolved	0.20	---	---	---	--	0.210	± 3	+ 5	42	---	---	---	--
	0.66	---	---	---	--	0.668	± 2	+ 1	44	---	---	---	--
Phosphorus, orthophosphate dissolved	0.052	0.050	± 20	- 4	49	0.050	± 7	- 4	27	0.050	± 28	- 4	22
	0.190	0.168	± 16	- 12	53	0.183	± 3	- 4	27	0.152	± 21	- 20	26

2.3 Data evaluation

2.3.1 The type of data evaluation will depend on the type of data. As examples of tabular presentation of data evaulation, note particularly table 12, in which the relative deviations were calculated for the two Geological Survey Central Laboratories (with the number of determinations reported) and the biases (with respect to the theoretical values) are indicated; table 13, in which both the standard and relative deviations are reported and biases on both the theoretical value and a multilaboratory determined value are tabulated; table 15, in which the frequency of "satisfactory," "unsatisfactory," "marginal," and "not determined" pH analyses is shown; and table 16, in which the "theoretical" relative deviation of the method has been used to calculate an artificial "acceptable range" using the means of the duplicates.

2.3.2 In order to determine the standard deviation and (or) the percent relative standard deviation (coefficient of variation) of the data, calculate:

Table 13.—Comparison of results of radiochemical analyses and most probable values

Determination	Theoretical value (pCi/L)	EPA "round-robin" results			Denver Central Laboratory					
		Mean (pCi/L)	Standard deviation (pCi/L)	Number of labs	Mean (pCi/L)	Standard deviation (pCi/L)	Number of analyses	Relative deviation (percent)	Bias (based on theoretical value) (percent)	Bias (based on multi-lab value) (percent)
Gross beta radioactivity, dissolved (as Sr-90)	12	16.3	6.0	59	12.2	4.0	4	27	+ 8	- 20
	15	15.9	3.6	42	16.3	.6	3	4	+ 9	+ 3
	49	51.2	9.5	65	52.3	1.5	3	3	+ 7	+ 2
Radium -226	3.5	----	---	--	3.12	.06	3	2	- 11	----
	5.1	----	---	--	4.80	.75	3	16	- 6	---
Strontium -89	14	14.9	4.3	28	16.7	.6	3	4	+ 19	+ 12
Strontium -90	10	9.2	2.2	28	9.3	.6	3	6	- 7	+ 1
Tritium	970	1008	197	52	1123	46	3	4	+ 16	+ 11
	980	1000	172	55	927	31	3	3	- 5	- 7
	1060	1098	219	50	1053	76.5	3	7	- 1	- 4
	1970	1988	258	50	2117	40.4	3	2	+ 7	+ 6

Table 14.—Comparison by WRD Region of field laboratory evaluation Round 1 pH data

Test sample	Central Region			Northeast Region			Southeast Region			Western Region			Combined data		
	Samples analyzed	MPV[1]	Standard deviation	Samples analyzed	MPV[1]	Standard deviation	Samples analyzed	MPV[1]	Standard deviation	Samples analyzed	MPV[1]	Standard Deviation	Samples Analyzed	MPV[1]	Standard deviation
P- 4	127	7.63	0.12	---	---	---	48	7.63	0.12	57	7.64	0.12	232	7.635	0.117
9	122	3.85	.08	86	3.88	0.08	49	3.87	.08	56	3.87	.06	313	3.861	.078
10	123	4.33	.09	89	4.32	.06	49	4.32	0.4	57	4.33	.06	318	4.315	.070
11	128	5.90	.07	89	5.90	.10	54	5.90	.06	54	5.89	.14	325	5.892	.065
12	123	7.45	.07	86	7.47	.09	52	7.46	.09	53	7.48	.09	314	7.458	.070
13	124	8.88	.17	100	8.89	.13	48	8.90	.15	54	8.95	.12	326	8.887	.132
14	---	---	---	---	---	---	3	3.00	.00	--	---	---	3	3.0 ± .02	2/
15	---	---	---	---	---	---	3	3.87	.15	--	---	---	3	4.0 ± .02	2/
16	---	---	---	---	---	---	2	5.05	.07	--	---	---	2	5.0 ± .02	2/
17	---	---	---	---	---	---	3	5.80	.00	--	---	---	3	5.8 ± .02	2/
18	---	---	---	---	---	---	3	7.37	.06	--	---	---	3	7.4 ± .05	2/
19	---	---	---	---	---	---	4	8.40	.02	--	---	---	4	8.4 ± .05	2/

1/ MPV = most probable value.
2/ Known Value at 25°C.

$$s = \sqrt{\frac{\Sigma(x_i - \bar{x})^2}{n-1}} = \sqrt{\frac{\Sigma x_i^2 - (\Sigma x_i)^2/n}{n-1}} \quad (34)$$

$$R.D. = \frac{s}{\bar{x}} \times 100 \text{ percent} \quad (35)$$

where
s = standard deviation of a sample,
x_i = concentration reported for a constituent in the sample,
$\bar{x}$ = mean concentration,
n = number of analyses made for the constituent, and
$R.D.$ = relative standard deviation, in percent.

Table 15.—Example of computer produced table of frequency distribution of pH and specific conductance results

[Produced by SAS computer program (Barr and others, 1976)]

COMMENTS	PARAMETER		
FREQUENCY PERCENT ROW PCT COL PCT	C[1]	P[2]	TOTAL
M[3]	47	57	104
	4.98	6.04	11.02
	45.19	54.81	
	9.25	13.07	
N[4]	30	8	38
	3.18	0.85	4.03
	78.95	21.05	
	5.91	1.83	
S[5]	265	308	573
	28.07	32.63	60.70
	46.25	53.75	
	52.17	70.64	
U[6]	166	63	229
	17.58	6.67	24.25
	72.49	27.51	
	32.68	14.45	
TOTAL	508	436	944
	53.81	46.19	100.00

C[1] = specific conductance at 25°C

P[2] = pH

M[3] = marginal

N[4] = not determined

S[5] = satisfactory

U[6] = unsatisfactory

2.3.3 In order to determine the bias (percent error) calculate:

$$B = \frac{x_{exp} - x_{acc}}{x_{acc}} \times 100 \text{ percent} \qquad (36)$$

where

B = bias

x_{exp} = experimental value,

x_{acc} = accepted value.

References

Barr, A. J., Goodnight, J. H., Sall, J. P., and Helwig, J. T., 1976, A user's guide to SAS: Raleigh, SAS Institute, 329 p.

Skougstad, M. W., Fishman, M. J., Friedman, L. C., Erdmann, D. E., and Duncan, S. S., eds., 1979, Methods for determination of inorganic substances in water and fluvial sediments: U.S. Geological Survey Techniques of Water-Resources Investigations, Book 5, Chapter A1, 626 p.

Table 16.—Results from duplicate analyses in which results are compared to ranges based on published precision data

Constituent	Published precision data (from Skougstad and others, 1979)			Duplicate Set No.1 Laboratory 1				Duplicate Set No. 2 Laboratory 2			
	For mean of (mg/L)	Relative deviation is (percent)	Based on data from (labs)	Sample A (mg/L)	Sample B (mg/L)	+1 std. dev. range (mg/L)	+2 std. dev. range (mg/L)	Sample C (mg/L)	Sample D (mg/L)	+1 std. dev. range (mg/L)	+2 std. dev. range (mg/L)
Calcium, dissolved	12.6	7	17	19	19	18-20	16-22	84	82	76-90	70-96
	110	8	23								
Magnesium, dissolved	22.0	5	20	10	9.5	9.2-10	8.8-11	39	39	32-46	26-52
	35.6	17	17								
Sodium, dissolved	3.44	9	26	1.4	1.7	1.4-1.7	1.3-1.8	4.7	4.6	4.0-4.7	3.6-5.1
Potassium, dissolved	0.8	14	15	.7	.7	.6-.8	.5-.9	2.4	2.4	2.1-2.7	1.9-2.9
	5.2	11	32								
Alkalinity as $CaCO_3$	96	8	19	75	77	70-82	64-88	180	180	164-196	148-212
	154	9	24								
Chloride, dissolved	1.7	16	7	.9	1.3	.9-1.3	.7-1.5	2.8	2.7	2.3-3.2	1.9-3.6
Fluoride, dissolved	0.78	12	3 (112 replicates)	.1	.0	.0-.1	.1	.9	.9	.8-1.0	.7-1.1
Sulfate, dissolved	13	13	7	6.3	6.9	5.7-7.5	4.9-8.3	190	190		
	68.7	4	3								
Silica, dissolved	17.4	7	5	13	14	13-14	12-15	22	22	20-24	19-25

Table 17.—Duplicate analyses of polychorinated biphenyls, total in bottom material

[1977 - 1979]

Mean (µg/kg)	Difference (µg/kg)	Mean (µg/kg)	Difference (µg/kg)
0.30	0.6	14.8	2.0
0.50	1.0	14.9	1.8
0.50	1.0	15.5	15.0
1.00	0.0	15.5	3.0
1.00	0.0	16.0	2.0
1.00	0.0	16.0	8.0
1.00	0.0	18.8	0.3
1.00	0.0	18.9	11.2
1.00	2.0	19.0	4.7
2.00	0.0	25.0	6.0
3.50	1.0	26.0	0.0
4.00	2.0	27.0	20.3
4.00	0.0	39.0	26.0
4.00	0.0	51.5	3.0
4.65	1.1	61.5	13.0
5.50	1.0	73.0	48.0
5.65	2.1	79.5	1.0
6.40	0.4	93.0	34.0
6.50	1.0	101.0	18.0
7.00	2.0	140.0	0.0
7.00	4.0	140.0	0.0
7.50	11.0	176.5	83.0
8.0	2.0	450.0	460.0
8.0	2.0	2250.	300.
8.0	2.0	4100.	200.
8.5	2.9	22500.	13000.
12.8	0.2	36000.	4000.
14.4	1.6	77500.	15000.

Table 18.—Radium-226 analyses of water by radon emanation method

Mean (pCi/L)	Relative deviation (percent)	Number of determinations
.036	58	4[c]
.008	36	5[c]
.124	27	5[d]
.221	13	5[d]
.522[a]	7	9[c]
.822	9	6[c]
1.415	9	7[c]
10.14[b]	5	5[e]
10.92	55	4[c]
12.85	5	6[f]
290	4	6[f]

[a] 0.50 pCi/L standard

[b] 10.0 pCi/L standard

[c] Different cell and different instrument used for each reading.

[d] Two of the five readings were made using the same cell. Instrument different in each case.

[e] All readings made using same cell; instruments different.

[f] Two of the five readings were made using the same cell.

Table 19.—Unknown replicates: gross alpha and beta radioactivity and uranium

Determination	Data submitted to laboratory										Mean	Standard deviation	Relative deviation (percent)
	6/11	6/17	6/22	6/30	7/7	7/14	7/19	7/26	8/3	8/9			
Gross alpha radioactivity dissolved (µg/L as U natural)	2.7	3.6	3.6	3.3	3.4	4.6	3.5	3.5	2.3	2.5	3.32	± 0.67	20
Gross beta radioactivity, dissolved (pCi/L as Cs-137)	3.2	2.8	3.5	3.2	3.3	2.7	2.8	3.1	5.9[a]	2.9	3.06	± .27	9
Uranium dissolved	2.4	1.7	1.9	2.1	2.2	2.4	2.3	3.0	2.1	2.3	2.24	± .35	16

[a] Outlier, not used in computation of standard deviation.

Methods for Data Evaluation: Graphical Presentations

1. Application or scope

1.1 This practice gives examples of types of graphs which may be used to evaluate quality assurance data. Such graphical presentations of quality assurance data may be effective aids to judging the quality of that data. Graphs may be used to estimate analytical precision, to compare results obtained by two analytical procedures, and to compare analyses from two or more laboratories.

1.2 Laboratory quality control charts, although meant to be plotted immediately after an analysis and used to indicate necessary corrections also can be used to look at the general precision and bias of a laboratory's data. The practice "Quality control charts" in the section "Laboratory Quality Control" should be referred to.

1.3 Other practices in this section which describe techniques to summarize and evaluate data should also be referred to.

2. Practice

2.1 Chart of analytical results from two samples.

2.1.1 In interlaboratory comparisons, analyses of two samples containing similar concentrations of the constituent being examined can be graphically compared and used to estimate laboratory bias (Youden, 1960, 1975, 1978) (NOTE 1). Concentration values for sample 1 are indicated along the x-axis and concentration values for sample 2 are indicated along the y-axis and the pair of values obtained from each laboratory is plotted on a graph (fig. 22). A vertical line is drawn at the mean concentration of sample 1 and a horizontal line is drawn at the mean concentration of sample 2 (NOTE 2).

NOTE 1. Similar concentrations are specified since both precision and bias may vary with concentration.

NOTE 2. It may be preferable to ignore points which are obviously separated from all other points when computing the mean concentrations (Youden, 1978).

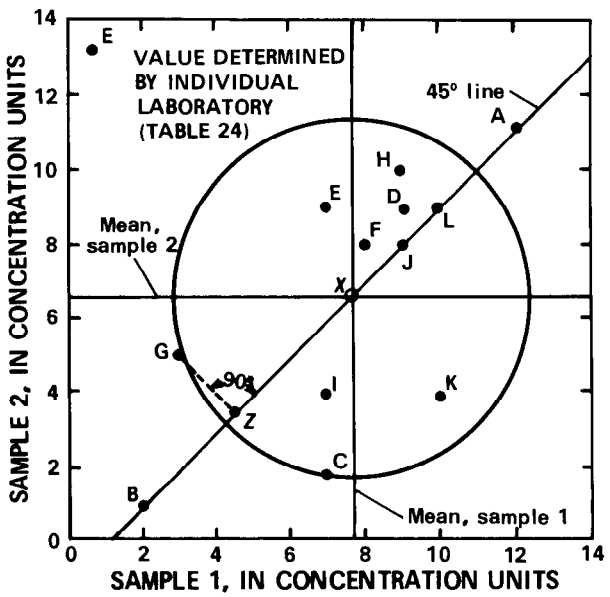

Figure 22.—Estimation of bias using two samples.

2.1.2 If systematic errors are not present, random errors will result in the points being equally distributed among the four quadrants (formed by the mean lines). On the other hand, in the hypothetical situation where only systematic errors are present, all values will be along a 45-degree line drawn though the intersection of the mean values. Generally, the data from all the participating laboratories will include both systematic and random errors and the majority of the data will be in the upper right or lower left-hand quadrants.

2.1.3 In order to estimate the standard deviation of a single result, first calculate the difference in the results submitted by each laboratory for samples 1 and 2. Then calculate the average difference and subtract it from each individual difference. The average of the absolute value of each individual difference minus the average difference, multiplied by $\sqrt{\pi/2}$ or .886 gives an estimate of the standard deviation (Youden, 1978).

2.1.4 If an estimate of the standard deviation is made, a circle whose radius is three times the estimated standard deviation should contain most of the points on the graph. Values outside of the circle indicate laboratory bias. A laboratory with a large, consistent bias will be represented by a point at one end of the 45-degree line (in the upper right quadrant for a positive bias or in the lower left quadrant for a negative bias).

2.1.5 If a numerical estimate of laboratory bias is desired, a perpendicular line can be drawn between each point and the 45-degree line. The difference between this intersection and the intersection of the two mean values divided by $\sqrt{2}$ will provide a numerical estimate of bias relative to the consensus values (Youden, 1960).

2.1.6 Illustrating this technique, data in table 20 are plotted in figure 22; points A to L represent the pairs of analytical results from the 12 laboratories. Point X represents the concentration values (of the consensus) for the two samples. Point Z is formed by the intersection of the 45-degree line (drawn through X) with a perpendicular line from point G. In order to estimate the standard deviation, the difference in results from each laboratory is calculated (12–11; 2–1; and so forth), and the average difference is determined to be 1.08. 1.08 is then subtracted from each difference, and the average of the absolute values of the results is calculated to be 1.79. Multiplying 1.79 by $\sqrt{\pi/2}$ gives 1.59, an estimate of the standard deviation, and 4.77 (3×1.59) gives the radius of the circle which should include most points; points A, B, and G all are outside the circle. The distance between point X and Z divided by $\sqrt{2}$ gives -3.2, an estimate of the overall bias of laboratory G with respect to the consensus values.

Table 20.—Example: Analytical results from 12 laboratories, tabulated prior to graphical evaluation

Laboratory	Sample 1 (concentration units)	Sample 2 (concentration units)
A	12	11
B	2	1
C	7	2
D	9	9
E	7	9
F	8	8
G	3	5
H	9	10
I	7	4
J	9	8
K	10	4
L	10	9

2.1.7 This graphical estimation of bias may be used to examine and evaluate data obtained by different analytical methods to determine which method is preferable. It may be used in the evaluation of data from laboratories; certainly if another set of samples was analyzed and the points representing laboratory A or B again were far away from the others and on the 45-degree line, there would be evidence of consistent, systematic laboratory error.

2.2 Quality-control type chart

2.2.1 If a variety of reference materials are analyzed over a period of time, a pictorial representation of bias and precision can be presented by using a quality control type of chart.

2.2.2 Figures 23 and 24 show results from analyses made by the laboratories on reference materials submitted as unknowns to the laboratories via field personnel. Although all values for the constituent plotted in figure 23 are less than two standard deviations from the theoretical (most-probable) value, a positive bias of results is clearly evident in the graph. Values for the constituent plotted in figure 24, on the other hand, show both a positive bias and a lack of precision. Charts showing the same type of "errors" for more than one laboratory indicate that there may be a problem with the analytical methodology itself.

2.2 Bar charts

2.3.1 A bar chart provides a simple means to graphically illustrate results. It can be used, for example, to compare results from laboratories participating in a "round-robin," or to show an increase or decrease in the percent of acceptable results produced by a laboratory (or Geological Survey district).

2.3.2 Figure 25 shows results from analysis of a standard reference water sample (see practice "Development of statistical data for standard reference water samples"); each point represents the values submitted by a laboratory, and points A, B, and C are in obvious disag-

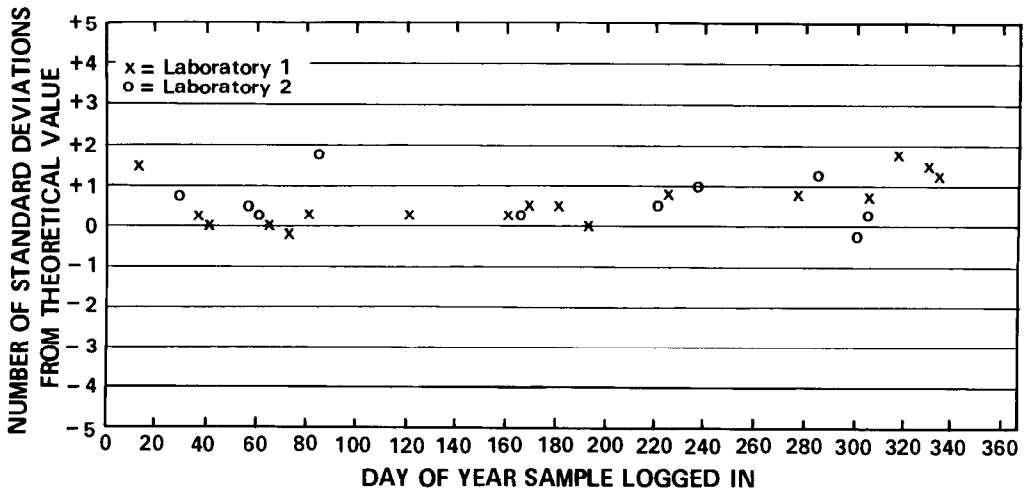

Figure 23.—Example of chart showing positive bias.

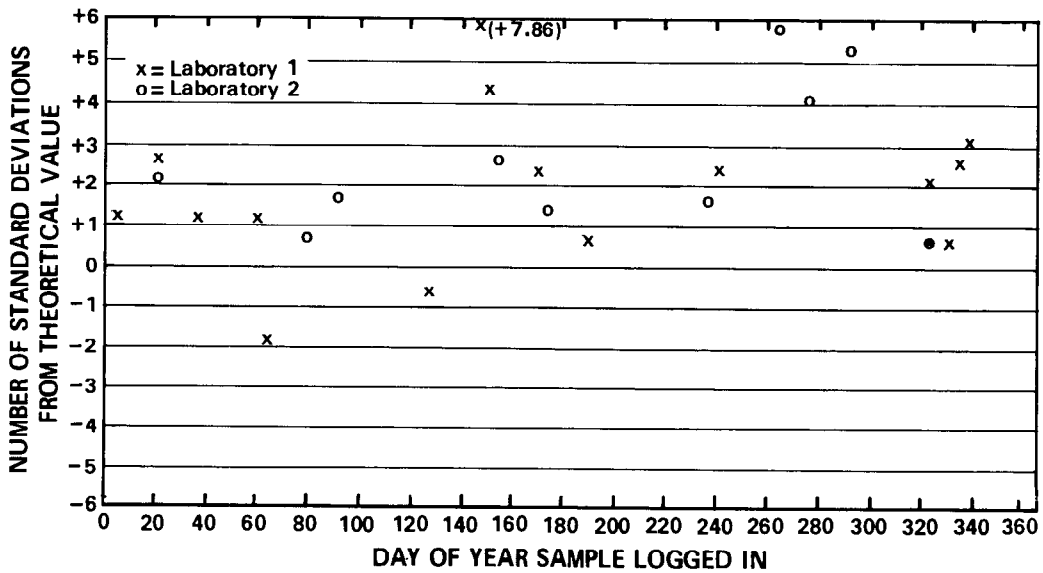

Figure 24.—Example of chart showing positive bias and lack of precision.

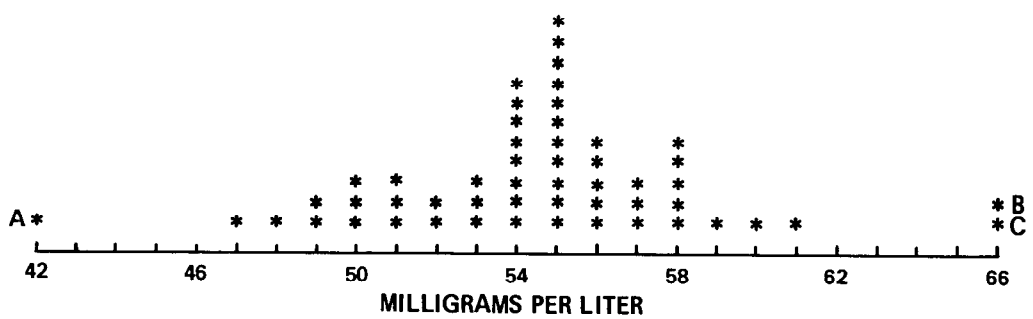

Figure 25.—Results from the analysis of magnesium in Standard Reference Water Sample 68. Each * equals a value from the laboratory; values marked A, B, and C are in obvious disagreement with the consensus.

reement with the consensus. Figure 26 demonstrates the use of a bar chart to show the percentage of correct results achieved by several different laboratories (or offices) after analyses of a round of reference materials and to show the percentage increase or decrease in correct results since the last round of analyses; this type of figure could be effectively used, for instance, to depict district results for the specific conductance field-monitoring program (see practice "Reference material use in monitoring field pH and specific conductance measurements" in section "Quality Assurance Monitoring").

2.4 Linear regression graph

2.4.1 If there is a linear relationship between two variables and if points representing the two variables are plotted on a graph, the relationship can be shown by drawing the line which best fits the points. This line can be written, $y = a + bx$, where y is the value which is observed for a given x value, a is the intercept of the line with the y-axis, and b is the slope of the line; it is often called a "least-squares" line since the sum of squares of vertical deviations of the points from it is smaller than the sum of squares of deviations from any other line. The line should not be extended beyond the limits supported by the data.

2.4.2 When a least squares equation is presented, it will be most useful if the correlation coefficient for the equation is also given so that anyone looking at the data will know how "valid" the stated relationship is. A correlation coefficient near 1 is an indication that there is a good fit of the points to the line, while a correlation coefficient near zero is an indication either of a poor fit of the points or of a relationship in which the y is constant for all x values and the line is horizontal.

2.4.3 Least-squares lines can be used, for instance, to show how the standard deviation of a method varies with the concentration of the constituent being tested, to show how differences between "duplicate" analyses vary with concentration, to compare results from two laboratories, to compare results obtained by two analytical procedures, or to compare results from field analyses with results from laboratory analyses. Figure 27, for example, shows a possible relationship between observed concentration differences and means for determination of polychlorinated biphenyls made on "duplicate" bottom sediment samples; in this case, more data needs to be collected.

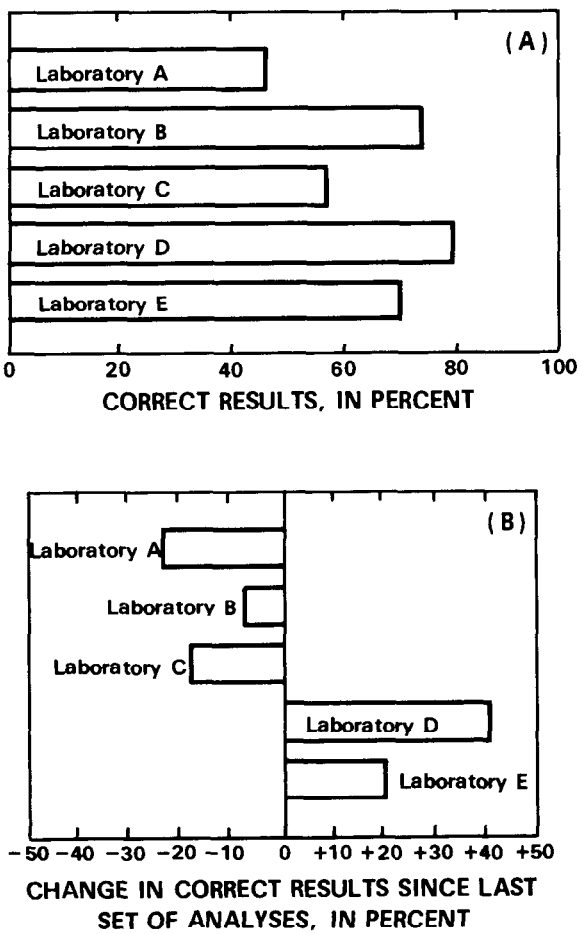

Figure 26.—Use of bar graph to depict (A) percentage of correct results achieved by five laboratories in an interlaboratory study and to show (B) the percent increase or decrease in correct results since last interlaboratory study.

References

Dixon, W. J., and Massey, F. J., Jr., 1969, Introduction to statistical analysis, (3d ed.): New York, McGraw-Hill, 638 p.

Draper, Norman, and Smith, Harry, 1966, Applied regression analysis: New York, John Wiley, 407 p.

Schmid, C. F., and Schmid, S. E., 1969, Handbook of graphic presentation, (2d ed.): New York, John Wiley, 308 p.

Youden, W. J., 1960, The sample, the procedure, and the laboratory: Analytical Chemistry, v. 32, no. 13, p. 23A–37A.

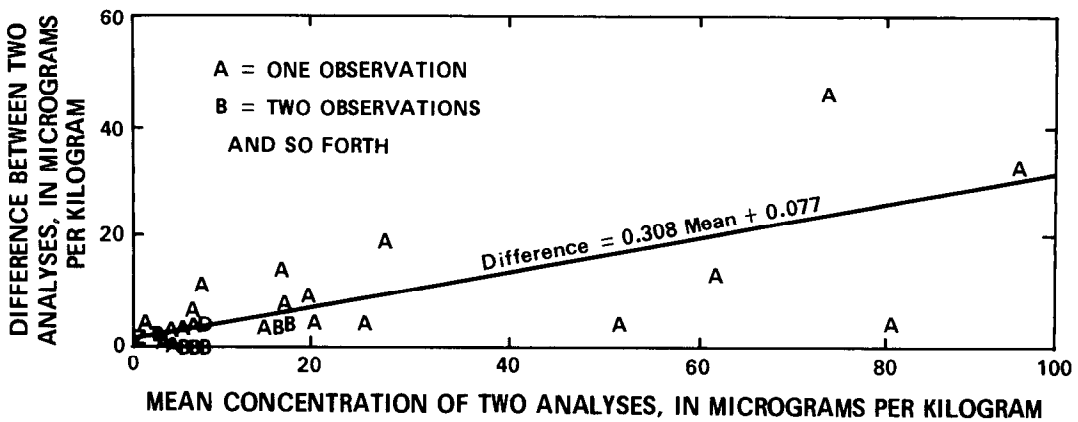

Figure 27.—Relationship between the concentration difference and mean for duplicate determinations of polychlorinated biphenyls in bottom material.

Youden, W. J., 1975, Statistical techniques for collaborative tests *in* Statistical Manual of the Association of Official Analytical Chemists: Washington D.C., Association of Official Analytical Chemists, p. 10–11.

Youden, W. J., 1978, Graphical diagnosis of interlaboratory test results *in* Chemical Division Technical Supplement Interlaboratory Testing Techniques: Milwaukee, American Society for Quality Control, p. 12–16.

Methods Used for Data Evaluation: *t*-Test

1. Application or scope

1.1 This practice gives examples of tests which are based on use of the statistical parameter "*t*" (NOTE 1). Other examples of the use of "*t*" are available in most books on statistics.

NOTE 1. Often called "Student's *t*," the distribution of this parameter was discovered by W. S. Gosset (Fraser, 1958).

1.2 The *t*-test may be used to determine if two means are statistically different.

1.3 If data are paired, a paired *t*-test can be made on the differences. The paired *t*-test can be used, for example, to compare data from samples which have been split in the field and mailed to two laboratories. It cannot be used if the data are not really paired (for example, to compare daily temperature data for two different years).

2. Practice

2.1 *t*-test example

2.1.1 The interlaboratory mean for cadmium for Standard Reference Water Sample (SRWS) number 56 was determined to be 9.9 μg/L. Analyzing the reference sample six times over a period of several months, the Denver Central laboratory obtained a mean and standard deviation of 8.2±3.0 μg/L. The *t*-test may be used to decide if the mean value obtained by Denver is different from the SRWS mean.

2.1.2 The hypothesis to be tested (H_o) is: $\bar{X}_{DCL}=\bar{X}_{SRWS}$. The alternative hypothesis (H_a) is: $\bar{X}_{DCL}\neq\bar{X}_{SRWS}$. The *t* is calculated:

$$t=\frac{\bar{X}_{DCL}-\bar{X}_{SRWS}}{s/\sqrt{n}} \qquad (37)$$

where

t = the t statistic,

$\bar{X}_{SRWS}$ = the SRWS mean

$\bar{X}_{DCL}$ = the mean obtained by the Denver laboratory

s = the standard deviation found by the Denver Laboratory, and

n = the number of times the Denver Laboratory analyzed the sample.

In this case:

$$t=\frac{8.2-9.9}{3.0/\sqrt{6}}=-1.388$$

2.1.3 In order to determine whether the means are different, the calculated value for *t* is compared with the *t* value found in table A11 in the appendix. At the 95 percent level with 5 degrees of freedom, $t=2.571$ or $t=-2.571$ (NOTE 2). For the calculated *t* to be rejected requires that it be greater than 2.571 or less than -2.571. In this case, *t* is not rejected and there is a less than 5 percent chance that the means are different.

NOTE 2. The "degrees of freedom" is $n-1$ for the examples discussed.

2.2 Paired *t*-test

2.2.1 Data in table 21 represent results from samples which were split and analyzed for constituent A in two laboratories, B, and C.

2.2.2 In order to compare the two laboratories, the differences between the values are computed and a mean and standard deviation of the differences are determined (note that the original values themselves are not considered).

2.2.3 The hypothesis to be tested, H_o, is: $\bar{d}=0$. The alternative hypothesis of H_a is: $\bar{d}\neq 0$. (In other words the hypothesis is that there is no difference in the data). The *t* is calculated:

$$t=\frac{\bar{d}-0}{s/\sqrt{n}}=\frac{\bar{d}}{s/\sqrt{n}} \qquad (38)$$

Table 21.—Paired data tabulation

Laboratory B (mg/L of A)	Laboratory C (mg/L of A)	Difference (mg/L of A)
19	15	+ 4
7	5	+ 2
10	8	+ 2
4	2	+ 2
23	20	+ 3
20	18	+ 2
18	19	- 1
65	63	+ 2
27	25	+ 2
25	26	- 1
3	3	0
	Average difference, $\bar{d}$ =	1.545
	Standard deviation, s =	1.572

where

t = the t statistic,

d = the mean of the differences,

s = the standard deviation of the differences, and

n = the number of pairs.

In this case

$$t = \frac{1.545}{1.572/\sqrt{11}} = 3.260$$

3. From the table at the 95 percent level with 10 degrees of freedom, t=2.228. Since the calculated t is greater than that found in the table, the hypothesis is rejected. There is difference between the data from the two laboratories with a less than 5 percent chance that the difference is due to random causes.

Selected References

Dixon, W. J., and Massey, F. J., Jr., 1969, Introduction to statistical analysis: (3d ed.): New York, McGraw-Hill, 638 p.

Miller, Irwin, and Freund, J. E., 1977, Probability and statistics for engineers (2d ed.): Englewood Cliffs, New Jersey, Prentice-Hall, 529 p.

Methods Used for Data Evaluation: A Test of Laboratory Variance

1. Application or scope

1.1 This practice describes a technique for analysis of variance.

1.2 The technique can be used to compare data submitted by several laboratories. This practice gives an example of the technique's use and presents several tests which may be made on the data. Other examples and tests are available in most books on statistics.

2. Practice

2.1 Example of analysis of variance

2.1.1 Consider a Geological Survey district office which has contracts with three laboratories and must monitor their work to ensure that the data are comparable to that of a Geological Survey Central Laboratory. A reference material is specially prepared in a matrix which is typical of water which the contract laboratories are analyzing. A portion of the reference water is sent to each of the three contract laboratories and also to a Central Laboratory. Over a period of several months, each laboratory receives and analyzes five such portions, and the data indicated in table 22 are reported.

2.1.2 In order to compare each laboratory's data, the following values are calculated:

$$SS_x = \Sigma X^2 - \frac{(\Sigma X)^2}{n} \tag{39}$$

Table 22.—Example: Data tabulation for a given constituent, as reported by four laboratories

Lab 1 (mg/L)	Lab 2 (mg/L)	Lab 3 (mg/L)	Central Laboratory (mg/L)
8	7	8	8
9	6	10	9
7	5	11	10
8	8	9	8
8	7	9	9

$$SS_L = \frac{\Sigma L^2}{n/m} - \frac{(\Sigma X)^2}{n} \tag{40}$$

$$SS_w = SS_x - SS_L \tag{41}$$

where

X = each value,

L = the total of the values reported by each laboratory,

n = the number of values,

m = the number of laboratories,

SS_x = the total sum of squares,

SS_L = the between laboratory sum of squares, and

SS_w = the within laboratory sum of squares.

In this case

$$SS_x = (8^2+9^2+7^2 \ldots +9^2) - \frac{(8+9+7+\ldots 9)^2}{20}$$

$$= 1{,}382 - \frac{(164)^2}{20} = 37.2$$

$$SS_L = \frac{40^2+33^2+47^2+44^2}{20/4} - \frac{(164)^2}{20}$$

$$= 1{,}366.8 - \frac{(164)^2}{20} = 22$$

$$SS_w = 37.2 - 22 = 15.2$$

2.1.3 These data are arranged in table 23, in a format which is typical of an analysis of variance table. The total degrees of freedom are one less than the total number of values, the between-

Table 23.—Typical data tabulation for analysis of variance

Type of variance	Degrees of freedom	Sum of squares	Mean squares
Total	19	37.2	
Between labs	3	22	7.333
Within labs	16	15.2	.950

lab degrees of freedom are one less than the number of laboratories and the within-lab degrees of freedom are obtained by subtraction. The mean square values are calculated by dividing the sum of squares value by the appropriate number of degrees of freedom.

2.2 *F*-test

2.2.1 In order to test the hypothesis that the laboratory means are equal (or that there is no variance between the laboratory means), the *F*-test is used (NOTE 1).

NOTE 1. The statistical parameter *F* is based on the distribution of the ratios of two variances (Dixon and Massey, 1969).

2.2.2 The value for *F* is calculated:

$$F=\frac{BMS}{WMS} \tag{42}$$

where

F = the F statistic,

BMS = the between laboratory mean squares, and

WMS = the within laboratory mean square.

The *F* calculated for the example is

$$F=\frac{7.333}{.950}=7.72$$

2.2.3 The *F* so computed is compared to the tabular values for *F* in table A6. Locating the correct value in the table requires using a set of degrees of freedom values which correspond to the number of "between-lab" and "within-lab" degrees of freedom. A computed value greater than the tabular value means the hypothesis can be rejected.

2.2.4 At the 95th percentile with 3 and 16 degrees of freedom, the tabular *F* value is 3.24. Thus, the *F* calculated from the data in the example is greater than the tabular *F* values. The hypothesis is rejected: There is less than a 5 percent chance that the laboratory means are equal.

2.3 *q*-test

2.3.1 This test can be used to compare all the means (Dunn and Clark, 1974). It requires that the *F*-test must have shown a significant difference and also requires that the number of values used to compute each mean be equal (NOTE 2).

NOTE 2. This test was developed by Tukey and is based on the studentized range, *q*.

2.3.2 The number which would indicate significant difference between two means is calculated:

$$SD=q\sqrt{\frac{WMS}{n}} \tag{43}$$

where

SD = the significant difference,

q = the q statistic, taken from table A12 using the number of laboratories and using the degrees of freedom associated with the "within" mean square.

WMS = the "within" mean square, and

n = the number of values used to compute a laboratory

2.3.3 From table A12, the *q*-statistic at the 95 percent level is 4.05 for four laboratories and 16 degrees of freedom. The significant difference for the example is:

$$SD=4.05\sqrt{\frac{.950}{5}}=1.77$$

2.3.4 This calculated significant difference may be used to compare means of all laboratories. For ease in comparison, the laboratories are first ranked by their mean values (table 24).

2.3.5 A difference between two laboratory means which is greater than the calculated value indicates a significant difference. Thus, for the example, the mean of laboratory 2 is significantly different from the mean of laboratory 3 or the Central Laboratory (9.4–1.8 = 7.6

Table 24.—Example: Ranking of mean data

Rank	Laboratory	Mean
1	3	9.4
2	Central	8.8
3	1	8.0
4	2	6.6

and 8.8–1.8 = 7.0), but is not significantly different from the mean of laboratory 1 (8.0–6.6 = 1.4). There is no statistically significant difference between the means of laboratories 1, 3, and the Central Laboratory.

2.4 Significant difference test using t

2.4.1 This test can be applied if it has been decided, before looking at the data, that one mean will be used as the "standard" and the other means will be compared with it (Dunn and Clark, 1974). For example, it is decided, before any samples are mailed to the laboratories, that each contract laboratory's data will be compared to data from a Geological Survey Central Laboratory.

2.4.2 The absolute difference between the central laboratory mean and each of the other means is calculated:

$$\left| \bar{X}_{cl} - \bar{X}_i \right|$$

where

$\bar{X}_{cl}$ = the Central Laboratory mean, and

$\bar{X}_i$ = laboratory means other than the Central Laboratory.

2.4.3 Using the data in table 24, the values are 0.8, 2.2, and 0.6 for the differences between the Central Laboratory mean and the means of laboratory 1, laboratory 2, and laboratory 3, respectively.

2.4.4 Each difference is compared to the significant difference value, calculated as follows:

$$SD = t \sqrt{\frac{WMS}{n_{cl}} + \frac{WMS}{n_i}} \qquad (44)$$

where

SD = the least significant difference,

t = the t statistic, taken from table A11 using the degrees of freedom associated with the "within" mean square,

WMS = the "within" mean square,

n_{cl} = the number of values used in calculating the Central Laboratory mean, and

n = the number of values used in calculating the mean being compared (NOTE 3).

NOTE 3, n_i does not have to equal n_{cl}, although in this example they are equal.

2.4.5 For the example:

$$SD = 2.12 \sqrt{\frac{.95}{5} + \frac{.95}{5}} = 1.31$$

Any mean difference which is larger than 1.31 is significant: The mean reported by laboratory 2 is statistically significantly different from the Central Laboratory mean.

References

Dixon, W. J., and Massey, F. J., 1969, Introduction to statistical analyses (3d ed.): New York, McGraw-Hill, 638 p.

Dunn, O. J., and Clark, V. A., 1974, Applied statistics: analysis of variance and regression: New York, John Wiley, 387 p.

Steiner, E. H., 1975, Planning and analyses of results of collaborate tests, *in* Statistical Manual of the Association of Official Analytical Chemists: Washington, D.C., Association of Official Analytical Chemists, p. 65–88.