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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

By Linda C. Friedman and David E. Erdmann

Book 5

Laboratory Analysis

Inorganic Quality Control

Atomic Absorption Analysis

1. Application or scope

1.1 This practice applies to the determination of constituents by atomic absorption spectrometry.

1.2 The practice "Atomic absorption spectrometers," in the section "Instrumental Techniques" and the applicable analytical procedures in Book 5, Chapter A1 of Techniques of Water-Resources Investigations of the U.S. Geological Survey (Skougstad and others, 1979) should be referred to.

2. Practice

2.1 Preparation of standards, blanks, and reagents

2.1.1 Prepare a stock solution and intermediate standards as specified in the analytical procedure. Intermediate standards should be prepared bimonthly (and dated) or at time intervals specified in the analytical procedure.

2.1.2 Prepare reagents, if any, as specified in the analytical procedure. If reagents deteriorate with age, prepare fresh daily or at time intervals specified in the method.

2.1.3 Prepare working standards and reagent blank, if any. Add all reagents which will be added to the samples. Extract standards and blanks if samples will be extracted. A minimum of five standards, equally spaced over the analytical range, should be prepared. In general, prepare working-level standards fresh each day.

2.2. Calibration and measurement

2.2.1 Adjust lamp current and aline lamp.

2.2.2 Adjust wavelength as specified in the analytical procedure and set the gain and slit width.

2.2.3 Adjust compressed gas regulators to achieve correct type of flame.

2.2.4 Aline burner.

2.2.5 Adjust nebulizer if necessary.

2.2.6 If the system has been automated with a sampler and pump, check pump tubing to make sure it is in good condition.

2.2.7 Aspirate a blank and adjust electronics, including recorder or digital read-out to read zero.

2.2.8 Aspirate a standard known to give a 0.2 to 0.6 absorbance and known to be within the linear portion of the analytical range. Keep a record of the sensitivity of each element for each instrument. A significant change ($\geq$10 percent) from previous results indicates that a problem exists which must be corrected.

2.2.9 Determine the concentration of the five standards, aspirating the solvent between each sample. If a direct-concentration read-out is used, the instrument is set with one standard, usually the highest, and the concentration in the other standards determined; concentrations must agree with their theoretical concentration or analyses discontinued until it is determined why they do not and until corrections are made.

2.2.10 Aspirate samples with solvent aspirated between each sample (NOTE 1).

NOTE 1. Demineralized water (or solvent such as methyl isobutyl ketone) is not to be considered the reagent blank unless no reagents have been added to standards and samples.

2.2.11 If concentrations of samples are outside of those specified as the range in the analytical procedure, dilute or run by an alternative procedure.

2.2.12 Use a standard addition technique when interferences cannot be avoided or are unknown. Use standard additions for all flameless and electrothermal-vaporization methods.

2.3 Calibration checks

2.3.1 Insert, in random order, a standard or reagent blank at every seventh or eighth sample or as specified in the method.

2.3.2 If there is a difference of over 2 percent from the initial readings or if there is noticeable baseline drift, recalibrate the instrument and reanalyze all samples that were analyzed after the last acceptable calibration check.

2.3.3 Use a standard reference material as the first sample to be analyzed and as every twentieth sample thereafter. The value for the reference material should fall within 1.5 standard deviation of the theoretical value. If it does not, the reason for the discrepancy must be determined and corrected and the concentration of all samples from the last "good" reference value should be reanalyzed.

2.3.4 Record reference sample values in a notebook, preferably kept near the instrument, along with the date of analysis. Also record the laboratory-assigned log-in numbers of all samples included in the set analyzed.

2.3.5 Plot values on a quality control chart as outlined in the practice "Quality control charts." If a bias appears to be developing in the results (for example, all reference sample results are greater than the theoretical), correct for it before continuing.

Reference

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.

Automated Colorimetric or Potentiometric Analysis

1. Application or scope

1.1 This practice applies to analyses, using the Technicon AutoAnalyzer, of samples in which the constituent of interest forms a unique colored complex with the reagent used.

1.2 This practice is also applicable to automated potentiometric analyses (such as fluoride). If specific conductance or pH are to be measured, refer to the practice "Inorganic quality control: automated measurements of specific conductance and pH."

1.3 Refer also to the practice "Automated analyzers" in the section "Instrumental Techniques," and the applicable analytical procedures in Book 5, Chapter A1 of Techniques of Water-Resources Investigations of the U.S. Geological Survey (Skougstad and others, 1979).

2. Practice

2.1 Preparation of standards, blanks, and reagents

2.1.1 Prepare a stock solution and intermediate standards as specified in the analytical method. Intermediate standards should be prepared at least bimonthly (and dated), or at time intervals specified in the analytical method.

2.1.2 Prepare reagents, if any, as specified in the analytical method. Prepare fresh daily, or at time intervals specified in the method, all reagents which deteriorate with age.

2.1.3 Prepare a minimum of five working-level standards, spaced evenly over the analytical range. If there is evidence of instability, working-level standards should be prepared fresh daily, or at time intervals specified in the method.

2.2 Calibration and measurement

2.2.1 Set up the manifold as specified in the appropriate analytical procedure. Select proper flow-cell length, sampling rate, sample-to-wash ratio, and heating bath temperature (if a heating bath is part of the manifold) as specified in the analytical procedure.

2.2.2 Check manifold tubing and glassware to make sure that they are clean and free of leaks, and that pump tubes are taut. Replace limp tubing.

2.2.3 Set wavelength, with the appropriate filter, as specified in the analytical procedure and allow colorimeter or potentiometer to warm up and stabilize (NOTE 1).

NOTE 1. Stabilization usually will take 20 to 60 minutes.

2.2.4 Set indicator control to zero and see if recorder reads zero; then set indicator control to full and see if recorder reads 100. For ion-selective electrodes (for example, for fluoride), set control to "Cal 1" and see if recorder reads zero; then set control to "Cal 2" and see if recorder reads 50. Adjust recorder if it does not give correct response (see practice "Automated analyzers").

2.2.5 With all reagents being pumped, with wash solution in the sample line, and after the chart recorder shows a stable reading indicating that the system has reached equilibrium, set the baseline of the recorder to read zero

or to a positive value if specified in the analytical method; the printer should give a reading similar to that of the recorder.

2.2.6 If the AutoAnalyzer is linked to and controlled by a computer system, activate the interface connection which links the colorimeter to the computer system. Follow any special instructions related to the computer (such as initially setting the colorimeter at full scale and then at normal operating conditions) (NOTE 2).

NOTE 2. Once control is turned over to the computer system, only minor adjustments may be made to Technicon equipment without restarting the entire analysis. No adjustment may be made without supervisor's knowledge.

2.2.7 Rinse the sample cups (NOTE 3).

NOTE 3. Keep sample cups sealed until ready to use and rinse immediately before use. If chloride is to be determined, avoid contamination of the cups with perspiration from hands; thin gloves are recommended.

2.2.8 Place a complete set of standards (minimum five) in the sampler.

2.2.9 For routine use of the Technicon AutoAnalyzer, place standards in descending order, beginning with the highest standard and ending with a blank (NOTE 4).

NOTE 4. The following scheme has been found to be helpful in setting up the first sample tray: highest standard, blank, highest standard, blank, all standards in decreasing order of concentration, two blanks. This scheme enables the analyst to adjust instrumental controls and to check that adjustment, and to rezero the printer and (or) recorder using the last blank.

2.2.9a If the AutoAnalyzer is linked to and controlled by a computer system, set up the tray as follows: three high standards, two blanks, all of the standards in ascending order, and two blanks (NOTE 5).

NOTE 5. Be sure that the computerized tray pattern correctly identifies the standards, blanks, and samples.

2.2.10 As the first standard is read, adjust the "STD CAL" control on the colorimeter so that the flat portion of the peak reads full scale. When the peak is at maximum, press the start print button on the printer.

2.2.11 Use subsequent high standards to check the adjustment and "fine tune" the system.

2.2.12 Keep a record of the STD CAL setting for each constituent for each instrument. A significant change ($\geq$10 percent) from previous results indicates that a problem exists which must be determined and corrected before proceeding (NOTE 6).

NOTE 6. This problem may be instrumental or it may be chemical (for example, a reagent has deteriorated or standards have been incorrectly prepared.)

2.2.13 Record and compare the results for the rest of the set of standards (that is for all of the standards except the initial one(s) used to adjust the STD CAL control) with those obtained previously. If they differ significantly (over 5 percent), a problem exists which must be determined and corrected before proceeding (NOTE 7).

NOTE 7. If a computerized system is used, the computer will make any curve corrections and will print out the calculated concentration of the standards; in this case, check to see if the concentration is within 5 percent of the theoretical value (rather than comparing previous results). The computer will also print a "CD" (correlation coefficient of the determination or r^2) value; if this value is not 0.99 or greater, a problem exists which must be determined and corrected before proceeding.

2.2.14 Analyze samples. If concentrations are outside those specified as the range in the analytical method, dilute or determine by an alternative procedure. If a computerized system is used, dilute to the amount specified by the computer and place the dilution in the tray at the location specified by the computer.

2.2.15 If interferences cannot be avoided, use a standard addition technique or select an alternative procedure.

2.2.16 If color is an interference, it may be possible to compensate for it by subtracting the concentration obtained when all reagents except the indicator reagent are used, or by using a bleaching or adsorption procedure. (See the section on "Instrumental Techniques.")

2.3 Calibration checks

2.3.1 Insert in random order a standard or reagent blank at every seventh or eighth sample or as specified in the analytical method.

2.3.2 If there is a difference of over 2 percent from the initial readings or if there is noticeable baseline drift, recalibrate the instru-

ment and reanalyze all samples analyzed after the last acceptable calibration check.

2.3.3 Use a standard reference material as the first sample to be analyzed and as every twentieth sample thereafter. The reference material should fall within 1.5 standard deviations of the theoretical value. If it does not, determine the reason for the discrepancy, make necessary corrections, and remeasure the concentration of all samples from the last "good" reference value.

2.3.4 Record determined reference sample values, along with the expected value and date of analysis. Also record the laboratory-assigned log-in numbers of all samples run in the set.

2.3.5 Plot values on a quality control chart as outlined in the practice "Quality control charts." If a bias appears to be developing in the results (for example, all reference sample results are greater than the theoretical), correct for it before continuing.

Reference

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.

Automated Measurement of Specific Conductance and pH

1. Application or scope

1.1 This practice applies to automated measurements of specific conductance and pH. The pH system uses a Technicon printer and recorder while the conductivity system employs a specially designed printer used in conjunction with a conductivity bridge. Both use a "flow-through" cell.

1.2 Refer to practices "Potentiometers," "Conductivity meters," and "Automated wet-chemical analyzers" in the section "Instrumental Techniques." Refer also to analytical methods I–1586–78 and I–1780–78 ("pH, electrometric, glass electrode" and "Specific conductance, electrometric, wheatstone bridge") in Skougstad and others (1979).

2. Practice

2.1 Preparation of standards and buffers

2.1.1 Prepare a minimum of three standards for specific conductance: 0.00702 *N* KCl (1,000 μmho/cm at 25°C), 0.02 *N* KCl (2,767 μmho/cm at 25°C), and 0.1 *N* KCl (12,900 μmho/cm at 25°C). See method I–1780–78 and also see Standard Methods (American Public Health Association and others, 1975).

2.1.2 Check the new KCl solutions against previous KCl standard solutions. If conductances of new and old solutions are different, check both solutions against a third solution (prepared by another analyst).

2.1.3 Prepare a minimum of three buffer solutions as specified in method I–1586–78. Date the solutions and prepare fresh every 3 months or when noticeable discoloration or deterioration of a buffer occurs (NOTE 1).

NOTE 1. Prepared buffer solutions or buffer concentrates are available from chemical and instrumental suppliers.

2.2 Calibration and measurement

2.2.1 Set up the manifold, check tubing, and glassware to make sure that they are clean and free of leaks and that pump tubes are taut. Replace limp tubing.

2.2.2 With wash solution being pumped through the sample line, allow the instruments to warm up and stabilize (usually 60 minutes).

2.2.3 In order to adjust the recorder and printer for pH, and the printer and bridge for conductance, to calibrate the system, and to check the accuracy of the determination, set up the first sample tray in the following manner: 1,000-μmho conductance standard, 1,000-μmho conductance standard, 12,900-μmho conductance standard, blank, 2,767-μmho conductance standard, 12,900-μmho conductance standard, blank, 2,767-μmho conductance standard, pH 4 buffer, pH 4 buffer, pH 7 buffer, blank, pH 9 buffer, blank, 3 reference materials, and samples.

2.2.4 Turn on the conductance system printer and start up the sampler. When the sampler is turned on, press the reset button on the printer. Watch the timer; when it reads 45 seconds, press the reset button on the printer again. Then press the event counter reset button to set the counter.

2.2.5 Calibrate the conductance system by adjusting the printer to read 1,000 with the temperature control knob on the conductivity bridge (after the first 1,000-μmho standard triggers the conductivity printer, wait 5 seconds and press the start-print button on the pH printer.) Adjust the printer to read 12,900 with the "span" control knob on the conductivity printer. Finally, adjust the printer to read 2,767 with the "offset" control knob on the conductivity printer.

2.2.6 Calibrate the pH system with the various standards. For the pH 4 standard, use the baseline control on the potentiometer; for the pH 7 standard, use the STD CAL control on the potentiometer.

2.2.7 If, at any time, the system cannot be calibrated following the procedures outlined above, do not proceed further. The problem may be instrumental and (or) chemical; determine its cause, correct it, and start again.

2.3 Calibration checks

2.3.1 Analyze a blank, 1,000-μmho conductance standard, and two pH buffers after every 20 samples.

2.3.2 If there is a difference of over 2 percent from the initial readings or if there is a noticeable baseline drift, recalibrate the instrument and reanalyze all samples that were analyzed after the last acceptable calibration check.

2.3.3 As indicated in paragraph 2.2.3, use three reference materials as the first three samples to be analyzed. Also use at least one reference material either as every 20th sample or immediately after the required standards in paragraph 2.3.1 (that is, either before or after the standards).

2.3.4 The reference material values should fall within 1.5 standard deviations of the theoretical value. If they do not, determine the reason for the discrepancy, make necessary corrections, and remeasure the concentration of all samples since the last "good" reference value.

2.3.5 Record reference sample values, along with the expected value and date of analysis. Also record the laboratory-assigned log-in numbers of all samples run in the set.

2.3.6 Plot values on a quality control chart as outlined in the practice "Quality control charts." If a bias appears to be developing in the results (for example, all reference sample results are greater than the theoretical), correct it before continuing.

2.3.7 At the end of each day's analyses, remeasure the specific conductance and pH of every 30th (nonreference) samples.

2.3.8 Record duplicate sample values along with their lab identification number and date of analysis.

2.3.9 Plot duplicate values on a quality control chart as outlined in the practice "Quality control charts." If differences are greater than warning limits, determine and correct the problem before continuing to make analyses. If differences are greater than control limits, reanalyze the appropriate portion, or all, of the samples.

References

American Public Health Association and others, 1975, Standard methods for the examination of water and wastewater (14th ed.): Washington D.C., American Public Health Association, 1193 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.

Colorimetric Analysis

1. Application

1.1 This practice applies to the analysis of samples in which a spectrometer is used to measure a unique colored complex formed between the constituent of interest and an appropriate reagent.

1.2 The practice "Inorganic quality control: automated colorimetric or potentiometric analysis," should be used instead of this one if the colored complexes are to be measured using the Technicon AutoAnalyzer.

1.3 Refer also to the practice "Colorimetric spectrometers," in the section "Instrumental Techniques" and the applicable methods in Book 5, Chapter A1, of Techniques of Water-Resources Investigations of the U.S. Geological Survey (Skougstad and others, 1979).

2. Practice

2.1 Preparation of standards, blanks and reagents

2.1.1 Prepare a stock solution and intermediate standards as specified in the analytical method. Intermediate standards should be prepared bimonthly (and dated) or at time intervals specified in the analytical method.

2.1.2 Prepare reagents, if any, as specified in the analytical method. If reagents deteriorate with age, prepare fresh daily, or at time intervals specified in the method.

2.1.3 Prepare working standards and reagent blank, if any. Add all reagents which will be added to the sample. Prepare a minimum of four standards, evenly spaced over the analytical range. If there is any evidence of instability, prepare all working-level standards fresh daily, or at time intervals specified in the method.

2.2 Calibration and measurement

2.2.1 Check light source and cell holder alignment as necessary (see practice "Colorimetric spectrometers" in section "Instrumental Techniques").

2.2.2 Check wavelength calibration every six months (see practice "Colorimetric spectrometers," in section "Instrumental Techniques").

2.2.3 Set wavelength as specified in the method.

2.2.4 Transfer the reagent blank to the cell and set spectrometer to zero absorbance. Record slit width.

2.2.5 Transfer standards to cells and record absorbance.

2.2.6 Keep a record of slit width and absorbance of each element for each instrument. A significant change ($\geq$10 percent) from previous results indicates that a problem exists which must be corrected. This problem may be instrumental (for example, the cell holder is out of alinement) or chemical (for example, a reagent has deteriorated or standards have been incorrectly prepared).

2.2.7 Analyze samples. If concentrations are outside those specified as the analytical range in the procedure, dilute or run by an alternative procedure.

2.2.8 If interferences cannot be avoided, use a standard addition technique or select an alternative procedure.

2.2.9 If color is an interference, it may be possible to compensate for it by using a sample containing all reagents except the indicator reagent or by using a bleaching or adsorption procedure (see section, "Instrumental Techniques").

2.3 Calibration checks

2.3.1 Read a blank and, if the color complex is stable, read in random order a standard after every 10th sample. If the color complex is unstable, sufficient standards must be prepared in the order in which they will be read, so that a standard can be inserted after every 10th sample.

2.3.2 If there is a difference of over 2 percent from the initial readings or if there is noticeable baseline drift, recalibrate the instrument and reanalyze all samples analyzed since the last acceptable calibration check.

2.3.3 For chemical oxygen demand and cyanide, analyze every 10th sample, in duplicate.

2.3.4 When determining boron, bromide, iodide and vanadium, repeat the analysis of every 10th sample either by diluting and using half the original concentration or by spiking with a standard to give double the original concentration.

2.3.5 Record the values in a notebook, along with date of analyses and the laboratory-assigned log-in numbers of all samples run in the set.

2.3.6 Plot values on a quality control chart as outlined in the practice "Quality control charts." If values exceed control limits or if a bias appears to be developing in the results, correct the problem before continuing.

Selected References

McClelland, N. I., Delfino, J. J., Greenberg, A. E., McDonald, D. B., and Morris, R. C., 1978, Water and wastewater analysis, *in* Inhorn, S. L., ed., Quality assurance practices for health laboratories: Washington, D. C., American Public Health Association, p. 1145–1188.

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.

U.S. Environmental Protection Agency, 1979, Handbook of analytical quality control in water and wastewater laboratories: U.S. Environmental Protection Agency EPA–600/4–79–019, Cincinnati, 104 p.

Determination of Color or Turbidity

1. Application

1.1 This practice applies to the measurement of color and turbidity.

1.2 Refer also to methods I–1250–78, "Color, electrometric, visual comparision," and I–3860–78, "Turbidity, nephlometric," in Skougstad and others (1979).

2. Practice

2.1 Preparation of standards

2.1.1 Prepare turbidity suspensions as specified in method I–3860–78. The working-level concentration (40 NTU) must be prepared fresh weekly (NOTE 1).

NOTE 1. Sealed suspensions are also available, usually from the instrument manufacturer.

2.2 Calibration and measurement

2.2.1 Measure color in color comparator and turbidity in turbidimeter. Be careful not to entrap bubbles in the glass tubes.

2.2.2 Follow the manufacturer's operating instructions in calibrating the turbidimeter. Prepare a calibration graph for each range of the instrument (unless a precalibrated scale is supplied) as specified in method I–3860–78.

2.3 Calibration checks

2.3.1 At the end of every set of samples, rerun every tenth sample. If possible, use a fresh portion of the sample.

2.3.2 Record duplicate values in a notebook along with the date of analysis and the laboratory-assigned log-in numbers of all samples in the set.

2.3.3 Plot control charts (see practice "Quality control charts").

Selected References

McClelland, N. I., Delfino, J. J., Greenberg, A. E., McDonald, D. B., and Morris, R. L., 1978, Water and wastewater analysis, *in* Inhorn, S. L., ed., 1978, Quality assurance practices for health laboratories: Washington D.C., American Public Health Association, p. 1145–1188.

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

Determination of pH

1. Application or scope

1.1 This practice applies to field and non-automated laboratory measurements of pH.

1.2 Refer also to the practice "Potentiometers," in the section "Instrumental Techniques," to method I–1586–78, "pH, electrometric, glass electrode" in Skougstad and others (1979), and to Water-Supply Paper 1535-H (Barnes, 1964).

2. Practice

2.1 Preparation of buffers

2.1.1 Prepare a minimum of three buffer solutions as specified in method I–1586–78 (NOTE 1).

NOTE 1. Prepared buffer solutions or buffer concentrates are available from instrument and chemical manufacturers.

2.1.2 Date all buffer solutions and prepare fresh every 3 months or when noticeable discoloration or deterioration occurs.

2.2 Calibration and measurement

2.2.1 Check electrodes visually for scratches or cracks and to see if they are filled sufficiently. Check connections between electrodes and meter.

2.2.2 Insert the electrodes in a pH 7.00 buffer.

2.2.3 Measure the temperature and adjust the temperature control.

2.2.4 Adjust the meter reading to give the correct pH value. Check the millivolt scale to be sure the electrode gives a reading that is 0 ± 10 mV.

2.2.5 After rinsing the electrodes thoroughly, insert them in a second buffer. If the reading is over 0.1 pH unit from its theoretical value, adjust the "slope adjustment," if the meter is equipped with one. If the slope adjustment is changed, always go back and recheck the first reading.

2.2.6 If it is known that the pH values of all samples will fall between the two buffers,

the use of a third buffer is unnecessary. In most cases, however, the third buffer should also be used in calibration. All three buffers should read correctly if meter and electrodes are in good condition.

2.2.7 Rinse the electrodes thoroughly between samples and between buffers (NOTE 2).

NOTE 2. It is relatively easy to contaminate a sample or a buffer of high pH with a low pH buffer. A pH of 9 indicates 10^{-9} hydrogen ions while a pH of 4 indicates 10^{-4} hydrogen ions (or 100,000 times the pH 9 hydrogen ion concentration). Electrodes should be rinsed using portions of the solution to be measured; particular care should be used in rinsing before measuring a sample which has a specific conductance of less than 50 μmho.

2.2.8 Be sure to calibrate the meter under the same agitation conditions that samples are to be read.

2.2.9 Measure the temperature of each sample. The sample temperature must not differ from that of the buffer by more than 5°C.

2.2.10 Begin pH measurements (NOTE 3).

NOTE 3. In measuring the pH of ground water, the well must be pumped until readings are stable. Similarly, care must be taken to achieve stable readings in measuring the pH of samples that have a specific conductance less than 50 μmho (such as precipitation samples).

2.3. Calibration checks

2.3.1 Check the calibration of the instrument at least every 3 hours with buffer solutions (NOTE 4). Record the readings in a notebook. Include the date and time of initial calibration and of the calibration checks.

NOTE 4. In the case of most field work, meter should be recalibrated with every site change.

2.3.2 If there has been a noticeable (>.02 pH units) shift in the readings for the buffers, recalibrate the instrument and measure the pH of all samples back to where the shift occurred (Wood, 1976).

2.3.3 Use a reference material as the first sample to be analyzed and as every 30th sample thereafter. The reference material should fall within 1.5 standard deviations of the theoretical value. If it does not, the reason for the discrepancy should be determined and corrected and the pH of all samples from the last "good" reference value should be remeasured.

2.3.4 Record reference sample values, along with the expected value. Also record the laboratory-assigned log-in numbers (or sample identification numbers for measurements made in the field) of all samples analyzed.

2.3.5 At the end of each set of measurements, recheck the pH of every 20th sample. If the set consists of less than 20th analyses, recheck the pH of the first nonreference sample at the end of the set.

2.3.6 Record the duplicate values, in a notebook, along with the date of analysis and all laboratory-assigned log-in numbers of samples run in the set.

2.3.7 Plot values on quality control charts as outlined in the practice "Quality control charts." If values exceed control limits or if a bias appears to be developing in the results (for example, all reference sample results are greater than the theoretical), correct for it before continuing.

Selected References

Barnes, Ivan, 1964, Field measurement of alkalinity and pH: U.S. Geological Survey Water-Supply Paper 1535-H, 17 p.

McClelland, N. J., Delfino, J. J., Greenberg, A. E., McDonald, D. B., and Morris F. L., 1978, Water and wastewater analysis, *in* Inhorn, S. L., ed., Quality assurance practices for health laboratories: Washington D.C., American Public Health Association, p. 1145–1188.

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.

U.S. Environmental Protection Agency, 1979, Handbook for analytical quality control in water and wastewater laboratories: U.S. Environmental Protection Agency EPA–600/4–79–019, Cincinnati, p. 3–3—3–4.

Wood, W. W., 1976, Guidelines for collection and field analysis of ground water samples for selected unstable constituents: U.S. Geological Survey Techniques of Water-Resources Investigations, Book 1, Chapter D2, 24 p.

Determination of Solids Concentration

1. Application

1.1 This practice applies to the gravimetric determination of dissolved, suspended, total, and volatile solids concentration.

1.2 Refer to practices "Gravimetry," and "Analytical balances," in the sections on "Standard Quantitative Analysis Techniques," and "Instrumental Techniques," respectively, and to the applicable analytical methods in book 5, chapter A1 of Techniques of Water Resources Investigations of the U.S. Geological Survey (Skougstad and others, 1979).

2. Practice

2.1 Calibration and measurement

2.1.1 Check desiccators to see if they have a good seal and if desiccant in them is still effective. Regrease top of desiccator and regenerate or replace desiccant as necessary.

2.1.2 Check temperature of oven to see if it is correct (NOTE 1).

NOTE 1. The setting on the outside may be incorrect and not reflect the actual temperature. The thermometer must be read.

2.1.3 Proceed with the determination following directions specified in the analytical method.

2.2 Calibration checks

2.2.1 Check calibration of oven thermometer with a U.S. National Bureau of Standards certified thermometer at least once a year. Record date checked in a notebook kept near the oven.

2.2.2 Check calibration of analytical balance at least every 3 months using class S weights. Record date of calibration check in a notebook. If recalibration is necessary, consult the manufacturer's directions.

2.2.3 For dissolved solids, analyze 1 reference sample for every 50 samples or 1 in every set if fewer than 50 samples are run.

2.2.4 Analyze every 20th sample, in duplicate (NOTE 2).

NOTE 2. If the amount of water in a sample selected to be analyzed in duplicate is not sufficient for a second analysis, analyze in duplicate the first sample (after the 20th sample) for which there is enough water.

2.2.5 Record the determined and theoretical values or the duplicate values in a notebook. Also record the date of analysis and the laboratory-assigned log-in numbers of all samples which were analyzed.

2.2.6 Plot values on a control chart (see practice "Quality control charts"). If values exceed control limits or if a bias appears to be developing in the results, correct it before continuing.

Selected References

McClelland, N. I., Delfino, J. J., Greenberg, A. E., McDonald, D. B., and Morris, R. C., 1978, Water and wastewater analysis, *in* Inhorn, S. L., ed., Quality assurance practices for health laboratories: Washington D.C., American Public Health Association, p. 1145–1188.

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.

U.S. Environmental Protection Agency, 1979, Handbook for analytical quality control in water and wastewater laboratories: U.S. Environmental Protection Agency EPA–600/4–79–019, Cincinnati, 104 p.

Determination of Specific Conductance

1. Application or scope

1.1 This practice applies to field and non-automated laboratory measurements of specific conductance.

1.2 Refer to the practice "Conductivity meters," in the section "Instrumental Techniques," and to method I–1780–78, "Specific conductance, electrometric, wheatstone bridge," in Skougstad and others (1979).

2. Practice

2.1 Preparation of standard

2.1.1 Prepare a 0.00702 *N* KCl solution as specified in method I–1780–78. This solution has a conductance 1,000 μmho/cm at 25°C.

2.1.2 Check the specific conductance of each new KCl solution against a previous KCl standard solution. If the specific conductances of the two solutions are different, check both solutions against a third solution prepared by another analyst.

2.2. Calibration and measurement

2.2.1 Visually inspect the electrodes. Platinized electrodes require replatinization every few months. Replatinize electrodes when

platinum black has noticeably flaked off or when readings become erratic; consult method I–1780–78 for directions.

2.2.2 Measure the temperature of the 0.00702 *N* KCl solution to the nearest 0.1°C, and record the temperature. Adjust temperature control knob if applicable.

2.2.3 If the meter is temperature-compensated, adjust it to read 1,000 μmho. If a table of conductance or resistance versus temperature has been prepared, check the meter reading against the value in the table.

2.2.4 Rinse the cell thoroughly with distilled water and then rinse and fill with the first sample (NOTE 1).

NOTE 1. In reading standard KCl solution or samples, care must be taken that air bubbles are not entrapped in the cell.

2.2.5 Measure the conductance (or resistance) of each sample as directed in method I–1780–78 (NOTE 2). Be careful to record or compensate for the temperature of each sample.

NOTE 2. In measuring ground waters, be sure wells are pumped until readings are stable.

2.2.6 Thoroughly rinse the cell with each sample before filling the cell and measuring the conductivity.

2.2.7 If, using different cells, more than one cell constant is used or if instrumental scale changes are available and used, other KCl standard solutions should also be used. See Standard Methods (American Public Health Association and others, 1976) for KCl solutions which have a specific conductance of from 14.94 to 111,900 μmho.

2.3. Calibration checks

2.3.1 Check the calibration of the instrument at least every 3 hours with standard KCl solution (NOTE 3). Record the reading in a notebook. Include the date and time of initial calibration and of the calibration check.

NOTE 3. For field work, recalibrate the meter at each location.

2.3.2 If there has been a noticeable shift in the measurement value of the standard KCl solution, recalibrate the instrument and remeasure the conductivity of all samples back to where the shift occurred.

2.3.3 Use a reference material as the first sample to be analyzed and as every 30th sample thereafter. The reference material should fall within 1.5 standard deviations of the theoretical value. If it does not, the reason for the discrepancy should be determined and corrected, and the specific conductance of all samples from the last "good" reference value reading should be remeasured.

2.3.4 Record reference sample values, along with the expected value. Also record the laboratory-assigned log-in numbers of all samples analyzed in the set.

2.3.5 At the end of each set of conductivity measurements, recheck the specific conductance of every twentieth sample. If the set consists of less than 20 samples, recheck the specific conductance of the first non-reference sample at the end of the set. Record values in a notebook.

2.3.6 Plot reference sample and duplicate results on quality control charts as outlined in the practice, "Quality control charts." If values exceed warning limits or if a bias appears to be developing in the results (for example, all reference sample results are greater than the theoretical), correct for it before continuing.

Selected References

American Public Health Association and others, 1976, Standard methods for the examination of water and wastewater (14th ed.): Washington, D.C., American Public Health Association, 1193 p.

McClelland, N. I., Delfino, J. J., Greenberg, A. E., McDonald, D. B., and Morris, R. C., 1978, Water and wastewater analysis, *in* Inhorn, S. L, ed., Quality assurance practices for health laboratories: Washington D.C., American Public Health Association, p. 1145–1188.

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.

U.S. Environmental Protection Agency, 1979, Handbook for analytical quality control in water and wastewater laboratories: U.S. Environmental Protection Agency EPA–600/4–79–019, Cincinnati, p. 3–6—3–7.

Wood, W. W., 1976, Guidelines for collection and field analysis of ground-water samples for selected unstable constituents: U.S. Geological Survey Techniques of Water-Resources Investigations, Book 1, Chapter D2, 24 p.

Electrometric Titration (alkalinity and acidity)

1. Application

1.1 This practice applies to measurements of alkalinity (as $CaCO_3$) and acidity.

1.2 Refer to the practices "Titrimetry," and "Potentiometry," in the sections "Standard Quantitative Analysis Techniques" and "Instrumental Techniques," respectively, and to methods I–1020–78, "Acidity, Electrometric Titration"; I–2030–78, "Alkalinity, Electrometric Titration, Automated"; and I–1568–78, pH, "Electrometric, Glass Electrode," in Skougstad and others (1979).

1.3 For determination of carbonate species concentration, refer to Water-Supply Paper 1535-H (Barnes, 1964).

2. Practice

2.1 Preparation of titrant and buffers

2.1.1 Prepare primary standard as specified in method I–1020–78 or I–2030–78, using potassium hydrogen phthalate for acidity and sodium carbonate for alkalinity.

2.1.2 Prepare standard base (NaOH) or acid (H_2SO_4) solutions as specified in the method. Either standardize to the exact specified normality or determine the normality and use the appropriate factor in subsequent calculations.

2.1.3 Prepare a minimum of three buffer solutions for pH meter calibration. Date all buffer solutions and prepare fresh every 3 months or when noticeable discoloration or deterioration of the buffer occurs (NOTE 1).

NOTE 1. Premixed buffer solutions and buffer concentrates are available from instrument and chemical manufacturers.

2.2. Calibration and measurement

2.2.1 Check electrodes visually for scratches or cracks and to see if they are filled sufficiently. Check connection between electrode and meter.

2.2.2 Standardize the potentiometer using the three buffer solutions.

2.2.3 Titrate the samples with the standard solution to the end point specified in the analytical method.

2.3 Calibration checks

2.3.1 Titrate a primary standard biweekly or in every set, whichever is less frequent.

2.3.2 Calculate and record the normality of the titrant and the date on which the primary standard was analyzed.

2.3.3 If the normality is found to have changed slightly, either restandardize the titrant or adjust the factor used in the calculation of concentrations to reflect the new normality.

2.3.4 For alkalinity, use a reference material as the first sample to be analyzed and as every 20th sample thereafter. The value for the reference material should fall within 1.5 standard deviations of the theoretical value. If it does not, the reason for the discrepancy should be determined and corrected and the concentration of all samples from the last "good" reference value should be remeasured.

2.3.5 For acidity, repeat the analysis of every 10th sample using double the original volume.

2.3.6 Record values, along with the date of analysis. Also record the laboratory-assigned log-in number of all samples analyzed in the set.

2.3.7 Plot the values on a control chart as outlined in the practice "Quality control charts." If values exceed control limits or if a bias appears to be developing in the results, isolate and correct the problem before continuing.

References

Barnes, Ivan, 1964, Field measurement of alkalinity and pH: U.S. Geological Survey Water-Supply Paper 1535, 17 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.

Organic Quality Control

Gas Chromatographic Analysis

1. Application or scope

1.1 This practice applies to measurement by gas chromatography of chlorinated phenoxy acid herbicides, organochlorine insecticides, and organophosphorus insecticides.

1.2 The practice "Gas chromatographs," in the section on "Instrumental Techniques," and the applicable analytical method in Book 5, Chapter A3, of this series should be referred to.

2. Practice

2.1 Preparation of standards, blanks, and reagents

2.1.1 Initially, obtain pesticide standards of the highest available purity from at least two sources. A source for most standards is the U.S. Environmental Protection Agency, Health Effects Research Laboratory, Research Triangle Park, North Carolina (see Watts, 1980).

2.1.2 Preferably, use standards with a purity guaranteed by the supplier and (or) checked in the laboratory. In all other cases, analyze standards from both sources; if results are not equivalent, obtain a standard from another source.

2.1.3 Use distilled water from an all-glass still. In order to obtain water with a low organic background, it may also be necessary to redistill from alkaline permanganate solution or to double extract with an appropriate solvent, such as benzene, followed by boiling to remove residual solvent.

2.1.4 Use "pesticide quality" or "distilled in glass" solvents. Test each lot by concentrating to as great a concentration factor as will ever be used, injecting into the gas chromatograph, and recording detector response for 20 to 30 minutes. There should be no extraneous peaks greater than 10 picograms of heptachlor epoxide on electron capture detectors or 50 picograms of diazinon with a flame photometric detector when the solvent is used as a reagent blank. If potentially interfering peaks are noticeable, redistill the solvent over sodium-lead amalgam or other suitable agent to remove interferences (NOTE 1).

NOTE 1. Some solvents need to be subjected to procedural treatment (such as esterification) to determine if derivatizable interferences exist.

2.1.5 Check all adsorbents and reagents prior to use to insure non-interference with the chromatographic procedure. The tests employed to determine suitability would include the most rigorous test at the lowest detection limit that will be reported by use of the procedure (NOTE 2).

NOTE 2. For example, concentrate hexane by at least a factor of 75 and inject 5 microliters into a gas chromatograph, both before and after cleanup with alumina. There should be no extraneous peaks greater than those indicated above and the width of the solvent peak must not exceed 60 seconds prior to cleanup or 30 seconds after cleanup. If these requirements are not met, redistill the solvent and prepare a different batch of alumina.

2.1.6 Using a microbalance, accurate to at least .001 mg, prepare stock solutions of pesticide standards by accurately weighing between 2.000 and 10.000 mg of appropriate standard. Quantitatively transfer the compound to a 25.0 mL glass-stoppered volumetric flask; dissolve in benzene or other appropriate solvent and dilute to 25.0 mL with the solvent (NOTE 3).

NOTE 3. Benzene is usually the preferred solvent since it is relatively nonvolatile, and the stock solutions can be stored under refrigeration for long periods (Goerlitz and Brown, 1972).

2.1.7 If the purity of the standard is less than 100 percent, apply an appropriate correction factor. For example, if 5.000 mg of a standard which is only 90 percent pure is weighed and diluted to 25.0 mL, the weight of pure material is $5.000 \times 0.90 = 4.500$ mg in the 25.0 mL.

2.1.8 Have concentration calculations checked by another person.

2.1.9 Record all data used in stock solution preparation in a notebook. Include weight, volume, solvent, source of standard, purity, date prepared, and name of analyst who prepared the solution. Stock solutions from both sources (see paragraph 2.1.2, above) must be prepared, preferably by different analysts.

2.1.10 Store stock solutions in the dark, under refrigeration (-15 to -18°C). In general, prepare organophosphorus insecticide stock solutions fresh at least every 4 months and prepare organochlorine insecticide stock solutions fresh at least every 6 months (NOTE 4). Prepare sooner if there is an obvious change, such as a major shift in response factor and the shift is determined not to be due to other causes (such as column failure).

NOTE 4. Specific compounds may not need stock solution prepared this frequently, but, if they are not, it must be documented that they are stable for longer periods. For example, some organophosphorus insecticides may be stable for 6 months and some organochlorine insecticides may be stable for 1 year.

2.1.11 Allow stock solutions to warm to room temperature. Partially fill 100 mL volumetric flasks with appropriate solvent, as specified in the analytical methods, and prepare a minimum of six concentrations of working standards from both original sources using micropipets to transfer stock solutions to flasks and diluting to volume with solvent (NOTE 5).

NOTE 5. Working standards are usually mixtures of several compounds. A DDT standard should be prepared in which DDD and DDE are not mixed since the appearance of these degradation products in a DDT standard solution can be used to monitor for on-column breakdown (Sherma, 1979, p. 66).

2.1.12 Store working solutions in an explosion-proof refrigerator (approximately 5°C) during the night and weekends. Warm to room temperature before each use. Prepare new organochlorine working standards monthly and new organophosphate working standards every 2 weeks. Record all data from preparation, including date, in notebook.

2.2 Calibration and measurement

2.2.1 Extract samples a minimum of three times using the solvent and following the procedure specified in the analytical method (NOTE 6).

NOTE 6. If emulsions form, small amounts of distilled water or acetone may be added to water extractions and small amounts of anhydrous sodium sulfate to sediment plus water mixture in order to break the emulsions.

2.2.2 Simultaneously with the extraction of samples, extract a blank.

2.2.3 Concentrate the extracts as specified in the analytical method (for example, using a Kuderna-Danish evaporator). Do not allow complete evaporation of solvent.

2.2.4 Follow cleanup procedures specified in the method. Generally this involves using at least one microcolumn containing an absorbent (for example, alumina or Florisil), washing with solvent, and concentrating the sample. In some cases, more than one clean-up column will be necessary.

2.2.5 Check tank pressure daily to see if it is sufficient for the days work. Check carrier-gas trap monthly.

2.2.6 Check flow rates daily to see if they are set to those specified in analytical method or instrument manual.

2.2.7 Check oven, inlet, and detector temperatures daily to see if they are set to those specified in the analytical method or instrument manual and if they are remaining stable.

2.2.8 Check septum, "O" rings, and glass injection inserts daily to see if they appear in good condition.

2.2.9 Check recorder daily to see if the gain and speed controls are set properly and if ink supply and paper are sufficient. Clean recorder slide wire monthly.

2.2.10 Check nickel-63 detector monthly using an electrometer to obtain detector profile as specified in the instrument manual. If a poor profile is noted, detector must be cleaned or repaired; installation of a spare detector is recommended to avoid loss of analytical time.

2.2.11 Calibrate the instrument with a series of four to six standards semiannually or when response factors have changed by more than 10 percent, a new column has been installed, or any other major changes have been made in the system. Prepare standard curve as

indicated in the practice "Gas chromatographs," in the section "Instrumental Techniques," and in the method "Pesticides-gas chromatographic analysis," in Goerlitz and Brown, 1972.

2.2.12 Analyze one set of two standards before any samples are analyzed. If a line drawn between the read-out values for these two standards does not parallel the original calibration line or if concentration values differ by more than 10 percent from the values for the same concentrations on the original calibration line, do not proceed with analysis until the problem has been isolated and corrected.

2.2.13 Inject a reagent blank.

2.2.14 At least twice a week, inject a p,p'-DDT standard at a concentration known to give about 50 percent full scale deflection. The standard should be free of p,p'-DDD and p,p'-DDE. Appearance of either of these degradation products indicates on-column breakdown.

2.2.15 Weekly inject an endrin standard at a concentration known to give about 50 percent full scale deflection. Appearance of additional peaks indicates on-column breakdown.

2.2.16 Proceed with the analysis. Inject sample extracts. Allow sufficient time between samples for the last compound to be eluted and for the baseline to return to normal (NOTE 7).

NOTE 7. When injecting standards, blanks, or samples, flush the syringe several times with the standard to be injected, overfill the syringe, withdraw it from the sample container, check it visually for bubbles, discharge the excess solution, and immediately and smoothly inject the extracts.

2.2.17 Analyze all samples, blanks, and standards using a minimum of two different columns. Because a column may not separate all pesticides present, report the lower value obtained.

2.2.18 Confirm the presence of pesticides in concentrations greater than 1.0 μg/L in water or 10.0 μg/kg in sediment by conductivity gas chromatography. Confirm the presence of pesticides in concentrations greater than 2.0 μg/L in water or 20 μg/kg in sediment by gas chromatography-mass spectrometry (unless definite foreknowledge of the presence of a specific compound obviates this need, as in the weekly monitoring of a pesticide known and confirmed to be in a steam).

2.3 Calibration checks

2.3.1 As noted in 2.2.12, analyze one set of two standards before any samples. If instrument conditions change or if the analyst suspects (possibly because of dirty or very concentrated samples) that there may be a problem, inject another set of standards.

2.3.2 If results indicate a problem exists (for example, concentration values differ more than 10 percent from initial values) remake the standards and reinject them. If this does not solve the problem, it must be isolated and corrected and all samples from the last set of standards must be reanalyzed.

2.3.3 Analyze a reagent blank after every set of standards. If baseline drift is indicated, take corrective measure before proceeding with the analysis.

2.3.4 Inject a reference material, if available, as every 20th sample.

2.3.5 If reference material is unavailable, spike extracts of every 20th sample with mixed standard(s) of constituents of interest. If reference material is available but includes very few of the constituents to be analyzed, alternate reference material and spikes on every 20 samples.

2.3.6 Analyze at least one reference material or spike per week.

2.3.7 Spike a natural water sample (tap water is acceptable if nothing else is available) with a suitable reference material or with standards prepared in an acetone matrix. Carry out a complete analysis (including extraction and cleanup) of the spiked and unspiked sample at least once every 30th sample or every 2 weeks, whichever occurs first.

2.3.8 If bottom materials are being analyzed, reanalyze at least one bottom material a week.

2.3.9 Record all values in a notebook. Include expected reference sample concentration, concentration of spike, and date of analysis. Also record the laboratory-assigned log-in numbers of "duplicates" and of all samples run between reference materials or spikes.

2.3.10 Plot values on a quality control chart as outlined in the practices, "Quality control charts." If a bias is noticeable or if the anal-

ysis is out of control, determine the reason and correct before continuing analyses. If a constant bias is known to be inherent in the methodology, adjust all concentrations in order to eliminate the bias and indicate the correction with the results.

Selected References

Goerlitz, D. F., and Brown, Eugene, 1972, Methods for analysis of organic substances in water: U.S. Geological Survey Techniques of Water-Resources Investigations, Book 5, Chapter A3, p. 24–40.

Sherma, Joseph, 1979, Manual of analytical quality control for pesticides and related compounds in human and environmental samples: U.S. Environmental Protection Agency EPA–600/1–79–008, Research Triangle Park, North Carolina, 401 p.

U.S. Environmental Protection Agency, 1979, Handbook for analytical quality control in water and wastewater laboratories: U.S. Environmental Protection Agency EPA–600/4–79–019, Cincinnati, p. 8–1—8–10.

Watts, R. R., 1980, Analytical reference standards and supplemental data for pesticides and other selected organic compounds: U.S. Environmental Protection Agency EPA–600/2–81–011, Research Triangle Park, North Carolina, 182 p.

Quality Control Charts

1. Application or scope

1.1 This practice describes the construction and use of several types of control charts. Control charts indicate trends and variability in analyses which may not be readily apparent from an examination of tabulated results (NOTE 1). They can be effectively used to monitor analytical results in order to determine if bias is developing or if precision is less than expected. When used to monitor the quality of results produced by a particular analyst, control charts can be a helpful training and supervisory tool.

NOTE 1. The scale of the abscissa is in increments of time. The date of analysis will probably be the most useful unit to plot, although other time units can be used.

1.2 If standard reference materials are available for a constituent in sufficient quantity to be analyzed routinely, quality control charts can be constructed from the resulting analytical data. In many cases, large quantities of stable "reference samples" may be prepared by a section head or analyst by adding constituents of interest to either demineralized or ambient water. Results from repeated analyses of spiked (with constituent of interest) or unspiked samples can also be used for control charts.

1.3 Results which fall outside of the established "warning limits" indicate that there may be a problem and should be investigated. Results which fall outside of the "control limits" require that analyses cease being made until the reason for lack of control is determined and corrections are made (NOTE 2).

NOTE 2. Warning limits for the charts in this practice are set at either 1.5 or 2 times and control limits at 3 times the standard deviation of the statistic used. If only normal random errors are present, approximately 86.6 percent of the values should be within 1.5 standard deviations, 95.5 percent should be within 2 standard deviations, and 99.7 percent of the values should be within 3 standard deviations. In general, there should be less than a 0.3 percent chance of deciding on lack of control when there is control.

1.4 Many of the charts described in this practice use average values; their use is desirable because "averages are more sensitive to change than are individuals" (Becking and Gryna, 1974). Such charts are useful if a fixed number of analyses are made on a reference sample in a given time period or for a given number of samples (NOTE 3).

NOTE 3. They can be used, for example, if three analyses of a reference material are always made per day or if one reference material analysis is made for each 20 samples and the results plotted after every 80 samples.

1.5 Other charts described in this practice use individual values and, although less sensitive, have the advantage of being able to be plotted as soon as an analysis is made. Such charts can be particularly useful when it is considered more desirable to make a single analysis of several reference materials containing different concentration levels of a particular constituent than to make several analyses of one reference material (and when time, money, and so forth, prohibit multiple analyses of several reference materials of different concentrations.)

1.6 A value outside of the control limits of a mean concentration chart suggests that there may be an overall change in the method (such as might result from a shift in alinement of the light source in a spectrometer). A value outside of the control limits of a standard deviation or range chart tends to indicate an increased variability in analyses (such as might result from dirty or limp tubing in an analysis using a Technicon AutoAnalyzer). Thus, using both types of charts increases the probability of spotting problems soon after they occur.

1.7 To determine what type of chart to use, consider whether average or individual values are to be plotted, whether the results to be plotted reflect analyses of reference materials or of ambient waters, whether the concentration or range is the parameter of interest, and so forth. Go to 2.1 and (or) 2.4 if values to be

plotted are from analysis of a reference material for a specified, fixed number of times per time period or per number of samples; go to 2.2 if values to be plotted are from individual measurements of up to three reference materials; go to 2.3 if values to be plotted are from a variety of reference materials which have a variety of most probable values and associated standard deviations; go to 2.1 and (or) 2.5 if values to be plotted are from replicate analyses of ambient samples; go to 2.6 if values to be plotted are from spiked samples and are to be used in looking at bias; and go to 2.7 if values to be plotted are from diluted samples and are to be used in looking at bias.

2. Practice

2.1 Mean concentration control chart:

2.1.1 Set up and use this chart if an ambient sample or a reference material is being analyzed a fixed number of times per time period or per given number of samples (for example, the reference sample is analyzed twice a day or twice for each set of 30 samples) (NOTE 4).

NOTE 4. Because there must be sufficient quantity of a stable sample available to be analyzed over a long time period, this chart will usually be more appropriate for use with a reference material.

2.1.2 Decide on the number of times the sample will be analyzed in an analytical sequence or per day (or other convenient numerical or time division).

2.1.3 Indicate concentration along the vertical axis and the date of analysis along the horizontal axis (fig. 5).

2.1.4 If repeated analyses are being made of a reference material, draw a horizontal line to indicate the theoretical (most-probable) concentration. If repeated analyses are being made of an actual sample or of a material prepared (usually by use of "spikes") for the constituent of interest (and the concentration is unknown), calculate:

$$\bar{\bar{x}} = \frac{\Sigma \bar{x}}{N} = \frac{\Sigma(\Sigma x_i/n)}{N} \qquad (22)$$

where

$\bar{\bar{x}}$ = the average of the means of the sets of results,

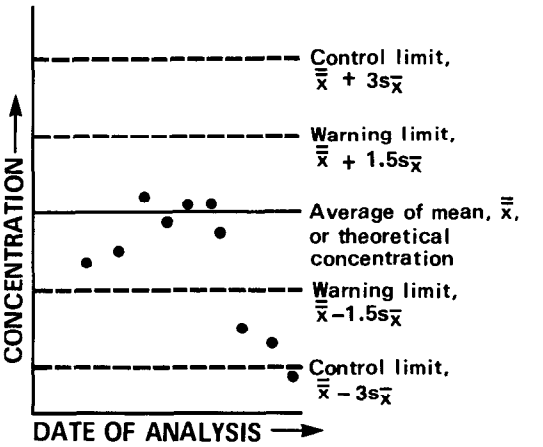

Figure 5.—Concentration control chart: plot of mean values.

$\bar{x}$ = the mean of each set of results,

N = the number of sets of results (NOTE 5),

x_i = the individual results of a set of analyses, and

n = the number of results in a set of analyses.

NOTE 5. In order to have a fairly reliable $\bar{\bar{x}}$, use a relatively large number of sets of results (20 to 30) and keep in mind that it may be necessary to later revise the value for $\bar{\bar{x}}$.

2.1.5 Estimate the standard error of the mean as follows:

2.1.5a If analyses are being made of a reference material and the value for the standard deviation (based on data from the original analyses of the material) which is supplied with the material is based on at least 20 analyses, calculate an estimate of the standard error of the mean (NOTE 6):

$$s_{\bar{x}} = \frac{s}{\sqrt{n}} \qquad (23)$$

where

$s_{\bar{x}}$ = the standard error of the mean,

s = the standard deviation, and

n = the number of results in a set of analyses.

NOTE 6. Since the standard deviation for results of analyses made on the reference material was based on a limited number of analyses, keep in mind that the upper and lower control limits may have to be revised after more analyses are made.

2.1.5b If the standard deviation for analysis is unknown or is likely to be unreliable (if, for instance it was based on only three or four results), calculate the standard deviation for each set of analyses and determine:

$$\bar{s}=\frac{\Sigma s_i}{N} \tag{24}$$

where

$\bar{s}$ = the average of the standard deviations of the sets of analyses,
s_i = the individual standard deviation of each set of analyses, and
N = the number of sets of results (see NOTE 5).

Then calculate an estimate of the standard error of the mean.

$$s_{\bar{x}}=\frac{s}{\sqrt{n}}=\frac{\bar{s}/c_2}{\sqrt{n}} \tag{25}$$

where

$s_{\bar{x}}$ = the standard error of the mean,
s = the standard deviation,
n = the number of results in each set of analyses,
$\bar{s}$ = the average of the standard deviations of the set of results, and
c_2 = factor from table A7 in the appendix.

2.1.5c Alternatively to calculating the standard deviations for each set of results, calculate the range:

$$R=x_H-x_L \tag{26}$$

where

R = the range for a set of results,
x_H = the highest concentration in a set of results, and
x_L = the lowest concentration in a set of results.

Calculate the average range:

$$\bar{R}=\frac{\Sigma R_i}{N} \tag{27}$$

where

$\bar{R}$ = the average range of the sets of results,
R_i = the individual range of each set of results, and
N = the number of sets of results (see NOTE 5).

Calculate an estimate of the standard error of the mean:

$$s_{\bar{x}}=\frac{\bar{R}/d_2}{\sqrt{n}} \tag{28}$$

where

$s_{\bar{x}}$ = the standard error of the mean,
$\bar{R}$ = average range of the sets of results,
n = the number of results in each set of analyses, and
d_2 = factor from table A8 in the appendix (NOTE 7).

NOTE 7. The control limits can be determined more directly by multiplying $\bar{R}$ by the factor A_2 also found in table A8. $A_2=3/d_2\sqrt{n}$(Grant and Leavenworth, 1974) and is, for example, 1.88, 1.02, and 0.73 for sets of 2, 3, and 4, respectively.

2.1.6 Draw short-dashed horizontal lines at ± 1.5 times the standard error of the mean and long-dashed lines at ± 3 times the standard error of the mean to mark warning and control limits, respectively (fig. 5).

2.1.7 After each set of analyses, plot the mean concentration. Use different symbols for values obtained by different analysts, if desired, in order to monitor the "quality control" of the analyst as well as that for the constituent.

2.1.8 If a bias appears to be developing (for example, all values are positive), or if several analyses are beyond the warning limits (even if some are positive and some are negative), investigate the analytical technique used and make necessary corrections. (See step 2.6.8 for more information on deciding on bias.) If an analysis is beyond the control limit, discontinue making analyses until the reason for lack of control has been determined and corrected.

2.2 Concentration control chart, using individual results

2.2.1 Set up and use this chart if reference materials are analyzed and individual results are to be plotted. Use, for example, if several different reference materials are analyzed each day (NOTE 8).

NOTE 8. It is desirable to use reference materials containing concentrations of the constituent to be analyzed in both the high and low areas of the analytical range. In order avoid confusion, it is recommended that the chart be limited to a maximum of three reference materials per constituent.

2.2.2 Indicate concentration along the vertical axis and the date of analysis along the horizontal axis (fig. 6).

2.2.3 Draw horizontal line(s) to indicate the theoretical (most-probable) concentrations of reference material(s). Draw short-dashed horizontal lines at ± 1.5 standard deviations from the theoretical concentration and long-dashed horizontal lines at ± 3 standard deviations to mark warning and control limits respectively.

2.2.4 Plot each analysis of a reference sample, immediately. Use a different symbol or different color for different reference samples. A different symbol or color can also be used for different analysts and the "quality control" of the analyst watched as well as monitoring each constituent.

2.2.5 If a bias appears to be developing (for example, all values are positive), or if several analyses are beyond the warning limits (even if some are positive and some negative), investigate the analytical technique used and make necessary corrections. (See step 2.6.8 for more information on deciding on bias.) If an analysis is beyond the control limit, discontinue making analyses until the reason for lack of control has been determined and corrected.

2.3 Standard deviation increment control chart

2.3.1 Set up and use this control chart if several different reference samples having different theoretical (most-probable) concentrations and standard deviations are to be used. Use this chart if a number of "reference materials" containing different concentrations of the constituent of interest are available (prepared, perhaps, by mixing different reference materials or by spiking deionized water) and if an estimate of the standard deviation can be made using the equations developed for interlaboratory or intralaboratory precision (see section "Analytical Methods Development Procedures").

2.3.2 Indicate number of standard deviations along the vertical axis and the date along the horizontal axis (fig. 7). Draw a horizontal line at 0 and draw short-dashed horizontal lines at ± 1.5 for warning limits and long-dashed horizontal lines at ± 3 for control limits.

2.3.3 Immediately following the analysis of a reference sample determine the sign (posi-

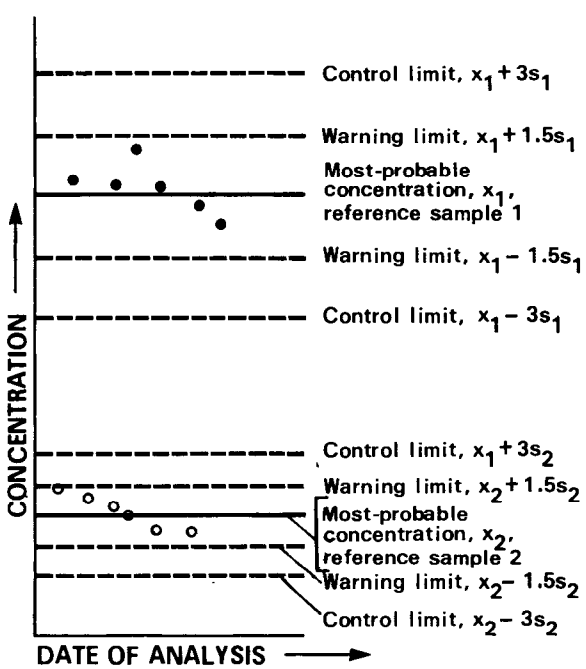

Figure 6.—Concentration control chart: plot of individual values.

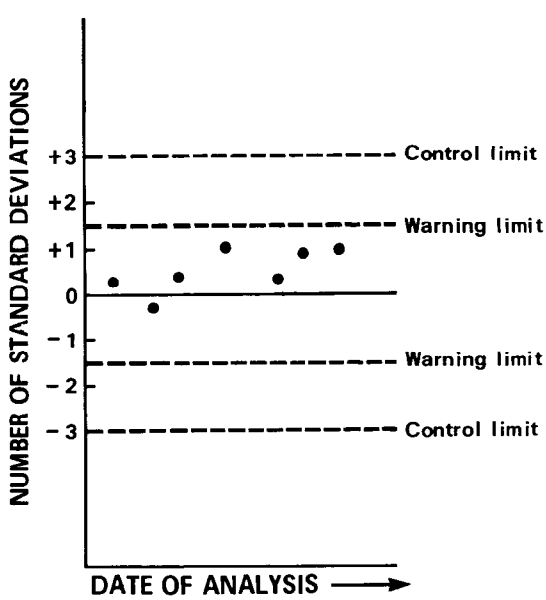

Figure 7.—Standard deviation increment control chart.

tive or negative) and number of standard deviations which the analyzed concentration is from the theoretical concentration:

$$V = \frac{x_a - x_t}{s_t} \qquad (29)$$

where

V = the value to be plotted,
x_a = the analyzed concentration,
x_t = the theoretical concentration, and
s_t = the theoretical standard deviation.

2.3.4 Plot the value.

2.3.5 If a bias appears to be developing (for example, all values are positive or negative) or if several analyses are beyond the warning limits (even if some are positive and some are negative), investigate the analytical technique used and make corrections. If an analysis is beyond the control limit, discontinue analysis until reason for lack of control has been determined and corrected.

2.4 Standard deviation or range control chart, using reference materials

2.4.1 Set up and use this control chart if a reference material is being analyzed a fixed number of times per time period or per number of samples. Use in conjunction with a mean concentration control chart (see paragraph 2.1).

2.4.2 Decide on the number of times the sample will be analyzed in an analytical series or per day (or other convenient numerical or time division).

2.4.3 Indicate increments of concentration along the vertical axis and the date along the horizontal axis (figs. 8 and 9).

2.4.4 Calculate the standard deviation or range for each set of analyses. Then calculate the average of the standard deviations of the set of results, $\bar{s} = \Sigma s_i/N$ (see 2.1.5b above) or calculate the average range, $\bar{R} = \Sigma R_i/N$ (see 2.1.5c above) (NOTE 9).

NOTE 9. Although for the mean concentration control chart, the standard deviation or range for each set of analyses will need to be calculated only when initially setting up the control chart, for this control chart (the standard deviation or range control chart) either the standard deviation or range must be calculated for each successive set of analyses. Because it is easier to calculate the range for each set than it is to calculate the standard deviation, it is recommended that the range control chart be used. As is pointed out in Grant and Leavenworth (1974, p. 89), the $\bar{R}$ control chart is also preferable, because it is easier to understand "range" than it is to understand "standard deviation."

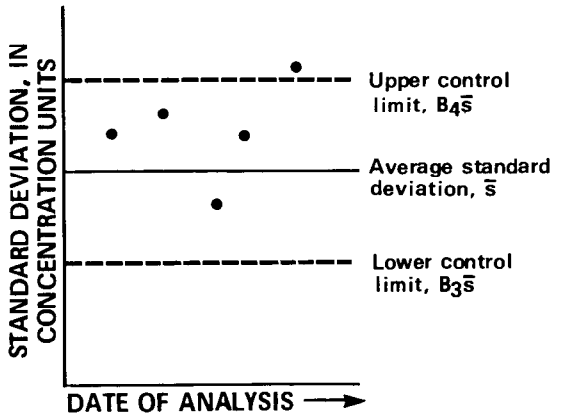

Figure 8.—Standard deviation control chart for replicate analyses.

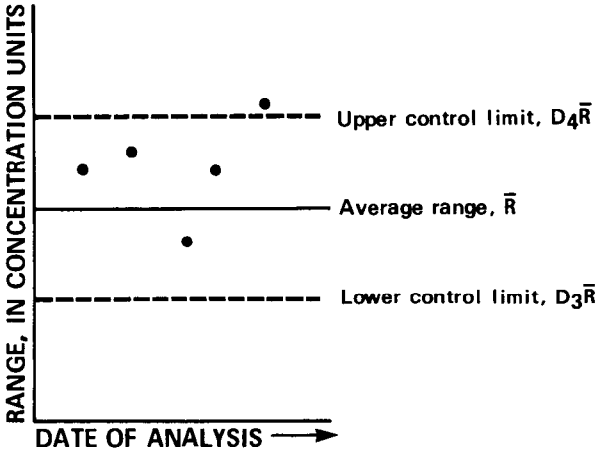

Figure 9.—Range control chart for replicate analyses.

2.4.5 Calculate and draw lines for control limits for the standard deviation or for the range:

Upper control limit = $B_4\bar{s}$
Lower control limit = $B_3\bar{s}$
Upper control limit = D_4R
Lower control limit = D_3R

where values for B_4 and B_3 are from table A9 and values for D_4 and D_3 are from table A10 (NOTE 10).

NOTE 10. For samples analyzed in duplicate, lower control limits are zero, and D_4 = 3.267 (fig. 10). A warning limit set to include 95 percent of the values can be drawn at 2.456 (Youden, 1975).

2.4.6 Immediately after analyzing a set of samples, calculate the range (or standard deviation) and plot on the control chart.

2.4.7 If a determined value is outside the upper control limit, discontinue further analyses until the reason for the lack of control has been determined and corrected. Values falling below the lower control limit suggest that the initial $\bar{s}$ or $\bar{R}$ is in error and that a smaller value could be used.

2.5 Range control chart, using duplicate or replicate analyses of actual samples.

2.5.1 Set up and use this control chart if a proportion of all analyses made are being repeated. Use to supplement charts prepared with reference samples in order to get an idea of the quality of analytical results for actual samples (since the actual samples have much more varied composition than is possible for a few reference materials) or use when a reference material is not available for the constituent of interest (if, for example, the constituent is not sufficiently stable for a reference material to be prepared).

2.5.2 After considering the analytical method, number of samples routinely run for the constituent, and so forth, determine both how many times a sample will be analyzed (often duplicate analyses will be specified) and the frequency of samples to be reanalyzed. (Analyze every 10th sample in duplicate, for example.)

2.5.3 Indicate increments of concentration along the vertical axis and the date along the horizontal axis.

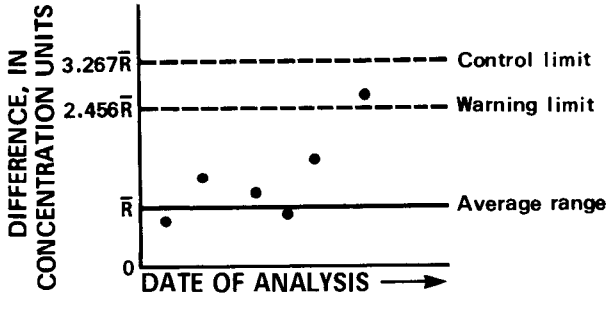

Figure 10.—Range control chart for duplicate analyses.

2.5.4 If the difference in concentrations of duplicate analyses (or the deviation of replicate analyses) is known or has been determined to be constant throughout the analytical range, follow the procedure outlined in paragraph 2.4 above to set up a control chart similar to figure 10. (Probably temperature measurements would fall into this category.)

2.5.5 If the differences in analytical results are known or suspected to vary with concentration (which is likely to be the case in environmental analyses), but the naturally occurring concentration range of the constituent is very narrow, it may be possible to consider the differences constant throughout the range and follow the procedure outlined in paragraph 2.4.

2.5.6 In most cases where the differences vary with concentration, it will be necessary to determine the appropriate regression model (NOTE 11).

NOTE 11. It may also be possible to set up several different concentration ranges and apply the appropriate factor for each range (see EPA, 1979). However, this will often cause interpretation problems in "border-line" cases. Thus, if 0.5 µg/L difference is allowed for concentrations less than 5 µg/L and 1.5 µg/L difference is allowed for concentrations between 5 and 10 µg/L, the limit of 1.5 µg/L might be considered suspect for a value of exactly 5 µg/L.

2.5.6a After a sufficient number of duplicate or replicate analyses have been made throughout the concentration range, plot the difference or range for each set on the vertical axis and the mean concentration for each set on the horizontal axis (fig. 11).

2.5.6b Apply appropriate factors to determine limits. For duplicates, apply 2.456 for warning limits and 3.267 for control limits (see fig. 11).

2.5.6c Set up a control chart by indicating proportion of "theoretical" difference along the vertical axis and the date along the horizontal axis (fig. 12). Draw a horizontal line at 1.0 (which would indicate the observed difference and difference determined from the regression model are the same). Draw a short-dashed horizontal warning line at 2.456 (for duplicates) and a long-dashed horizontal control line at 3.267 (for duplicates), or at appropriate values if more than two analyses will be made on the sample.

2.5.6d Each time "duplicate" (or replicate)

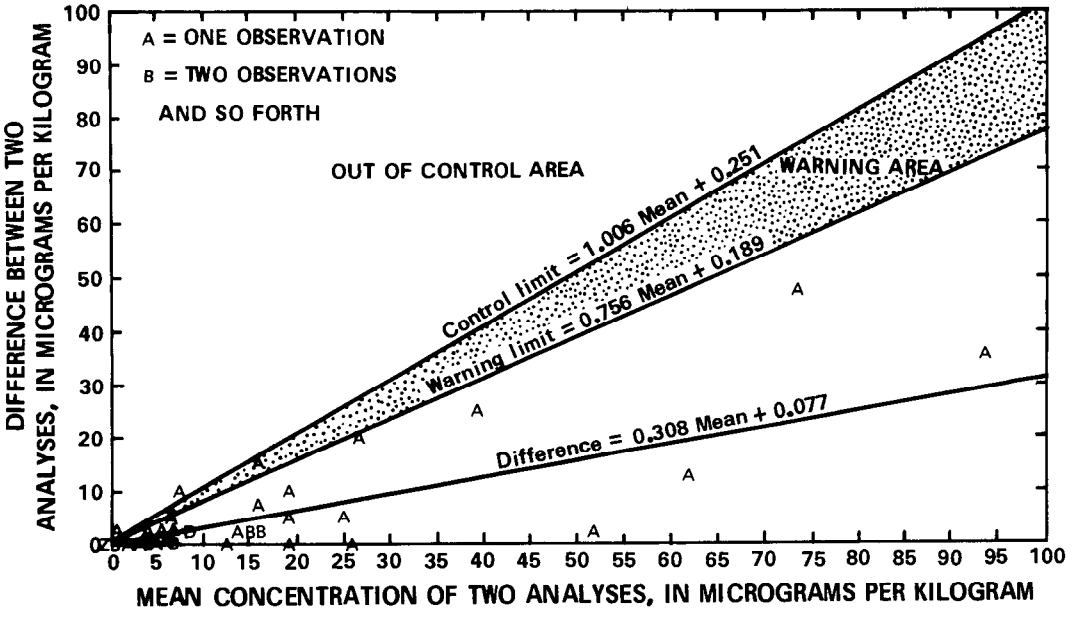

Figure 11.—Tentative model for duplicate analyses of polychlorinated biphenyls, total in bottom material.

analyses are made, determine the mean concentration:

$$\bar{x}=\frac{x_1+x_2}{2} \qquad (30)$$

where

$\bar{x}$ = the mean concentration of constituent of interest,

x_1 = the concentration of constituent of interest found in sample 1, and

x_2 = the concentration of constituent of interest found in sample 2.

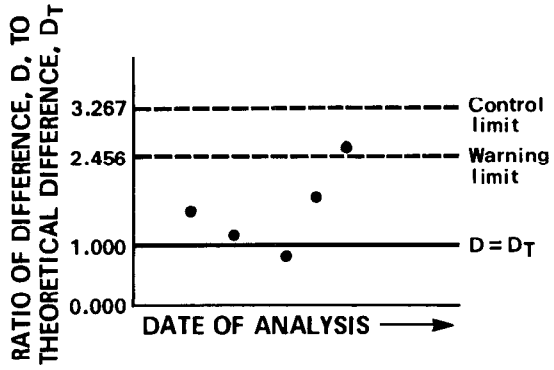

Figure 12.—Control chart for difference in duplicate analyses, for cases in which the difference between analyses varies with mean concentration.

2.5.6e Using the appropriate regression model, calculate the most-probable difference, D_t.

2.5.6f Calculate the difference between the "duplicate" analyses:

$$D=|x_1-x_2| \qquad (31)$$

where

D = the difference between duplicate analyses, and

x_1 and x_2 are as previously defined.

2.5.6g Determine the value to be plotted:

$$V=\frac{D}{D_t} \qquad (32)$$

where

V = the value to be plotted, the proportion of the theoretical difference,

D = the difference between duplicate analyses, and

D_t = the theoretical (most-probable) difference.

2.5.6h Plot the value after each set of analyses. If several values are outside of the warning limits, investigate the analytical technique used and make corrections. If an analysis

is beyond the control limit, discontinue analyses until the reason for lack of control has been determined and corrected (NOTE 12).

NOTE 12. If values are consistently less than "one," the regression model may be in error and allow differences which are "too large."

2.6 Bias control charts, using spikes

2.6.1 Set up and use this control chart if samples are to be analyzed both with and without a spike (known amount of constituent of interest).

2.6.2 Determine the frequency of samples to be spiked (for example, every 20th sample in an analytical series) depending on the method, instrument, number of samples analyzed per day, and so forth.

2.6.3 Analyze samples prior to spiking.

2.6.4 For a sample in which the original concentration is in the low portion of the range, add a spike which is sufficient to double the concentration. For a sample in which the original concentration is relatively high, add a spike small enough to ensure that the final concentration is not near the top of or outside of the analytical range. If it has been determined that the original concentration of the sample requires that a one-half dilution be made in order to be analyzed, add a spike such that the resulting concentration will also require a one-half dilution (NOTE 13).

NOTE 13. In quality control monitoring, usually only one spike concentration is added for a sample. This should not be confused with the method of standard additions in which multiple spikes of several concentrations are added.

2.6.5 Prepare a control chart. Indicate concentration (both "+" and "−") along the vertical axis and the date along the horizontal axis (fig. 13). Draw a solid horizontal line at "0" difference.

2.6.6 After the analyses, plot the difference between the known and determined concentrations of the spike (NOTE 14).

NOTE 14. Always subtract the known concentration from the determined concentration of the spike.

2.6.7 Use the binomial distribution to determine criteria for assuming positive or negative bias (NOTE 15). For a risk of about 1 percent of assuming bias where there is none (compared to a 0.3 percent risk for a 3 standard deviation limit), check to see if 7 out of 7 successive positive or negative points, 10 out of 11, 12 out of 14, 14 out of 17, or 16 out of 20 successive positive or negative points are either positive or negative (Grant and Leavenworth, 1974, p. 97–98). Similarly check for 19 out of 25, and 22 out of 30 positive or negative successive points. If the number of points on one side of the zero line meet or exceed these criteria, investigate (and correct if necessary) the reason for the possible bias before continuing with the analysis (NOTE 16).

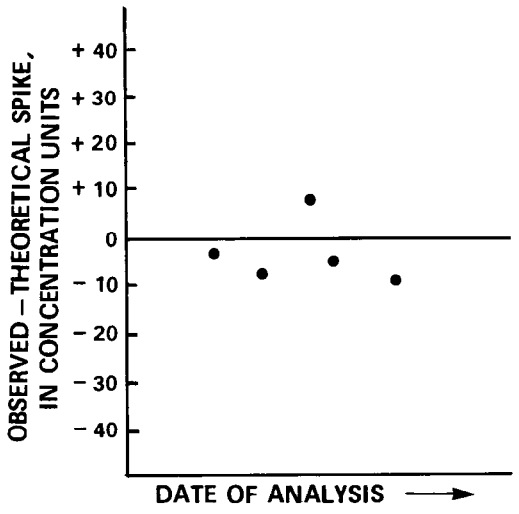

Figure 13.—Control chart for bias, based on recovery of spike.

NOTE 15. Use the formula:

$$P(x)=2\left\{\sum_{i=x}^{N}\frac{N!}{i!(N-i)!}(\tfrac{1}{2})^{i}(\tfrac{1}{2})^{N-i}\right\} \qquad (33)$$

where

$P(x)$ = the probability of having x or more points on the same side of the zero line,

N = the number of successive points, and

i = the number of points on the same side of the zero line.

The 2 is used to multiply the sum because a run of points above or below the line must be considered. See Grant and Leavenworth (1974, p. 235–236) for further explanation.

NOTE 16. The bias of results from a single sample could be due to factors such as an unsuspected matrix interference or glassware contamination. Note also that any inherent bias in an analytical method should have been determined during the development of the method and applied when reporting results.

2.7 Bias control chart, using diluted replicates

2.7.1 Set up and use this control chart instead of the spike recovery control chart if the use of spikes is undesirable for some reason (for example, the pure constituent is difficult to obtain) (NOTE 17).

NOTE 17. The bias must be constant over the analytical range.

2.7.2 Determine the number and (or) intervals of samples to be run as a dilution depending on the method, instrument, number of samples analyzed per day, etc. For example, a dilution of every 10th sample might be made and analyzed.

2.7.3 Determine an estimate of the bias for a sample using the following example as a guide: Consider a sample which contains a "true" concentration of 440 mg/L of a constituent. Analysis of the sample yields a result of 500 mg/L (a positive 60 mg/L bias) and a repeat analysis still gives 500 mg/L. However, when a one-half dilution is made, rather than finding the expected concentration of 250 mg/L, the concentration is found to be 280 mg/L (220 mg/L + 60 mg/L). The amount of the bias may be estimated by plotting the results (fig. 14). Rather than going through the origin, the line will intercept the y-axis at a point equal to the "bias concentration."

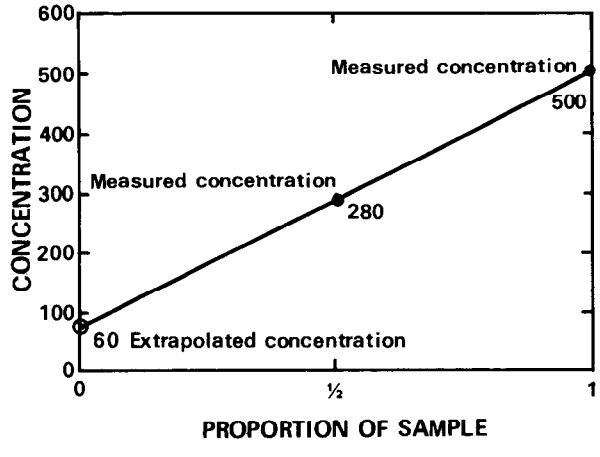

Figure 14.—Determination of bias using a diluted duplicate sample.

2.7.4 Indicate concentration (both "+" and "−") along the vertical axis and the date along the horizontal axis (see fig. 13).

2.7.5 After the analyses, plot the estimated bias for the sample.

2.7.6 Proceed as in step 2.6.8 to determine whether there is reason to assume a positive or negative analytical bias.

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Quality Control Duties and Responsibilities of Section Leader

1. Application or scope

1.1 This practice describes quality control responsibilities of the section leader or, in small laboratories, of the laboratory chief. In general, it also applies to field operations. Although many of the duties may be delegated, the responsibility may not.

1.2 Refer also to the quality control and quality assurance practices outlined in this manual, and to the appropriate analytical methods.

2. Practice

2.1 Methods

2.1.1 Be familiar with all methods and equipment in use.

2.1.2 Be sure each analyst has a written copy of methods to be used.

2.1.3 Know which methods should be used and when.

2.1.4 Be aware of samples that require special handling or analysis and ensure that they are analyzed by the correct procedure.

2.1.5 If a sample requires a slight method modification, approve, have recorded, and initial the results. Be sure that the effect of a modification has been tested and recorded.

2.1.6 Do not allow major methodology changes in the section, unless there has been formal documentation of data and approval has been obtained.

2.1.7 Be sure any required qualitative or quantitative confirmation of analysis (such as in gas chromatography) is made.

2.2 Training

2.2.1 Train or assign an experienced analyst to training new employees. If delegated, this duty is performed by one or at the most two senior analysts who have a formal, recognized function of training all new employees.

2.2.2 Until the quality of work of a new employee is at least equivalent to existing employees, do not allow new employee to work alone. Use quality control charts or other data review procedures to verify quality.

2.2.3 Be sure that training is sufficient before allowing new methods or new instruments to be used. Take advantage of training courses offered by instrument manufacturers.

2.2.4 Become familiar with each new method, instrument and technique; do not simply assign an analyst to learn about it.

2.3 Standard and reagent preparation

2.3.1 Be sure all standards and reagents are of correct quality grade.

2.3.2 Record lot number and "date-opened" of each standard and reagent.

2.3.3 Prepare (or assign an experienced analyst to prepare) stock standard solutions.

2.3.4 Check or have a different experienced analyst check all calculations relating to stock standard preparation.

2.3.5 Whenever possible, insure the correct preparation of stock standards by cross-checking. For example, a chloride standard of sodium chloride can be analyzed for sodium, and a new standard solution can be compared against an old standard solution.

2.3.6 Date all stock, intermediate, and working standards and reagents and record the dates in a notebook along with data pertaining to their preparation. Set up a system for monitoring the stability of standards. Discard all solutions immediately on reaching the expiration date specified in the method.

2.4 Instrumental

2.4.1 Be sure that required operational and calibration procedures are performed, that required checks are performed, and that all data are recorded in a notebook.

2.4.2 If an instrument is shared by more than one section, one section leader should be responsible for primary calibration check; be sure it is clear to which section the responsibility is assigned. For example, analytical balances

must be checked at least every 3 months using Class S weights and a record of this check kept; unless each section maintains its own balance, checking to ensure that this recalibration check is done would probably fall under the jurisdiction of the section most likely to use the balances.

2.4.3 Be sure any maintainence is promptly done and that any instrument not in proper working order is not used.

2.5 Analyst quality control

2.5.1 Be sure all required standards, blanks, reference materials, spikes, duplicates, and so forth, are analyzed.

2.5.2 Be sure all quality control information is recorded in a notebook, along with the date of analysis and all laboratory-assigned log-in numbers of samples that were analyzed.

2.5.3 Be sure required quality control charts are maintained.

2.5.4 At least weekly, check and initial all quality control data. Be sure that problems (such as bias or lack of control) are being caught and corrected.

2.5.5 Monitor quality of work of all analysts in section, especially of newer analysts. A quality control chart for each analyst or one in which all analyst's data are recorded is a good way to conduct this monitoring.

2.6 Investigation of quality control problem

2.6.1 If a quality control problem is noticed by the section leader or is reported by the laboratory's quality control staff, personally investigate to find the cause.

2.6.2 Ensure that corrective action is taken. In making any necessary changes, clearly explain to the analyst(s) why such changes are being made (NOTE 1).

NOTE 1. Often quality control problems continue, because the analyst is unaware that there is a problem, because an improper modification of a method has been made and has existed for so long that it is accepted by the analyst, or because analysts are convinced that if they report a problem, nothing will be done. Clear explanations often solve the problem.

Selected Reference

American Society for Quality Control, 1977, Guide for reducing quality costs: Milwaukee, American Society for Quality Control, p. 27–28.