EPA-600/4-86-024

Method 200.6 – Dissolved Calcium, Magnesium, Potassium, and Sodium in *N*et Deposition by Flame Atomic Absorption Spectrophotometry

[METHOD ONLY]

Method 200.6 -- Dissolved Calcium, Magnesium, Potassium, and Sodium in Wet Deposition by Flame Atomic Absorption Spectrophotometry

March 1986

Performing Laboratory:

Loretta M. Skowron
Carla Jo Brennan
Mark E. Peden

Illinois State Water Survey
Analytical Chemistry Unit
2204 Griffith Drive
Champaign, Illinois 61820

Sponsoring Agency:

John D. Pfaff, Project Officer

Inorganic Analysis Section
Physical and Chemical Methods Branch
United States Environmental Protection Agency
Office of Research and Development
Environmental Monitoring and Support Laboratory
Cincinnati, Ohio 45268

INDEX

Section Number	Subject
1	Scope and Application
2	Summary of Method
3	Definitions
4	Interferences
5	Safety
6	Apparatus and Equipment
7	Reagents and Consumable Materials
8	Sample Collection, Preservation, and Storage
9	Calibration and Standardization
10	Quality Control
11	Procedure
12	Calculations
13	Precision and Bias
14	References

TABLES

1. Method Detection Limits and Concentration Ranges for Flame Atomic Absorption Spectrophotometric Analysis of Wet Deposition.
2. Operating Conditions and Suggested Calibration Standard Concentrations for the Determination of Calcium, Magnesium, Potassium, and Sodium in Wet Deposition Samples.
3. Single-Operator Precision and Bias for Calcium, Magnesium, Potassium, and Sodium Determined from Analyte Spikes of Wet Deposition Samples.
4. Single-Operator Precision and Bias for Calcium, Magnesium, Potassium, and Sodium Determined from Quality Control Check Samples.

FIGURES

1. Percentile Concentration Values Obtained from Wet Deposition Samples: Calcium, Magnesium, Potassium, and Sodium.

1. SCOPE AND APPLICATION

1.1 This method is applicable to the determination of calcium, magnesium, potassium, and sodium in wet deposition by flame atomic absorption spectrophotometry (FAAS).

1.2 The term "wet deposition" is used in this method to designate rain, snow, dew, sleet, and hail.

1.3 The method detection limits (MDL) for the above analytes determined from replicate analyses of quality control check solutions containing 0.053 mg/L calcium, 0.018 mg/L magnesium, 0.012 mg/L sodium, and 0.013 mg/L potassium are 0.007, 0.002, 0.003, and 0.003 mg/L, respectively. The concentration range of this method is outlined in Table 1.

1.4 Figure 1 represents cumulative frequency percentile concentration plots of calcium, magnesium, potassium, and sodium obtained from the analysis of over five thousand wet deposition samples. These data should be considered during the selection of appropriate calibration standard concentrations.

2. SUMMARY OF METHOD

2.1 A solution containing the element(s) of interest is aspirated as a fine mist into a flame where it is converted to an atomic vapor consisting of ground state atoms. These ground state atoms are capable of absorbing electromagnetic radiation over a series of very narrow, sharply defined wavelengths. A distinct line source of light, usually a hollow cathode lamp specific to the metal of interest, is used to pass a beam through the flame. Light from the source beam, less whatever intensity was absorbed by the atoms of the metal of interest, is isolated by the monochromator and measured by the photodetector. The amount of light absorbed by the analyte is quantified by comparing the light transmitted through the flame to light transmitted by a reference beam. The amount of light absorbed in the flame is proportional to the concentration of the metal in solution. The relationship between absorption and concentration is expressed by Beer's Law:

$$\log(I_o/I) = abc = A$$

where: I_o = incident radiant power
I = transmitted radiant power
a = absorptivity (constant for a given system)
b = sample path length
c = concentration of absorbing species (mg/L)
A = absorbance

The atomic absorption spectrophotometer is calibrated with standard solutions containing known concentrations of the element(s) of interest. Calibration curves are constructed from which the concentration of each analyte in the unknown sample is determined.

3. DEFINITIONS

3.1 ABSORBANCE (A) -- the logarithm to the base ten of the reciprocal of the transmittance, (T):

$$A = \log(1/T)$$

$$0.0044\ A = \text{the absorption of 1\% of the transmitted light.}$$

The absorbance is related to the analyte concentration by Beer's Law (Sect. 2.1) where $1/T = I_o/I$

3.2 ATOMIC ABSORPTION -- the absorption of electromagnetic radiation by an atom resulting in the elevation of electrons from their ground states to excited states. Atomic absorption spectrophotometry involves the measurement of light absorbed by atoms of interest as a function of the concentration of those atoms in a solution.

3.3 SPECTRAL BANDWIDTH -- the wavelength or frequency interval of radiation leaving the exit slit of a monochromator between limits set at a radiant power level half way between the continuous background and the peak of an emission line or an absorption band of negligible intrinsic width (14.1).

3.4 SPECTROPHOTOMETER -- an instrument that provides the ratio, or a function of the ratio, of the radiant power of two light beams as a function of spectral wavelength. These two beams may be separated in time and/or space.

3.5 For definitions of other terms used in this method, refer to the glossary. For an explanation of the metric system including units, symbols, and conversion factors see American Society for Testing and Materials (ASTM) Standard E 380, "Metric Practices" (14.2).

4. INTERFERENCES

4.1 Chemical interference is the most frequently encountered interference in atomic absorption spectrophotometry. A chemical interference may prevent, enhance, or suppress the formation of ground state atoms in the flame. For example, in the case of calcium determinations, the presence of phosphate or sulfate can result in the formation of a salt that hinders proper atomization of the solution when it is aspirated into the flame. This decreases the number of free, ground state atoms in the flame, resulting in lowered absorbance values. Aluminum can cause a similar interference when measuring magnesium. The addition of appropriate complexing agents to the sample solution reduces or eliminates chemical interferences and may increase the sensitivity of the method.

4.2 Alkali metals such as sodium and potassium may undergo ionization in an air-acetylene flame resulting in a decrease in ground state atoms available for measurement by atomic absorption. Addition of a large excess of an easily ionizable element such as cesium will eliminate this problem, since cesium will be preferentially ionized. The preferential ionization of the cesium solution results in an enhanced atomic absorption signal for both potassium and sodium (14.3).

4.3 If a sample containing low concentrations of the metal being measured is analyzed immediately after a sample having a concentration exceeding the highest calibration standard, sample carry-over will result in elevated readings. To prevent this interference, routinely aspirate water (Sect. 7.2) for about 15 seconds after a high concentration sample. Depending on the concentration of metal in the last sample analyzed, it may be necessary to rinse for longer time periods. Complete purging of the system is ascertained by aspirating water until the absorbance readout returns to the baseline.

4.4 Wet deposition samples are characterized by low ionic strength and rarely contain enough salts to cause interferences due to nonspecific background absorbance. The use of background correction techniques is not necessary and will decrease the signal to noise ratio and lessen precision.

5. SAFETY

5.1 The calibration standards, sample types, and most reagents used in this method pose no hazard to the analyst. Use a fume hood, protective clothing, and safety glasses when handling concentrated hydrochloric acid (Sect. 7.5-6).

5.2 Use a fume hood, protective clothing, and safety glasses when preparing the lanthanum solution. The reaction between the lanthanum oxide and acid (Sect. 7.7) is extremely exothermic.

5.3 A permanent ventilation system is required to eliminate the large quantity of hot exhaust gases produced during instrument operation. Since acetylene is a flammable gas, take precautions when using it. To avoid explosions, never pass acetylene through copper or high-copper alloy (brass, bronze) fittings or piping.

5.4 The operator must wear safety glasses to avoid eye damage from the ultraviolet light emitted by the flame.

5.5 To avoid in-line explosions, do not allow the pressure of acetylene being delivered to the instrument to exceed 15 psig (10.6 g/m^2). In the event of a flashback, turn off the gas control switch, the instrument power, and the gas tanks.

5.6 Follow manufacturer's operating guidelines carefully when optimizing gas flow rates. Too low gas flow rates can result in a combustion within the gas mixing chamber and therefore a flashback.

5.7 Check that the drain tube from the gas mixing chamber, fitted with a safety trap, is filled with water before igniting the flame. Keep the drain tube filled to prevent explosion in the chamber. The safety trap may be either looped or valved.

5.8 Avoid any contact with a hot burner head. Serious tissue burns will result.

5.9 Follow American Chemical Society guidelines regarding safe handling of chemicals used in this method (14.4).

6. APPARATUS AND EQUIPMENT

6.1 ATOMIC ABSORPTION SPECTROPHOTOMETER -- Select a double-beam instrument having a dual grating monochromator, photodetector, pressure-reducing valves, adjustable spectral bandwith, wavelength range of 190-800 nm, and provisions for interfacing with a strip chart recorder or a suitable data system.

6.1.1 Burner -- Use a long path, single slot air-acetylene burner head supplied by the manufacturer of the spectrophotometer.

6.1.2 Hollow Cathode Lamps -- Single element lamps are recommended. Multi-element lamps are available but are not recommended. They generally have a shorter lifespan, are less sensitive, require a higher operating current, and increase the chances of spectral interferences. When available, electrodeless discharge lamps (EDL) may also be used.

6.1.3 Monochromator -- To increase sensitivity of calcium and potassium determinations, use a monochromator equipped with a blaze grating in the range of 500-600 nm (14.5). For the analysis of sodium and magnesium, a blaze grating in the range of 200-250 nm is adequate.

6.1.4 Photomultiplier Tube -- A wide spectral range (160-900 nm) phototube is recommended. Select a red-sensitive phototube to detect potassium at 766.5 nm and to increase sensitivity to calcium at 422.7 nm.

6.2 The first time any glassware is used for making stock solutions and standards, clean with 0.6 N HCl and rinse thoroughly with water (Sect. 7.2) before use. Maintain a set of Class A volumetric flasks to be used only when making dilute working standards for the analysis of wet deposition samples. Store filled with water (Sect. 7.2) and covered.

6.3 LABORATORY FACILITIES -- Laboratories used for the analysis of wet deposition samples should be free from external sources of contamination. The use of laminar flow clean air workstations is recommended for sample processing and preparation to avoid the introduction of airborne contaminants. If a clean air bench is unavailable, samples must be capped or covered prior to analysis. A positive pressure environment within the laboratory is also recommended to minimize the introduction of external sources of contaminant gases and particulates. Windows within the laboratory should be kept closed at all times and sealed if air leaks are apparent. The use of disposable tacky floor mats at the entrance to the laboratory is helpful in reducing the particulate loading within the room.

7. REAGENTS AND CONSUMABLE MATERIALS

7.1 PURITY OF REAGENTS -- Use chemicals of reagent grade or better for all solutions. All reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society (ACS) where such specifications are available.

7.2 PURITY OF WATER -- Use water conforming to ASTM Specification D 1193, Type II (14.6). Point of use 0.2 micrometer filters are recommended for all faucets supplying water to prevent the introduction of bacteria and/or ion exchange resins into reagents, standard solutions, and internally formulated quality control check solutions.

7.3 ACETYLENE (C_2H_2) -- Fuel -- Minimum acceptable acetylene purity is 99.5% (v/v). Change the cylinder when the pressure reaches 75 psig (53 g/m^2) if the acetylene is packed in acetone. Pre-purified grades that contain a proprietary solvent can be used to 30 psig (21 g/m^2) before replacement. Avoid introducing these solvents into the instrument. Damage to the instrument's plumbing system can result. Solvent in the system is indicated by abnormally high pulsating background noise. To prevent solvent carryover, allow acetylene cylinders to stand for at least 24 hours before use.

CAUTION: Acetylene is a highly flammable gas. Follow the precautions in Sect. 5.3-6 regarding safe operating pressures, suitable plumbing, and operator safety.

7.4 CESIUM SOLUTION (1.0 mL = 100.0 mg Cs) -- Ionization Suppressant -- Dissolve 126.7 g of cesium chloride (CsCl), dried at 105°C for one hour, in water (Sect. 7.2) and dilute to 1 L. Store at room temperature in a high density polyethylene or polypropylene container. Add to samples and standards as directed in Sect. 9.4 and 11.4 for the determination of potassium and sodium.

7.5 HYDROCHLORIC ACID (6.0 N) -- Carefully add 1 volume of concentrated hydrochloric acid (HCl, sp gr 1.19) to an equal volume of water (Sect. 7.2).

7.6 HYDROCHLORIC ACID (0.6 N) -- Add 50 mL of concentrated hydrochloric acid (HCl, sp gr 1.19) to 900 mL of water (Sect. 7.2) and dilute to 1 L.

7.7 LANTHANUM SOLUTION (1.0 mL = 100.0 mg La) -- Releasing Agent -- In a glass 1 L volumetric flask, place 117.0 g of lanthanum oxide (La_2O_3), dried at 105°C for one hour. Add 6 N HCl very carefully to the solid in increments of about 0.5 mL. Cool the solution between additions. Continue adding the acid solution to the flask in increasing increments until a total of 500 mL of 6 N HCl has been added. Dilute to 1 L with water (Sect. 7.2). Store at room temperature in a high density polyethylene or polypropylene container. Add to samples and standards as directed in Sect. 9.4.3 and 11.4 for the determination of calcium and magnesium.

CAUTION: Dissolving lanthanum oxide in hydrochloric acid is a violently exothermic reaction; use extreme caution when dissolving the reagent. Refer to Sect. 5.2 for proper safety precautions when preparing this solution.

7.8 OXIDANT (air) -- The air may be provided by a compressor or commercially bottled gas supply. Remove oil, water, and other foreign matter from the air using a filter recommended by the manufacturer. Refer to the manufacturer's guidelines for recommended delivery pressure.

7.9 STOCK STANDARD SOLUTIONS -- Stock standard solutions may be purchased as certified solutions or prepared from ACS reagent grade materials as detailed below. Store the solutions at room temperature in high density polyethylene or polypropylene containers.

7.9.1 Calcium Solution, Stock (1.0 mL = 1.0 mg Ca) -- Add 2.497 g of calcium carbonate ($CaCO_3$), dried at 180°C for one hour, to approximately 600 mL of water (Sect. 7.2). Add concentrated hydrochloric acid (HCl, sp gr 1.19) slowly until all the solid has dissolved. Dilute to 1 L with water (Sect. 7.2).

7.9.2 Magnesium Solution, Stock (1.0 mL = 1.0 mg Mg) -- Dissolve 1.000 g of magnesium ribbon in a minimal volume of 6 N HCl and dilute to 1 L with water (Sect. 7.2).

7.9.3 Potassium Solution, Stock (1.0 mL = 1.0 mg K) -- Dissolve 1.907 g of potassium chloride (KCl), dried at 105°C for one hour, in water (Sect. 7.2) and dilute to 1 L.

7.9.4 Sodium Solution, Stock (1.0 mL = 1.0 mg Na) -- Dissolve 2.542 g of sodium chloride (NaCl), dried at 105°C for one hour, in water (Sect. 7.2) and dilute to 1 L.

7.10 SAMPLE CONTAINERS -- Use polyolefin sample cups that have been thoroughly rinsed with water (Sect. 7.2) before use.

8. SAMPLE COLLECTION, PRESERVATION, AND STORAGE

8.1 Collect samples in high density polyethylene (HDPE) containers that have been thoroughly rinsed with ASTM Type II water (7.2). Do not use strong mineral acids or alkaline detergent solutions for cleaning collection vessels. Residual acids may remain in the polyethylene matrix and slowly leach back into the sample. Alkaline detergents may also leave residues that may affect the sample chemistry. Cap collection bottles after cleaning to prevent contamination from airborne contaminants; air dry collection buckets in a laminar flow clean air workstation and wrap in polyethylene bags prior to use. If a laminar flow workstation is not available, pour out any residual rinse water and bag the buckets immediately. Do not dry the bucket interior by any method other than air drying in a laminar flow clean air workstation.

8.2 The frequency of sample collection and the choice of sampler design are dependent on the monitoring objectives. In general, the use of wet-only samplers is recommended to exclude dry deposition contributions, minimize sample contamination, retard evaporation, and enhance sample stability. Sample collection frequency may vary from subevent to monthly sampling periods. Collection periods of more than one week are not recommended since sample integrity may be compromised by longer exposure periods.

8.3 The dissolution of particulate materials can affect the stability of calcium, magnesium, sodium, and potassium in wet deposition samples (14.7). This instability generally results in a concentration increase for these constituents. Measurements should be made immediately after sample collection to obtain representative data. Refrigeration of samples at 4°C will minimize but not eliminate concentration changes.

8.3.1 Filtration of samples through a 0.45 micrometer membrane leached with water (Sect. 7.2) is effective at stabilizing samples that are influenced by the dissolution of alkaline particulate matter (14.7). Monitoring of the filtration procedure is necessary to ensure that samples are not contaminated by the membrane or filtration apparatus. Filtered samples are stable for six weeks when stored at room temperature.

9. CALIBRATION AND STANDARDIZATION

9.1 SETTING INSTRUMENT PARAMETERS

9.1.1 Lamp Current -- Refer to manufacturer's guidelines for optimization of this parameter. The use of excessively high currents will shorten lamp life. High currents also cause line broadening, resulting in a reduction in sensitivity and calibration curve linearity, especially in the determination of magnesium. The use of currents that are too low will cause lamp instability and insufficient throughput of energy through the instrument's optical system. The result is increased signal noise due to excess electrical gain applied to the photodetector.

9.1.2 Light Beam -- Position a small card over the burner slot to intercept the light beam from the hollow cathode lamp. Check that the beam is focused midway along the slot and, if necessary, focus according to the manufacturer's guidelines. Rotate the lamp within its holder for maximum energy output readings.

9.1.3 Burner/Beam Alignment -- Position a small card over the burner slot to intercept the light beam from the hollow cathode lamp. For optimal sensitivity when analyzing calcium, magnesium, potassium, and sodium, adjust the burner height so that the center of the light beam is approximately 6 mm above the surface of the burner slot. By adjusting the burner alignment and rotation, set the light beam to coincide with the burner slot. While observing from above, move the card along the full length of the burner slot to ensure that the beam is centered over the slot for the entire length of the burner. Optimize this parameter for maximum instrumental sensitivity as directed in Sect. 9.2.

9.1.4 Wavelength -- Set the wavelength of the spectrophotometer for each analyte according to Table 2 by following the manufacturer's operating guidelines. After the instrument has warmed up with the flame burning (about 30 minutes), check the wavelength and readjust if necessary.

Note: The sodium spectrum is characterized by a doublet at 589.0 nm and 589.5 nm. The wavelength chosen for sodium determinations depends on the degree of analytical sensitivity desired by the operator. A setting of 589.0 nm will provide maximum sensitivity in the concentration range of most wet deposition samples. For those samples with higher sodium concentrations, a less sensitive setting of 589.5 nm is more appropriate. Refer to Tables 1 and 2 for information regarding working ranges, standards, and detection limits for sodium at each wavelength setting.

9.1.5 Spectral Bandwidth -- The selection of optimum bandwidth depends upon the spectrum of the particular element being analyzed. For the determination of calcium, magnesium, and potassium, a relatively wide (1.0 nm) bandwidth is appropriate. Because the sodium spectrum is characterized by a doublet, use a smaller bandwidth of 0.5 nm.

9.1.6 External Gas Settings -- Follow manufacturer's recommended delivery pressures for air and acetylene. Never allow acetylene pressure to exceed 15 psig (10.6 g/m^2).

9.1.7 Nebulization Rate -- Set the acetylene and air flow rates as recommended by the manufacturer. Adjust the nebulizer sample uptake rate to approximately 5 mL/min. If an adjustable glass bead nebulizer is used, adjust it according to manufacturer's guidelines. Exact placement of the glass bead is critical to ensure that a uniform vapor of the smallest size particles is introduced into the flame. Improper spacing of the bead from the nebulizer end will result in poor precision and sensitivity. Optimize the sample uptake rate for maximum sensitivity as directed in Sect. 9.2.

Note: The nebulizer can clog easily if particulates are present in the samples. Symptoms of this are decreased sensitivity and/or dramatically increased signal noise, especially noticeable at the higher concentration levels. A thorough cleaning with a small diameter wire is usually sufficient to unclog the nebulizer.

9.1.8 Flame Conditions -- If the flame temperature is too low, compounds containing the analyte will not be completely dissociated. Alternatively, too high a flame temperature may result in ionization. In both cases, a decrease in the apparent concentration of the analyte will result. In general, calcium exhibits maximum sensitivity at higher fuel and oxidant flow rates. Maximum sensitivity for potassium is obtained with minimal gas flow rates, resulting in lower flame temperature and allowing longer residence time of the atomic vapor in the flame. The MDLs stated in Sect. 1.3 for magnesium and sodium are obtained over a wide range of flame conditions. Optimize this parameter for maximum instrumental sensitivity as directed in Sect. 9.2.

CAUTION: Follow manufacturer's operating guidelines carefully when setting gas flow rates since combustion within the gas mixing chamber can occur if caution is not exercised.

9.2 Optimization -- Allow the instrument to warm up for 30 minutes before beginning the optimization. Set the instrument readout to absorbance units and set the integration time to <0.5 seconds. Use either a strip chart recorder or set the display in a continuous read mode to monitor absorbance readings. Aspirate a calibration standard at a concentration near the midpoint of the working range (Sect. 9.4). While watching the absorbance readings, adjust the instrument parameters with small, discrete changes until maximum values are obtained. Parameters such as flame conditions, nebulization rate, and the region of maximum atom concentration in the flame are interrelated. Adjustment of any of these three parameters usually requires adjustment of the other two.

9.3 Instrument Response Time -- Determine the minimum sample uptake time before taking a reading on a sample or standard solution. Use either a strip chart recorder or set the display in a continuous read mode to monitor absorbance readings. After purging the system with water (Sect. 7.2), aspirate the highest calibration standard (Sect. 9.4) and measure the length of time necessary to obtain a stable reading. Aspirate water (Sect. 7.2) and measure the time it takes for the baseline to return to zero.

Note: If the time necessary for the baseline to return to zero is longer than 15 seconds, a clogged nebulizer may be suspect. If purging time begins to increase during sample analysis, this may also be an indication of nebulizer clogging.

9.4 CALIBRATION SOLUTIONS

9.4.1 Five calibration solutions and one zero standard are needed to generate a suitable calibration curve. The lowest calibration solution should contain the analyte of interest at a concentration greater than or equal to the method detection limit. The highest solution should approach the expected upper limit of concentration of the analyte in wet deposition. Prepare the remaining solutions such that they are evenly distributed throughout the concentration range. Suggested calibration standards for each analyte are listed in Table 2.

9.4.2 Prepare all calibration standards by diluting the stock standards (Sect. 7.9) with water (Sect. 7.2). Use glass (Class A) or plastic pipettes that are within the bias and precision tolerances specified by the manufacturer. The calibration standards are stable for three months if stored at room temperature in high density polyethylene or polypropylene containers.

9.4.3 After preparing the calibration standards to volume, add the lanthanum solution (Sect. 7.7) to the calcium and magnesium standards to yield 1000 mg/L La. Add the cesium solution (Sect. 7.4) to the potassium and sodium standards for 1000 mg/L Cs. Mix well. Use the same stock of ionization suppressant or releasing agent for the samples and the calibration standards.

Note: The final volume of each working standard solution exceeds the nominal volume by 1%. This adjustment is necessary to maintain consistency when the appropriate volume of suppressor solution is added to the wet deposition samples.

9.5 CALIBRATION

9.5.1 To establish a baseline, aspirate the zero standard and set the absorbance readout to 0.000. Aspirate the calibration standards, allowing time for each standard to equilibrate in the flame and gas mixing chamber before measuring the absorbance (Sect. 9.3). Construct calibration curves for each of the four analytes according to Sect. 12.

9.5.2 Analyze all the calibration standard solutions. The apparent concentration values must agree with the nominal concentrations within the predetermined control limits (Sect. 10.2.1) of three times the standard deviation ($\pm 3s$). If results fall outside of these limits, recalibrate the instrument. If there is a consistent bias greater than $\bar{x} \pm 2s$ and less than $\bar{x} \pm 3s$, for all of the concentration values measured, reestablish the baseline with the zero standard and reanalyze the calibration standards.

9.5.3 Verify the calibration curve after every ten samples and at the end of each day's analyses according to Sect. 10.7.

10. QUALITY CONTROL

10.1 Each laboratory using this method should develop formalized quality control protocols to continually monitor the bias and precision of all measurements. These protocols are required to ensure that the measurement system is in a state of statistical control. Estimates of bias and precision for wet deposition analyses cannot be made unless these control procedures are followed. Detailed guidelines for the development of quality assurance and quality control protocols for precipitation measurement systems are published in a manual available from the United States Environmental Protection Agency, Research Triangle Park, NC 27711 (14.8). Included in this manual are procedures for the development of statistical control charts for use in monitoring bias and precision as well as recommendations for the introduction of reagent blanks, laboratory duplicates, field duplicates, spike samples, and performance evaluation samples. These guidelines are to be used by all laboratories involved with wet deposition measurements.

10.2 ESTABLISHMENT OF WARNING AND CONTROL LIMITS -- Warning and control limits are used to monitor drift in the calibration curve, analyses of quality control check samples (QCS), and measured recoveries from laboratory spikes.

10.2.1 Calibration Curve -- After a calibration curve has been constructed according to Sect. 12, reanalyze additional aliquots of all the standards. Calculate the concentrations using the previously derived calibration curve. Repeat this procedure until at least ten

determinations at each concentration level have been made. These data should be collected on ten different days to provide a realistic estimate of the method variability. Calculate a standard deviation (s) at each concentration level. Use the nominal standard concentration as the mean value ($\bar{x}$) for determining the control limits. A warning limit of $\bar{x} \pm 2s$ and a control limit of $\bar{x} \pm 3s$ should be used. Reestablish these limits whenever instrumental operating conditions change.

10.2.2 Quality Control Check Samples (QCS) -- Calculate warning and control limits for QCS solutions from a minimum of ten analyses performed on ten days. Use the calculated standard deviation (s) at each QCS concentration level to develop the limits as described in Sect. 10.2.1. Use the certified or NBS traceable concentration as the mean (target) value. Constant positive or negative measurements with respect to the true value are indicative of a method or procedural bias. Utilize the data obtained from QCS measurements as in Sect. 10.6 to determine when the measurement system is out of statistical control. The standard deviations used to generate the QCS control limits should be comparable to the single operator precision reported in Table 4. Reestablish new warning and control limits whenever instrumental operating conditions are varied or QCS concentrations are changed.

10.2.3 Laboratory Spike Solutions -- A minimum of ten analyte spikes of wet deposition samples is required to develop a preliminary data base for the calculation of warning and control limits for spike recovery data. Select the spike concentration such that the working range of the method will not be exceeded. Samples selected for the initial spike recovery study should represent the concentration range common to wet deposition samples in order to reliably estimate the method accuracy. Calculate a mean and standard deviation of the percent recovery data using the formulas provided in the glossary. Determine warning and control limits using $\pm 2s$ and $\pm 3s$, respectively. If the data indicate that no significant method bias exists (14.9), the 100 percent recovery is used as the mean percent recovery. Where a significant bias is determined at the 95% confidence level, the control limits are centered around the bias estimate. Routine spiked sample analyses that yield percent recovery data outside of the control limits are an indication of matrix interferences that should be resolved before routine analyses are continued.

10.2.4 All warning and control limits should be reevaluated on a continual basis as additional data are collected during routine analyses. The limits should be broadened or narrowed if a recalculated standard deviation under similar operating conditions provides a different estimate of the procedure variability.

10.3 Monitor the cleaning procedure by pouring a volume of water (Sect. 7.2) that approximates the median sample size into the collection vessel. Allow the water to remain in the sealed or capped collection container for at least 24 hours and determine the concentration of the analytes of interest. If any of the measured concentrations exceed the MDL, a contamination problem is indicated in the cleaning procedure. Take corrective action before the sampling containers are used for the collection of wet deposition.

10.4 Keep daily records of calibration data and the instrument operating parameters used at the time of data acquisition. Use these historical data as general performance indicators. Gross changes in sensitivity, curve linearity, or photomultiplier tube voltage are indicative of a problem. Possibilities include instrument malfunction, clogged nebulizer, incomplete optimization, bad hollow cathode lamp, contamination, and inaccurate standard solutions.

10.5 Precision will vary over the analyte concentration range. Standard deviation (s) increases as concentration increases while relative standard deviation (RSD) decreases. At approximately 100 times the MDL, the RSD should remain less than 1%.

10.6 Analyze a quality control check sample (QCS) after a calibration curve has been established. This sample may be formulated in the laboratory or obtained from the National Bureau of Standards (NBS Standard Reference Material 2694, Simulated Rainwater). The check sample(s) selected must be within the range of the calibration standards. Prepare according to Sect. 11.4. If the measured value for the QCS falls outside of the $\pm 3s$ limits (Sect. 10.2.2), or if two successive QCS checks are outside of the $\pm 2s$ limits, a problem is indicated with the spectrophotometer or calibration curve. Reestablish the baseline with the zero standard and/or recalibrate. If the QCS analysis is still beyond control limits, inaccurate working standards might be the problem. Prepare new standards. Plot the data obtained from the QCS checks on a control chart for routine assessments of bias and precision.

10.7 Verify the calibration curve after a maximum of ten samples and at the end of each day's analyses. Analyze a zero standard and calibration standards at the low and high ends of the working range. If the routine calibration checks do not meet the criteria described in Sect. 10.6, recalibrate the system and reanalyze all samples from the last time the system was in control. Verify the new calibration curve with the QCS according to Sect. 10.6 and reanalyze all samples from the last time the measurement system was in control.

10.8 Submit a Field Blank (FB) to the laboratory for every 20 samples. The FB may consist of a water sample (Sect. 7.2) or a known reference solution that approximates the concentration levels characteristic of wet deposition. The FB is poured into the sampling vessel at the field site and undergoes identical processing and analytical protocols as the wet deposition sample(s). Use the analytical data obtained from the FB to determine any contamination introduced in the field and laboratory handling procedures. The data from the known reference solution can be used to calculate a system precision and bias.

10.9 Prepare and analyze a laboratory spike of a wet deposition sample according to the guidelines provided in "Quality Assurance Manual for Precipitation Measurement Systems" (14.8). Compare the results obtained from the spiked samples to those obtained from identical samples to which no spikes were added. Use these data to monitor the method percent recovery as described in Sect. 10.2.3.

10.10 Participation in performance evaluation studies is recommended for precipitation chemistry laboratories. The samples used for these performance audits should contain the analytes of interest at concentrations within the normal working range of the method. The true values are unknown to the analyst. Performance evaluation studies for precipitation chemistry laboratories are conducted semiannually by the USEPA Performance Evaluation Branch, Quality Assurance Division, Research Triangle Park, NC 27711.

10.11 INSTRUMENT MAINTENANCE -- Strictly adhere to manufacturer's maintenance schedule.

10.11.1 Exposed optical mirrors should be replaced yearly to maintain optimal sensitivity and precision.

10.11.2 If the instrument is used for other sample types that have high analyte concentrations it may be necessary to disassemble the entire burner-nebulizer system for cleaning before analyzing wet deposition samples. This is best accomplished by placing the components in a water (Sect. 7.2) bath in an ultrasonic cleaner for a half hour. Rinse with water (Sect. 7.2) after cleaning and allow to air dry in a dust-free environment before reassembly. Check o-rings for wear and replace if necessary.

11. PROCEDURE

11.1 Set instrument parameters and optimize the instrument each day according to Sect. 9.1-2.

11.2 Prepare all standards and construct calibration curves according to Sect. 9.4-5.

11.3 After the calibration curve is established, analyze the QCS. If the measured value for the QCS is not within the specified limits (Sect. 10.2.2), refer to Sect. 10.7.

11.4 Pipette the appropriate cesium or lanthanum solution into the empty sample cup (Cs or La:Sample = 1:100). For the determination of calcium and magnesium, use the lanthanum solution described in Sect. 7.7. For potassium and sodium determinations, add cesium solution (Sect. 7.4). Pour the sample into the sample cup containing Cs or La; 3 mL of sample for 30 uL of Cs or La is suggested. Mix well, aspirate, wait for equilibration in the flame (Sect. 9.3), and record the measured absorbance (or concentration).

11.5 If the absorbance (or concentration) for a given sample exceeds the working range of the system, dilute a separate sample with water (Sect. 7.2). Prepare and analyze according to Sect. 11.4.

11.6 When analysis is complete, rinse the system by aspirating water (Sect. 7.2) for ten minutes. Follow the manufacturer's guidelines for instrument shut-down.

12. CALCULATIONS

12.1 For each analyte of interest, calculate a linear least squares fit of the standard concentration as a function of the measured absorbance. The linear least squares equation is expressed as follows:

$$y = B_0 + B_1 x$$

where: y = standard concentration in mg/L
x = absorbance measured
B_0 = y-intercept calculated from: $\bar{y} - B_1\bar{x}$
B_1 = slope calculated from:

$$\sum_{i=1}^{n} (x_i - \bar{x})(y_i - \bar{y}) / \sum_{i=1}^{n} (x_i - \bar{x})^2$$

where: $\bar{x}$ = mean of absorbances measured
$\bar{y}$ = mean of standard concentrations
n = number of samples

The correlation coefficient should be 0.9995 or greater. Determine the concentration of analyte of interest from the calibration curve.

12.2 If the relationship between concentration and absorbance is nonlinear, use a second degree polynomial least squares equation to derive a curve with a correlation ≥ 0.9995. The second degree polynomial equation is expressed as follows:

$$y = B_2x^2 + B_1x + B_0$$

A computer is necessary for the derivation of this function. Determine the concentration of analyte of interest from the calibration curve.

12.3 An integration system or internal calibration software may also be used to provide a direct readout of the concentration of the analyte of interest.

12.4 Report concentrations in mg/L as Ca^{+2}, Mg^{+2}, Na^{+}, and K^{+}. Do not report data lower than the lowest calibration standard.

13. PRECISION AND BIAS

13.1 The mean percent recovery and mean bias of this method were determined from the analysis of spiked wet deposition samples according to ASTM Standard Practice D4210, Annex A4 (14.9). The results are summarized in Table 3. No statistically significant biases were found for any of the metal cations.

13.2 Single-operator precision and bias were obtained from the analysis of quality control check samples that approximated the levels common to wet deposition samples. These results reflect the accuracy that can be expected when the method is used by a competent operator. These data are presented in Table 4.

14. REFERENCES

14.1 Annual Book of ASTM Standards, Part 42, "Standard Definitions of Terms and Symbols Relating to Molecular Spectroscopy," Standard E 131-81, 1981, p. 66.

14.2 Annual Book of ASTM Standards, Section 11, Vol. 11.01 (1), "Excerpts from Standard for Metric Practice," Standard E 380-79, 1983, pp. 679-694.

14.3 Van Loon, J. C., Analytical Atomic Absorption Spectroscopy, Selected Methods Academic Press, Inc., New York, N. Y., 1980, p. 42.

14.4 "Safety in Academic Chemistry Laboratories," American Chemical Society Publication, Committee on Chemical Safety, 3rd Edition, 1979.

14.5 Instrumentation Laboratory, Inc., Operator's Manual Model IL951, AA/AE Spectrophotometer, Instrumentation Laboratory, Inc., Wilmington, Massachusetts, 1982, pp. 3-4.

14.6 Annual Book of ASTM Standards, Section 11, Vol. 11.01 (1), "Standard Specification for Reagent Water," Standard D 1193-77, 1983, pp. 39-41.

14.7 Peden, M. E. and Skowron, L. M., 'Ionic Stability of Precipitation Samples," Atmos. Environ. 12, 1978, pp. 2343-2349.

14.8 Topol, L. E., Lev-On, M., Flanagan, J., Schwall, R. J., Jackson, A. E., Quality Assurance Manual for Precipitation Measurement Systems, 1985, U.S. Environmental Protection Agency, Environmental Monitoring Systems Laboratory, Research Triangle Park, NC 27711.

14.9 Annual Book of ASTM Standards, Section 11, Vol. 11.01 (1), "Practice for Intralaboratory Quality Control Procedures and a Discussion of Reporting Low-Level Data," Standard D4210 Annex A4, 1983, pp. 15-16.

Table 1. Method Detection Limits and Concentration Ranges for Flame Atomic Absorption Spectrophotometric Analysis of Wet Deposition.

Analyte	Method Detection Limit, mg/L	Concentration Range, mg/L
Calcium	0.007	0.030 - 3.00
Magnesium	0.002	0.010 - 1.00
Potassium	0.003	0.010 - 1.00
Sodium	0.003[a]	0.010 - 1.00[a]
	0.007[b]	0.020 - 2.00[b]

a. 589.0 nm wavelength setting
b. 589.5 nm wavelength setting

Table 2. Operating Conditions and Suggested Calibration Standard Concentrations for the Determination of Calcium, Magnesium, Potassium, and Sodium in Wet Deposition Samples.[a]

Analyte	Wavelength Setting, nm	Spectral Bandwidth, nm	Working Standards, mg/L
Calcium	422.7	1.0	zero
			0.03
			0.75
			1.50
			2.25
			3.00
Magnesium	285.2	1.0	zero
			0.01
			0.25
			0.50
			0.75
			1.00
Potassium	766.5	1.0	zero
			0.01
			0.25
			0.50
			0.75
			1.00
Sodium[b]	589.0	0.5	zero
			0.01
			0.25
			0.50
			0.75
			1.00
	589.5	0.5	zero
			0.02
			0.50
			1.00
			1.50
			2.00

a. Based on the MDL and 95th percentile concentration of each analyte obtained from analyses of over five thousand wet deposition samples from the NADP/NTN precipitation network.
b. Refer to Sect. 9.1.2 for details on wavelength selection

Table 3. Single-Operator Precision and Bias for Calcium, Magnesium, Potassium, and Sodium Determined from Analyte Spikes of Wet Deposition Samples.

Analyte	Amount Added, mg/L	n[a]	Mean Percent Recovery	Mean Bias, mg/L	Standard Deviation, mg/L	Statistically Significant Bias?[b]
Calcium	0.087	20	101.5	0.001	0.010	No
	0.221	20	98.3	-0.003	0.011	No
Magnesium	0.018	20	97.2	-0.001	0.001	No
	0.045	20	96.6	-0.002	0.002	No
Potassium	0.021	18	145.2	0.010	0.006	No
	0.052	13	108.1	0.004	0.002	No
Sodium[c]	0.099	19	107.1	0.007	0.011	No
	0.249	20	100.2	0.000	0.008	No

a. Number of replicates
b. 95% Confidence Level
c. 589.0 nm wavelength

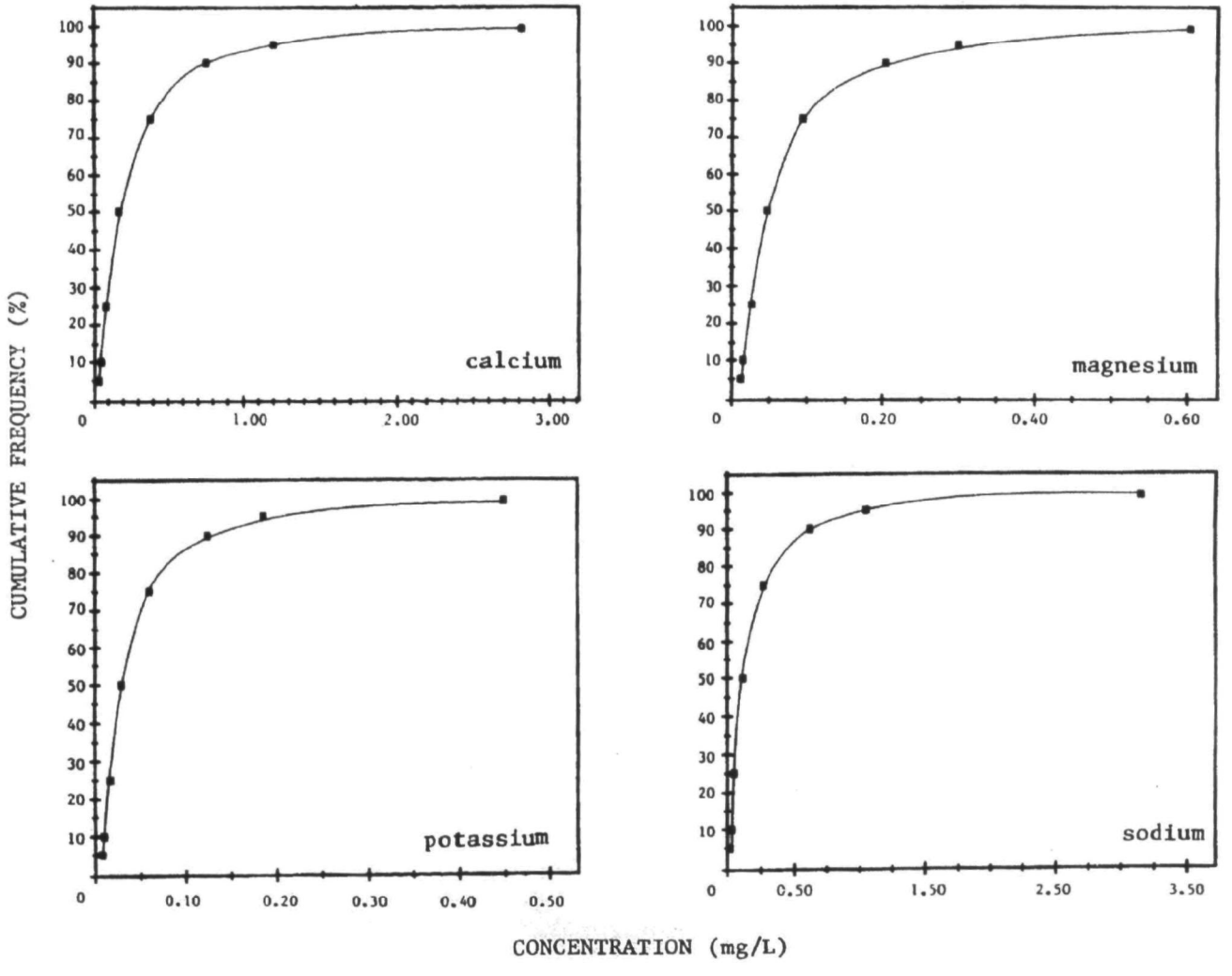
Table 4. Single-Operator Precision and Bias for Calcium, Magnesium, Potassium, and Sodium Determined from Quality Control Check Samples.

Analyte	Theoretical Concentration, mg/L	Measured Concentration, mg/L	n[a]	Bias, mg/L	Bias, %	Precision, s, mg/L	Precision, RSD, %
Calcium	0.053	0.051	145	-0.002	-3.8	0.002	3.9
	0.406	0.413	145	0.007	1.7	0.003	0.7
Magnesium	0.018	0.017	145	-0.001	-5.6	0.001	5.9
	0.084	0.083	145	-0.001	-1.2	0.001	1.2
Potassium	0.021	0.020	127	-0.001	-4.8	0.001	5.0
	0.098	0.095	122	-0.003	-3.1	0.001	1.0
Sodium[b]	0.082	0.084	123	0.002	2.4	0.001	1.2
	0.465	0.479	122	0.014	3.0	0.003	0.6

The above data were obtained from records of measurements made under the direction of the NADP quality assurance program.

a. Number of replicates
b. 589.0 nm wavelength

Figure 1. Percentile Concentration Values Obtained from Wet Deposition Samples: Calcium, Magnesium, Potassium, and Sodium.



Libraries

OLS Record

RECORD NUMBER: 2

Main Title	Development of Standard Methods for the Collection and Analysis of Precipitation
Author	Peden, M E. ; Bachman, S R ; Brennan, C J , Demir, B. , James, K O. ;
CORP Author	Illinois State Water Survey Div , Champaign ,Environmental Monitoring and Support Lab.-Cincinnati, OH.
Year Published	1986
Report Number	EPA-R-810780; EPA/600/4-86/024;
Holdings	**LIBRARY** **CALL NUMBER** NTIS MOST EPA LIBRARIES HAVE FICHE COPY. CHECK WITH INDIVIDUAL LIBRARY ABOUT PAPER COPY.
Owner Libraries	- National Technical Information Service
Stock Number	PB86-201365
Document Type	NT
Control Number	619921977
Cataloging Source	NTIS/MT
NTIS Title Notes	Rept. for May 83-Apr 86.
PUB Date Free Form	May 86
Collation	278p
Supplementary Notes	Sponsored by Environmental Monitoring and Support Lab.-Cincinnati, OH.
Subjects	Standards, Precipitation(Meteorology); Water pollution, Evaluation; Collecting methods; Manuals; Preserving, Processing; Accuracy, Flame photometry, Colorimetric analysis; Spectrophotometry, Chromatographic analysis; Volumetric analysis; Laboratories, Comparison; Acid precipitation
Category Codes	13B; 4B; 7D, 68A; 68D; 55C; 99A
NTIS Prices	PC A13/MF A01
Primary Description	600/06
Abstract	To provide the scientific community with a set of standardized procedures for the collection and analysis of wet precipitation samples, an analytical methods manual for use in acid deposition studies has been developed The manual includes detailed methods documentation for the major inorganic constituents of interest in wet deposition as well as guidelines for the collection, preservation, and processing of samples. The analytical methodologies include

preservation, and processing of samples. The analytical methodologies include flame atomic absorption spectrophotometry, ion selective electrode, automated colorimetry, ion chromatography, and titrimetric procedures.

Search Terms Summary Prior Next Manual Help *Display Records as Bibliography*

If there is an AREA footer, put it here

EPA Home | Privacy and Security Notice | Contact Us

Last updated on Tuesday, December 31st, 2069
URL http //cave epa gov/cgi/nph-bwcgis/BASIS/ncat/lib/ncat/DDW