Designation: D 5086 – 01

Standard Test Method for Determination of Calcium, Magnesium, Potassium, and Sodium in Atmospheric Wet Deposition by Flame Atomic Absorption Spectrophotometry[1]

This standard is issued under the fixed designation D 5086; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ϵ) indicates an editorial change since the last revision or reapproval.

1. Scope

1.1 This test method is applicable to the determination of calcium, magnesium, potassium, and sodium in atmospheric wet deposition (rain, snow, sleet, and hail) by flame atomic absorption spectrophotometry (FAAS). **(1)**[2]

1.2 The concentration ranges are listed below. The range tested was confirmed using the interlaboratory collaborative test (see Table 1 for a statistical summary of the collaborative test).

	MDL (mg/L) **(2)**	Range of Method (mg/L)	Range Tested (mg/L)
Calcium	0.009	0.03–3.00	0.168–2.939
Magnesium	0.003	0.01–1.00	0.039–0.682
Potassium	0.003	0.01–1.00	0.029–0.499
Sodium	0.003	0.01–2.00	0.105–1.84

1.3 The method detection limit (MDL) is based on single operator precision **(2)** and may be higher or lower for other operators and laboratories. Many workers have found that this test method is reliable at lower levels than were tested, but the precision and bias data presented are insufficient to justify their use at lower levels.

1.4 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.* Specific warning statements are given in 8.3, 8.7, 12.1.8, and Section 9.

2. Referenced Documents

2.1 *ASTM Standards:*

D 883 Terminology Relating to Plastics[3]

D 1129 Terminology Relating to Water[4]

D 1193 Specification for Reagent Water[4]

D 1356 Terminology Relating to Sampling and Analysis of Atmospheres[5]

D 2777 Practice for Determination of Precision and Bias of Applicable Methods of Committee D-19 on Water[4]

D 4453 Practice for Handling of Ultra-Pure Water Samples[4]

D 4691 Practice for Measuring Elements in Water by Flame Atomic Absorption Spectrophotometry[4]

D 5012 Guide for Preparation of Materials Used for the Collection and Preservation of Atmospheric Wet Deposition[5]

E 131 Terminology Relating to Molecular Spectroscopy[6]

E 275 Practice for Describing and Measuring Performance of Ultraviolet, Visible, and Near Infrared Spectrophotometers[6]

E 694 Specification for Laboratory Glass Volumetric Apparatus[7]

IEEE/ASTM SI 10 Standard for Use of the International System of Units (SI): The Modern Metric System[7]

3. Terminology

3.1 *Definitions*—For definitions of terms used in this test method, refer to Terminologies D 883, D 1129, D 1356, E 131, and Practices D 4691, E 275, and IEEE/ASTM SI 10.

3.1.1 *method detection limit, MDL*—the minimum concentration of an analyte that can be reported with 99 % confidence that the value is above zero based on a standard deviation of greater than seven repetitive measurements of a solution containing the analyte at a concentration near the low standard. The analyte concentration of this solution should not be greater than ten times the estimated MDL.

4. Summary of Test Method

4.1 A solution containing the metal(s) of interest is aspirated as a fine mist into an air acetylene 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 from a distinct line source of light, usually a hollow

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[1] This test method is under the jurisdiction of ASTM Committee D22 on Sampling and Analysis of Atmospheres and is the direct responsibility of Subcommittee D22.06 on Atmospheric Deposition.

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[2] The boldface numbers in parentheses refer to a list of references at the end of this test method.

[3] *Annual Book of ASTM Standards*, Vol 08.01.

[4] *Annual Book of ASTM Standards*, Vol 11.01.

[5] *Annual Book of ASTM Standards*, Vol 11.03.

[6] *Annual Book of ASTM Standards*, Vol 03.06.

[7] *Annual Book of ASTM Standards*, Vol 14.04.

TABLE 1 Interlaboratory Precision and Bias for Calcium, Magnesium, Potassium, and Sodium Determined from Analyte Spikes of Synthetic Atmospheric Wet Deposition Samples

Element	Number of Observations	Amount Added, mg/L	Mean Recovery, mg/L	S_t [A]	95 % Reproducibility Limit	S_o [B]	95 % Repeatability Limit	Bias, mg/L	Bias, %	Significant at 5 % Level
Ca	18	0.168	0.160	0.0062	0.017	0.0063	0.018	−0.008	−4.76	yes
	21	0.382	0.332	0.027	0.076	0.011	0.031	−0.030	−7.85	yes
	19	0.769	0.722	0.018	0.050	0.0091	0.025	−0.047	−6.11	yes
	21	1.448	1.334	0.038	0.106	0.025	0.070	−0.114	−7.87	yes
	20	2.939	2.770	0.047	0.132	0.037	0.104	−0.169	−5.75	yes
Mg	18	0.039	0.037	0.0033	0.0092	0.0016	0.0045	−0.002	−5.13	yes
	17	0.089	0.090	0.0061	0.017	0.0019	0.0053	0.001	1.12	no
	15	0.178	0.180	0.0057	0.016	0.0029	0.0081	0.002	1.12	no
	17	0.336	0.336	0.014	0.039	0.0038	0.011	0.00	0.00	no
	17	0.682	0.696	0.012	0.034	0.0037	0.010	0.014	2.05	yes
K	16	0.029	0.043	0.0036	0.010	0.0032	0.0090	0.014	48.3	yes
	16	0.065	0.068	0.0046	0.013	0.0012	0.0034	0.003	4.62	yes
	15	0.130	0.132	0.013	0.036	0.0038	0.011	0.002	1.54	no
	17	0.246	0.239	0.020	0.056	0.010	0.028	−0.007	−2.84	no
	17	0.499	0.507	0.025	0.070	0.014	0.039	0.008	1.60	no
Na	18	0.225	0.219	0.014	0.039	0.0056	0.016	−0.006	−2.67	no
	22	0.105	0.104	0.0010	0.027	0.0021	0.0059	−0.001	−0.95	no
	20	0.239	0.235	0.0053	0.015	0.0038	0.011	−0.004	−1.67	yes
	17	0.481	0.475	0.0070	0.020	0.0046	0.013	−0.006	−1.24	yes
	18	0.906	0.856	0.0087	0.024	0.0073	0.020	−0.050	−5.52	yes
	22	1.84	1.85	0.041	0.115	0.021	0.059	0.01	0.54	no

[A] Between laboratory precision, reproducibility.

[B] Within laboratory precision (pooled single operator precision), repeatability.

cathode lamp specific to the metal of interest, passed 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:

$$\log (I_o/I) = abc = A \qquad (1)$$

(1)

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, and
A = absorbance.

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

5. Significance and Use

5.1 This test method may be used for the determination of calcium, magnesium, potassium, and sodium in atmospheric wet deposition samples.

5.2 Emphasis is placed on the easily contaminated quality of atmospheric wet deposition samples due to the low concentration levels of dissolved metals commonly present.

5.3 Annex A1 represents cumulative frequency percentile concentration plots of calcium, magnesium, potassium, and sodium obtained from analyses of over five thousand wet deposition samples. These data may be used as an aid in the selection of appropriate calibration standard concentrations. **(3)**

6. Interferences

6.1 A chemical interference can 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, such as lanthanum, to the sample solution reduces or eliminates chemical interferences and may increase the sensitivity of this test method.

6.2 Alkali metals, such as potassium and sodium, can undergo ionization in an air-acetylene flame resulting in a decrease in ground state atoms available for measurement by atomic absorption. The 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 results in an enhanced atomic absorption signal for both potassium and sodium.

6.3 If a sample containing low concentrations of the metal being measured is analyzed immediately after a sample having a concentration exceeding the concentration of the highest calibration standard, sample carryover can result in elevated readings due to residual metal from the previous sample. To prevent this interference, routinely aspirate water for about 15 s 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.

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

7. Apparatus

7.1 *Atomic Absorption Spectrophotometer*—Select a double-beam instrument having a monochromator, photodetector, pressure-reducing valves, adjustable spectral bandwidth, and a wavelength range of 190 to 800 nm. Peripheral equipment may include a strip chart recorder or a suitable data system.

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

7.1.2 *Hollow Cathode Lamps*—Single element lamps are recommended. Multi-element lamps are available but are not recommended. They have a shorter lifespan, are less sensitive, require a higher operating current, and increase the chances of spectral interferences.

7.1.3 *Monochromator*—To increase the sensitivity for calcium and potassium measurements, a monochromator equipped with a blaze grating in the range of 500 to 600 nm is recommended. For the analysis of magnesium and sodium, a blaze grating in the range of 200 to 250 nm is adequate.

7.1.4 *Photomultiplier Tube*—A wide spectral range (160 to 900 nm) photomultiplier tube is recommended. Select a red-sensitive photomultiplier tube to detect potassium at 766.5 nm and to increase sensitivity for calcium at 422.7 nm.

7.2 *Volumetric Pipets*—Maintain a set of Class A volumetric pipets (see Specification E 694) to be used only when making dilute calibration solutions for the analysis of atmospheric wet deposition samples. Alternatively, disposable tip pipets may be used.

7.3 *Volumetric Flasks*—Maintain a set of Class A volumetric flasks (see Specification E 694) to be used only when making dilute calibration solutions for the analysis of atmospheric wet deposition samples.

7.3.1 The first time any glassware is used for making stock solutions and standards, clean with HCl (1+1) and rinse thoroughly with water before use.

7.3.2 Store clean glassware filled with water and covered.

7.4 *Laboratory Facilities*—Laboratories used for the analysis of atmospheric wet deposition samples should be free from external sources of contamination.

7.4.1 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 workstations is unavailable, samples must be capped or covered prior to analysis.

7.4.2 A positive pressure environment within the laboratory is 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 leaks are apparent.

7.4.3 The use of disposable tacky floor mats at the entrance to the laboratory is helpful in reducing the particulate loading within the room.

8. Reagents and Materials

8.1 *Purity of Reagents*—Use reagent grade or higher grade chemicals 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.[8]

8.2 *Purity of Water*—Unless otherwise indicated, references to water shall be understood to mean reagent water as defined by Type I of Specification D 1193. Point of use 0.2 µm filters are recommended for all faucets supplying water to prevent the introduction of bacteria and/or ion exchange resins into reagents.

8.3 *Acetylene (Fuel)*—Minimum acceptable acetylene purity is 99.5 % (*v/v*). Change the cylinder when the pressure reaches 517 kPa (75 psig) if the acetylene is packed in acetone. Pre-purified grades that contain a proprietary solvent can be used to 207 kPa (30 psig) before replacement. Avoid introducing these solvents into the instrument. Damage to the instrument's plumbing system can result. To prevent solvent carryover, allow acetylene cylinders to stand for at least 24 h before use. (**Warning—**Acetylene is a highly flammable gas. Follow the precautions in 9.3-9.6 regarding safe operating pressures, suitable plumbing, and operator safety.)

8.4 *Cesium Solution (Ionization Suppressant)*—Dissolve 126.7 g cesium chloride (CsCl), dried at 105°C for 1 h, in water and dilute to 1 L. Store at room temperature in a high density polyethylene or polypropylene container.

8.5 *Hydrochloric Acid* (1+1)—Carefully add one volume of concentrated hydrochloric acid (HCl, sp gr 1.19) to an equal volume of water.

8.6 *Hydrochloric Acid* (1+19)—Carefully add 50 mL of concentrated hydrochloric acid (HCl, sp gr 1.19) to 900 mL of water and dilute to 1 L.

8.7 *Lanthanum Solution (Releasing Agent)*—In a glass 1 L volumetric flask, place 117.3 g of lanthanum oxide (La_2O_3), dried at 105°C for 1 h. Wet with water and add HCl (1+1) in small increments until a total of 500 mL of HCl (1+1) has been added. Cool the solution between additions. Dilute to 1 L with water. Store at room temperature in a high density polyethylene or polypropylene container. (**Warning—**Dissolving lanthanum oxide in hydrochloric acid is a strongly exothermic reaction; use extreme caution when dissolving the reagent. Refer to 9.1 for proper safety precautions when preparing this solution.)

8.8 *Oxidant (air)*—The air may be provided by a compressor or commercially bottled 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.

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[8] *Reagent Chemicals, American Chemical Society Specifications,* American Chemical Society, Washington, DC. For suggestions on the testing of reagents not listed by the American Chemical Society, see *Analar Standards for Laboratory Chemicals*, BDH Ltd., Poole, Dorset, U.K., and the *United States Pharmacopeia and National Formulary*, U.S. Pharmacopeial Convention, Inc. (USPC), Rockville, MD.

8.9 *Stock Standard Solutions*—Stock standard solutions may be purchased as certified solutions or prepared from ACS reagent grade materials as detailed in 8.9.1-8.9.4. Store the solutions at room temperature in high density polyethylene or polypropylene containers.

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

8.9.2 *Magnesium Solution, Stock* (1.0 mL = 1.0 mg Mg)—Dissolve 1.000 g of magnesium ribbon in a minimal volume of HCl (1+1) and dilute to 1 L with water.

8.9.3 *Potassium Solution, Stock* (1.0 mL = 1.0 mg K)—Dissolve 1.907 g of potassium chloride (KCl), dried at 105°C for 1 h, in water and dilute to 1 L.

8.9.4 *Sodium Solution, Stock* (1.0 mL = 1.0 mg Na)—Dissolve 2.542 g of sodium chloride (NaCl), dried at 105°C for 1 h, in water and dilute to 1 L.

8.10 *Sample Containers*—Use polyolefin or polystyrene sample cups that have been thoroughly rinsed with water before use.

9. Hazards

9.1 Use a fume hood, protective clothing, and safety glasses when handling acids or preparing the lanthanum solution.

9.2 A permanent ventilation system is required to eliminate the large quantity of hot exhaust gases produced during instrument operation.

9.3 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.

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

9.5 To avoid in-line explosions, do not allow the pressure of the acetylene being delivered to exceed about 100 kPa (15 psig). In the event of a flashback, turn off the gas control switch, the instrument power, and the acetylene tanks.

9.6 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.

9.7 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.

9.8 Avoid contact with a hot burner head to prevent serious tissue burns.

10. Sampling, Test Samples, and Test Units

10.1 Some chemical constituents found in atmospheric wet deposition are not stable and must be preserved before analysis. For additional information on collection and preservation of atmospheric wet deposition, refer to Guide D 5012.

10.2 Proper selection and cleaning of sampling containers are required to reduce the possibility of contamination. **(3,4)** See Practice D 4453 for information regarding sample containers.

11. Calibration

11.1 *Calibration Solutions*:

11.1.1 Five uniformly distributed calibration solutions and one zero standard are needed to generate a suitable calibration curve. The lowest calibration solution should contain the analyte(s) of interest at a concentration approaching or equal to the MDL. The highest solution should slightly exceed the expected upper limit of concentration of the analyte. Suggested calibration standard concentrations for each analyte are listed in the Annex A1.

11.1.2 Calibration solutions are prepared by diluting the stock standard solutions with water. Dedicated volumetric glass pipets and volumetric flasks meeting the requirements for Class A items given in Specification E 694 should be used to obtain the required accuracy. Calibrated volumetric pipets with disposable tips, may also be used.

NOTE 1—It is recommended that the precision and bias of pipets with disposable tips be validated. **(5)**

11.1.3 Calibration solutions may be prepared using two different methods. Serial dilutions are necessary when using glass volumetric pipets. Disposable tipped pipets may be utilized for direct dilution of stock solutions.

11.1.3.1 Do not use more than three dilutions in a series when preparing calibration solutions utilizing glass pipets.

11.1.3.2 When using pipets with disposable tips, select either fixed or variable volume pipets. Rinse each new tip before use by running a stream of water over the exterior and then aspirating and discarding a minimum of four separate aliquots of water. Add the amount of stock solution, calculated from the following equation, to a volumetric flask partially filled with water. Dilute to volume and mix well.

$$\text{amount of stock solution to use, mL} = \frac{(\text{desired end volume, mL})(\text{desired concentration, mg/L})}{\text{stock solution concentration, mg/L}} \tag{2}$$

11.1.4 After preparing the calibration standards to volume, add the lanthanum solution to the calcium and magnesium standards to yield a final concentration of 1000 mg/L lanthanum (1+100). Add the cesium solution to the potassium and sodium standards for a final concentration of 1000 mg/L cesium (1+100). Mix well. Use the same stock of releasing agent or ionization suppressant for samples and calibration standards.

NOTE 2—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 or releasing solution is added to the atmospheric wet deposition samples.

11.2 Set instrument parameters and optimize according to Section 12.

11.3 *Calibration Curve*:

11.3.1 Establish a baseline by aspirating the zero standard and setting the absorbance readout to 0.000.

11.3.2 Aspirate the calibration standards, allowing time for each standard to equilibrate in the flame and gas mixing chamber before measuring the absorbance. Construct absorbance versus concentration calibration curves for each of the analytes according to Section 13.

11.4 Standards are stable for eight weeks when stored at room temperature in high density polyethylene or polypropylene containers.

12. Procedure

12.1 Set instrument parameters and optimize.

12.1.1 *Hollow Cathode 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 gain applied to the photomultiplier tube.

12.1.2 *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.

12.1.3 *Burner Alignment*—Position a small card over the burner slot to intercept the light beam from the hollow cathode lamp. For optimal sensitivity when measuring 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. Adjust the burner alignment and rotation such that the light beam coincides with the full length of the burner slot. Optimize this parameter for maximum instrumental sensitivity as directed in 12.2.

12.1.4 *Wavelength*—Set the wavelength of the spectrophotometer for each analyte according to Annex A1 by following the manufacturer's operating guidelines. After the instrument has warmed up with the flame burning (about 30 min) check the wavelength and readjust if necessary.

12.1.5 *Spectral Bandwidth*—The selection of optimum bandwidth depends upon the spectrum of the particular metal 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.

12.1.6 *External Gas Settings*—Follow manufacturer's recommended delivery pressures for air and acetylene. Never allow acetylene pressure to exceed about 100 kPa (15 psig).

12.1.7 *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, position 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 12.2.

NOTE 3—The nebulizer can easily clog if particulates are present in the samples. Symptoms of clogging are decreased sensitivity or dramatically increased signal noise, or both, especially noticeable at the higher concentration levels. A thorough cleaning with a small diameter wire is usually sufficient to unclog the nebulizer.

12.1.8 *Flame Conditions*—Incomplete compound dissociation or analyte ionization can occur if the flame temperature is too low or too high, respectively, causing a decrease in the apparent concentration of the analyte. In general, calcium exhibits maximum sensitivity at higher fuel and oxidant flow rates. Maximum sensitivity for potassium is obtained with minimal gas flow rates which produce a lower temperature and allow a longer residence time of the atomic vapor in the flame. Sufficient sensitivities for magnesium and sodium are obtained over a wide range of flame conditions. Optimize this parameter for maximum instrumental sensitivity as directed in 12.2. (**Warning—**Follow manufacturer's operating guidelines carefully when setting gas flow rates to prevent combustion within the gas mixing chamber. See Section 9.)

12.2 *Optimization*—Allow the instrument to warm up (about one half hour) with the flame burning before optimizing. Set the instrument readout to absorbance units and set the signal integration time to < 0.5 s. Use either a strip chart recorder or set the instrument display to a continuous read mode to monitor absorbance readings. Aspirate a calibration standard at a concentration near the midpoint of the working range. While watching the absorbance readings, adjust the instrument parameters with small discrete changes until maximum values are obtained.

NOTE 4—Parameters such as flame condition, nebulization rate, and the region of maximum atom concentration in the flame are interrelated. Adjustment of any of these three parameters usually requires the adjustment of the other two.

12.3 *Instrument Response Time*—Determine the minimum sample uptake time before making a measurement on a sample or standard solution. Use either a chart recorder or set the instrument display in a continuous read mode to monitor absorbance readings. After purging the system with water, aspirate the highest calibration standard and measure the length of time necessary to obtain a stable reading. Aspirate water and measure the time it takes for the baseline to return to zero.

NOTE 5—If the time necessary for the baseline to return to zero is longer than 15 s or increases during sample analysis, it is an indication of nebulizer or sample uptake tube clogging.

12.4 Prepare all standards and construct calibration curves according to Section 11.

12.5 Pipet the appropriate cesium or lanthanum solution into the empty sample cup (1+100). For the determination of calcium and magnesium, use the lanthanum solution described in 8.7. For potassium and sodium determinations, use the cesium solution described in 8.4. Pour the sample into the sample cup containing cesium or lanthanum solutions; 3 mL of sample for 30 µL of cesium or lanthanum are appropriate amounts.

12.6 Aspirate the sample, wait for equilibration in the flame, and record the measured absorbance (or concentration).

12.7 If the absorbance (or concentration) for a given sample exceeds the working range of the system, dilute a separate aliquot of the sample with water. Prepare and measure according to 12.5 and 12.6.

12.8 Verify the calibration curve by analyzing a quality control check solution (QCS) immediately after calibration.

The concentration must agree within the predetermined control limits of two times the standard deviation of the QCS. If results of the calibration check fall outside of these guidelines, analyze an additional aliquot of the standard. If problems persist, recalibrate the instrument and reanalyze all samples measured since the last time the system was in control. **(3,4)**

12.9 When analysis is complete, rinse the system by aspirating water for 10 min. Follow the manufacturer's guidelines for instrument shutdown.

13. Calculation

13.1 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:

$$y = B_o + B_1 x \quad (3)$$

(3)

where:

y = standard concentration in mg/L,
x = absorbance measured,
B_o = y-intercept, and
B_1 = slope.

NOTE 6—If the relationship between concentration and absorbance is nonlinear, use a second degree polynomial least squares equation to derive a curve.

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

13.3 Report concentrations in mg/L as Ca^{+2}, Mg^{+2}, Na^{+}, and K^{+}. Report all data. Data lower than the method detection limit, (MDL), must be identified as such.

14. Precision and Bias [9]

14.1 A collaborative test of this test method was performed using synthetic wet deposition samples. Eight laboratories participated with triplicate determinations made at each concentration level.

14.2 The precision and bias of this test method for calcium, magnesium, potassium, and sodium were determined according to Practice D 2777 and are summarized in Table 1.

14.3 These data may not apply to waters of other matrices and are for atmospheric wet deposition only.

15. Keywords

15.1 atmospheric wet deposition; atomic absorption; calcium; magnesium; potassium; precipitation; sodium

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[9] Supporting data providing the results from the interlaboratory test have been filed at ASTM Headquarters, Request RR: D22-1022.

ANNEX

(Mandatory Information)

A1. OPERATION CONDITIONS AND SUGGESTED CALIBRATION STANDARD CONCENTRATIONS

A1.1 Operation Conditions and Suggested Calibration Standard Concentrations

A1.1.1 See Table A1.1.

TABLE A1.1 Operation Conditions and Suggested Calibration Standard Concentrations for the Measurement of Calcium, Magnesium, Potassium, and Sodium in Atmospheric Wet Deposition Samples[A]

Analyte	Wavelength Setting, nm	Approximate Spectral Bandwidth, nm	Working Standards mg/L
Calcium	422.7	1.0	0 0.03 0.75 1.50 2.25 3.00
Magnesium	285.2	1.0	0 0.01 0.25 0.50 0.75 1.00
Potassium	766.5	1.0	0 0.01 0.25 0.50 0.75 1.00
Sodium	589.0	0.5	0 0.01 0.25 0.50 0.75 1.00

[A] Based on the MDL and 95th percentile concentration of each analyte obtained from analyses of over 5000 wet deposition samples from the NADP/NTN precipitation network. **(3)**

REFERENCES

(**1**) Intersociety Committee, *Methods of Air Sampling and Analysis, Third Edition*, J. P. Lodge, Jr., editor, Lewis Publishers, Inc., Chelsea, Michigan, 1989.

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