Designation: D5086 – 20

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 D5086; 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) as given in 1.2 is based on single operator precision. Detection limits vary by instrumentation. Laboratories may be able to achieve lower detection limits. The method detection limit for this method as described in 1.2 was determined in 1987 (**2**).

1.4 The values stated in SI units are to be regarded as standard. No other units of measurement are included in this standard.

1.5 *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, health, and environmental 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.

1.6 *This international standard was developed in accordance with internationally recognized principles on standardization established in the Decision on Principles for the Development of International Standards, Guides and Recommendations issued by the World Trade Organization Technical Barriers to Trade (TBT) Committee.*

2. Referenced Documents

2.1 *ASTM Standards:*[3]

D883 Terminology Relating to Plastics
D1129 Terminology Relating to Water
D1193 Specification for Reagent Water
D1356 Terminology Relating to Sampling and Analysis of Atmospheres
D2777 Practice for Determination of Precision and Bias of Applicable Test Methods of Committee D19 on Water
D4453 Practice for Handling of High Purity Water Samples
D4691 Practice for Measuring Elements in Water by Flame Atomic Absorption Spectrophotometry
D5012 Practice for Preparation of Materials Used for the Collection and Preservation of Atmospheric Wet Deposition
E131 Terminology Relating to Molecular Spectroscopy
E275 Practice for Describing and Measuring Performance of Ultraviolet and Visible Spectrophotometers
E694 Specification for Laboratory Glass Volumetric Apparatus
IEEE/ASTM SI-10 Standard for Use of the International System of Units (SI): The Modern Metric System

2.2 *ISO Standard:*[4]

ISO 8655 Piston-Operated Volumetric Apparatus — Part 2: Piston Pipettes

3. Terminology

3.1 *Definitions:*

[1] This test method is under the jurisdiction of ASTM Committee D22 on Air Quality and is the direct responsibility of Subcommittee D22.03 on Ambient Atmospheres and Source Emissions.

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

[3] For referenced ASTM standards, visit the ASTM website, www.astm.org, or contact ASTM Customer Service at service@astm.org. For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

[4] Available from International Organization for Standardization (ISO), ISO Central Secretariat, BIBC II, Chemin de Blandonnet 8, CP 401, 1214 Vernier, Geneva, Switzerland, http://www.iso.org.

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.

3.1.1 For definitions of terms used in this test method, refer to Terminologies D883, D1129, D1356, E131, and Practices D4691, E275, and IEEE/ASTM SI-10.

3.1.2 *method detection limit, MDL*—the minimum concentration of an analyte that can be reported with 99 % confidence is not a false positive. Laboratories must perform detection limit studies or detection limit verification studies at least once every 12 months and any time changes to the analytical system have occurred which could affect sensitivity. Laboratories must document the statistical basis for the derived method detection limit. The procedure by which the detection limit is determined or verified must include a statistical assessment of a minimum of seven low level standards estimated to be at three- to five-times the detection limit and seven method blanks. Both the standards and the blanks must be processed through the entire method. One method by which this may be achieved is by following the EPA Method "Definition and Procedure for the Determination of the Method Detection Limit, Revision 2" (**3**).

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 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:

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

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 constructed 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.

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 *Analytical Apparatus:*

7.1.1 *Flame Atomic Absorption Spectrophotometer,* equipped with air/acetylene and nitrous oxide/acetylene burner heads.

7.1.2 *Hollow Cathode or Electrodeless Discharge Lamp,* for each element to be determined.

7.1.3 *Deuterium Continuum Lamp.*

7.1.4 *Compressed Air*—Appropriate pressure reducing regulator with base connections (see instrument manufacturer's instructions).

7.1.5 *Acetylene Gas and Regulator*—A cylinder of acetylene equipped with a two-gage, two-stage pressure-reducing regulator with hose connections (see instrument manufacturer's instructions).

7.2 *Volumetric Pipets*—Maintain a set of Class A volumetric pipets (see Specification E694) to be used only when making dilute calibration solutions for the analysis of atmospheric wet deposition samples. Alternatively, variable or fixed volume piston operated disposable tip pipets may be used if they comply with ISO 8655.

7.3 *Volumetric Flasks*—Maintain a set of Class A volumetric flasks (see Specification E694) 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 better. All reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society (ACS) where such specifications are available.[5]

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 D1193. 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

[5] *ACS Reagent Chemicals, Specifications and Procedures for Reagents and Standard-Grade Reference Materials*, 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.

polyethylene or polypropylene container. Alternatively, commercially available Cesium ionization suppressants/buffers may be purchased.

8.5 *Hydrochloric Acid (1+1, Volume to Volume)*—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, Volume to Volume)*—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.) Alternatively, commercially available lanthanum releasing agent solutions may be purchased.

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.

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 D5012.

10.2 Proper selection and cleaning of sampling containers are required to reduce the possibility of contamination (**4**, **5**). See Practice D4453 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 flasks meeting the requirements for Class A items given in Specification E694 should be used to obtain the required accuracy.

NOTE 1—It is recommended that the precision and bias of piston operated pipets be validated (**6**).

11.1.3 Calibration solutions may be prepared using two different methods.

11.1.3.1 Serial dilutions are necessary when using glass volumetric pipets. Do not use more than three dilutions in a series when preparing calibration solutions utilizing glass pipets.

11.1.3.2 Piston operated pipets may be utilized for direct dilution of stock solutions. When using piston operated pipets,