U. S. Department of Commerce
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National Bureau of Standards

Report of Investigation

Research Material 8409

Simulated Rainwater

Research Material (RM) 8409 has been developed to aid in the analysis of acidic rainwater by providing a stable, homogeneous material as a control standard. It consists of two 50 mL solutions in polyethylene bottles. It was prepared by the dissolution of high-purity salts and acids in high-purity distilled/deionized water. Recommended values are given in Table 1. Transition and heavy metals are not included in RM 8409 as they are not stable in solutions at this pH level. Analysts are referred to SRM 1643b "Trace Elements in Water" for applications involving trace metal determinations.

Table 1

Recommended Values for RM 8409

Simulated Rainwater

	RM 8409-I	RM 8409-II
pH	4.32 ±0.03	3.61 ± 0.03
Specific Conductance (μS/cm @25.0 °C)	25 ±1	128 ± 1
Acidity, μeq/L	55 ±4	280 ±10
Fluoride, mg/L	0.058 ±0.002	0.102 ± 0.004
Chloride, mg/L	0.230 ±0.006	1.00 ± 0.04
Nitrate, mg/L	0.535 ±0.008	7.18 ± 0.20
Nitrate-Nitrogen, mg/L	0.121 ±0.002	1.62 ± 0.04
Sulfate, mg/L	2.62 ±0.02	10.5 ± 0.1
Sulfate-Sulfur, mg/L	0.875 ±0.004	3.49 ± 0.04
Sodium, mg/L	0.208 ±0.012	0.410 ± 0.008
Potassium, mg/L	0.058 ±0.006	0.112 ± 0.002
Ammonium, mg/L	- - -	1.07 ± 0.05
Ammonium-Nitrogen, mg/L	- - -	0.83 ± 0.04
Calcium, mg/L	0.027 ±0.008	0.05 ± 0.01
Magnesium, mg/L	0.026 ±0.002	0.05 ± 0.01

NOTE: The ammonium concentration in RM 8409-I has been found to be unstable. RM 8409 will be periodically monitored and any other change in the recommended values will be reported to purchasers.

The values listed above are based on measurements using a single method or technique and are reported as *recommended values only*. The estimated uncertainties are 2 standard deviations of a single determination, except for uncertainties associated with the pH measurements, which are one standard deviation of a single determination. No attempt has been made to derive exact statistical measures of imprecision.

The preparation and analyses of these solutions were performed by W.F. Koch, G. Marinenko, and T.C. Rains, NBS Inorganic Analytical Research Division.

The overall direction and coordination of the technical measurements leading to this report were performed under the direction of J.R. DeVoe, Chief, NBS Inorganic Analytical Research Division.

The technical and support aspects involved in the preparation, analysis, and issuance of this Research Material were coordinated through the Office of Standard Reference Materials by T.E. Gills and L.J. Powell.

Gaithersburg, MD 20899
March 1, 1985
(Revision of Certificate
dated 11-14-84)

Stanley D. Rasberry, Chief
Office of Standard Reference Materials

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Notice and Warnings to Users:

Expiration of Certification: The data included in this Report of Investigation are invalid one year after the shipping date.

Note: This is not a Standard Reference Material and none of the data presented in this Report of Investigation are certified. However, the values supplied herein are based on proven NBS methods. Standard Reference Material (SRM) 2694, Simulated Rainwater, is in preparation and is scheduled for issue in July, 1985. The certificate for SRM 2694 will contain NBS *certified* values for pH, specific conductance, acidity, and the various cations and anions included in RM 8409.

Precautions: The solutions of RM 8409 are very dilute, unbuffered solutions and as such are very susceptible to contamination. Therefore, the solutions should be used immediately upon opening. No assurances can be made as to the composition or stability of the solutions after being opened and recapped.

If conductance and pH are to be measured on the same sample, then conductance must be measured first to prevent leakage from the pH reference electrode filling solution from affecting the conductance. The measurement of pH should be performed according to the guidelines set forth in the attachment to this document to minimize the bias caused by residual liquid junction potentials. Acidimetric titrations should be performed on samples that have been purged of dissolved carbon dioxide to prevent drifting end points and high results. Care must be exercised in the determination of chloride and fluoride by ion chromatography to avoid possible errors associated with the negative water-dip in the baseline.

GUIDELINES FOR THE MEASUREMENT OF pH IN ACIDIC RAINWATER

This report presents a recommended procedure for the measurement of pH in acidic rainwater. The intent of this guideline is to improve the accuracy and precision of the pH measurement with special emphasis on reducing the effect of the residual liquid junction potential. It consists of three major parts: Calibration Sequence, Control Sequence, and Rainwater Measurement Sequence. Each sequence should be executed in stepwise order with strict adherence to detail.

Note: This guideline is applicable only to the measurement of pH in acidic rainwater and acidic low ionic strength aqueous solutions. It should not be used for any other applications as inaccuracies may ensue.

General Directions

Make all pH measurements between 20 and 26 °C. Report the solution temperature to within 1 °C. Report all pH values to at least 0.01 pH unit. Make all measurements in a quiescent solution. Fully document all calibration and control standards.

Calibration Sequence

1) Standardize the pH electrodes and meter using SRM 185f, Potassium Hydrogen Phthalate [pH(S) 4.006 at 25.0 °C, 0.05 molal], or equivalent.[A] Refer to ASTM D1293, "Standard Test Methods for pH of Water" for guidance. Record the value. Rinse the electrodes with distilled water (ASTM Type II or better).

2) With the slope adjustment of the meter set at 100 percent, and the temperature adjustment set at the temperature of the buffer solution, check the Nernstian response of the pH measurement system with a second buffer, SRM 186Ic/186IIc, Potassium Dihydrogen Phosphate/Disodium Hydrogen Phosphate [pH(S) 6.863 at 25.0 °C], or equivalent.[A] Refer to ASTM D1293 for guidance. If the reading for the second buffer is not within 0.03 pH units of the prescribed value, recheck the calibration of the system. DO NOT CONTINUE until the conditions for calibration and Nernstian response have been satisified.[B] If the reading for the second buffer is within 0.03 pH units of the prescribed value, record the value and continue.

Control Sequence

3) Rinse the electrodes thoroughly with distilled water (ASTM Type II or better). Remove drops of water on the electrode by blotting gently (Do Not Rub!) with a clean lab tissue.

4) Insert the electrodes into a clean beaker (10-20 mL capacity) containing a portion (10-20 mL) of the rainwater control standard (e.g., RM 8409-I[C]). Be certain that the reference junction and glass bulb are completely immersed. Do not insert the electrodes directly into the polyethylene bottles.

5) Stir or swirl the solution to ensure homogeneity and contact with the electrodes.

6) Allow the solution to settle to a quiescent state (approx. 30 seconds). Record the pH after the reading has stabilized[D].

7) Discard this portion of the control standard. Do not use for subsequent control checks or for other analytical determinations such as specific conductance, anions, cations, and acidity.

8) Repeat steps 3 through 7 with a second rainwater control standard (e.g., RM 8409-II[C]).

9) Calculate the differences between the true pH values of the rainwater control standard and the values as determined by the pH measurement system.[E] Average the differences and apply this bias correction to subsequent rainwater measurements. (For example, if the pH measurement system displays the pH of the control 0.13 pH units lower than the true value, add 0.13 pH units to the subsequent pH measuremenents of rainwater.)

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Rainwater Measurement Sequence

10) Rinse the electrodes thoroughly with distilled water (ASTM Type II or better). Remove drops of water on the electrode by blotting gently (Do Not Rub!) with a clean lab tissue.

11) Insert the electrodes into a clean beaker containing a portion (10-20 mL) of the rainwater sample. Be certain that the reference junction and glass bulb are completely immersed.

12) Stir or swirl the solution to ensure homogeneity and contact with the electrodes.

13) Allow the solution to settle to a quiescent state (approx. 30 seconds). Record the pH after the reading has stabilized.[D]

14) Apply the bias correction as determined in step 9 and report this corrected value as the pH of the rainwater sample.

15) Discard this portion of the rainwater sample. Do not use it in other analytical tests.

16) Repeat steps 10 through 15 for subsequent rainwater samples.

17) Repeat the Control Sequence at regular intervals, based upon quality control guidelines, performance history of the measurement system, frequency of measurements, and required accuracy.

Storage of Electrodes

18) When not in use, soak the electrodes in a solution which is 0.1 mol/L potassium chloride and 1×10^{-4} mol/L hydrochloric acid. Do not store the electrodes in buffers, concentrated acids, concentrated potassium chloride, basic solutions, or distilled water. Do not allow the electrodes to dry out.

19) Use these electrodes exclusively for rainwater measurements.

Notes

A) For the highest accuracy and the most direct traceability to the National Bureau of Standards, it is recommended that freshly prepared solutions of Standard Reference Materials (SRM's) be used.

B) Possible causes for deviation from Nernstian response include:

   i) improper calibration,
   ii) old or contaminated buffer solutions,
   iii) insufficient rinsing of the electrodes between solutions,
   iv) plugged reference junction,
   v) defective electrodes,
   vi) defective meter.

   It may be necessary to replace the electrodes with a new pair if the non-Nernstian behavior persists even with accurately and freshly prepared buffer standards.

C) Research Material RM 8409-I/RM 8409-II, Simulated Rainwater, is issued by the National Bureau of Standards, Office of Standard Reference Materials.

D) Some systems may require five minutes or more to stabilize. If drifting persists, record the reading after 10 minutes and annotate the data accordingly. With such severe drift, it would be advisable to acquire a different type of pH electrodes which do not exhibit this adverse characteristic.

E) The difference should agree to within 0.05 pH units. If not, repeat the Control Sequence.