

National Bureau of Standards

Certificate of Analysis

Standard Reference Material 2694

Simulated Rainwater

This Standard Reference Material (SRM) has been developed to aid in the analysis of acidic rainwater by providing homogeneous materials as control standards at each of two levels of acidity. SRM 2694 consists of four 50 mL solutions, two at each level, in polyethylene bottles. It was prepared by the dissolution of high-purity salts and acids in high-purity distilled/deionized water. Certified values and method(s) used for certification are given in Table 1. Values in parentheses are *not* certified, but are included for information only. Transition and heavy metals are not included in SRM 2694 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

Simulated Rainwater

<u>Constituent Elements/ Parameters</u>	<u>Methods</u>	<u>2694-I</u>	<u>2694-II</u>
pH @ 25 °C	c	4.27 ± 0.03	3.59 ± 0.02
Specific Conductance (μS/cm @ 25.0 °C)	b	26 ± 2	130 ± 2
Acidity, meq/L	d	0.050 ± 0.002	0.284 ± 0.005
Fluoride, mg/L	a,c	0.054 ± 0.002	0.098 ± 0.007
Chloride, mg/L	a,c	(0.24)	(1.0)
Nitrate, mg/L	a,f	—	7.06 ± 0.15
Sulfate, mg/L	a,e	2.75 ± 0.05	10.9 ± .2
Sodium, mg/L	a,g,h	0.205 ± 0.009	0.419 ± 0.015
Potassium, mg/L	a,g,h	0.052 ± 0.007	0.106 ± 0.008
Ammonium, mg/L	a,c	—	(1.0)
Calcium, mg/L	g,i,k	0.014 ± 0.003	0.049 ± 0.011
Magnesium, mg/L	g,j	0.024 ± 0.002	0.051 ± 0.003

The certified values are based on proven reliable methods of analysis. The estimated uncertainties are 2 standard deviations of the certified values, except for uncertainties associated with SO₄, acidity, pH, and specific conductance which are based on scientific judgment and are roughly equivalent to 2 standard deviations of the certified value.

Note: The nitrate value for 2694-I is not certified because of instability. It is believed that bacterial or fungal activity contributes to that instability.

Techniques:

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| a. Ion Chromatography | f. Spectrophotometry |
| b. Conductimetry | g. Laser Enhanced Ionization Spectrometry |
| c. Potentiometry/Ion Selective Electrodes | h. Flame Emission Spectrometry |
| d. Coulometry | i. Inductively Coupled Plasma Spectrometry |
| e. Isotope Dilution Thermal Ionization Mass Spectrometry | j. Flame Atomic Absorption Spectrometry |
| | k. Direct Current Plasma Spectrometry |

The overall direction and coordination of the technical measurements leading to this certificate 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 Standard Reference Material were coordinated through the Office of Standard Reference Materials by T.E. Gills and L.J. Powell.

Gaithersburg, MD 20899
 April 23, 1986
 (Revision of Certificate
 dated 9-19-85)

Stanley D. Rasberry, Chief
 Office of Standard Reference Materials

The preparation and analyses of these solutions were performed by W.F. Koch, G. Marinenko, T.C. Rains, R.W. Burke, M. Knoerdel, W.R. Kelly, G.C. Turk, Mo De-Ming, M.S. Epstein, T.A. Rush, T.A. Butler, K. Han and M.V. Smith in the NBS Inorganic Analytical Research Division.

The statistical analysis of the certification data was performed by R.C. Paule of the National Measurement Laboratory.

Notice and Warnings to Users:

Expiration of Certification: The data included in this Certificate of Analysis are valid for 6 months from the shipping date.

Precautions: The solutions of SRM 2694 are very dilute, unbuffered, 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. SRM 2694 should be stored in an area free from acid and/or ammonia fumes or vapors. Refrigeration of the solutions is not necessary; however, they should not be exposed to extreme heat.

Additional Information: 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 endpoints 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.

Ammonium ion is not certified in these solutions because of the instability of ammonium ion, particularly in 2694-I. The concentration of ammonium ion in 2694-I was originally 0.1 $\mu\text{g/L}$, but is gradually decreasing. Thus no value is given for ammonium in this solution. The concentration of ammonium in 2694-II appears to be more stable than in 2694-I. Thus a value of 1.0 mg/L is given *for information only*. However the user should be aware of the possible unreliability of this value. The cause of the instability is not known at this time. It does not appear to affect significantly any other component in the solutions.

The temperature coefficient for the specific conductance of both solutions in SRM 2694 has been determined experimentally to be 1.5 percent per degree Celsius at 25 °C. The density of the solutions is 0.997 g/mL at 23 °C.

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. The purposes of the Calibration Sequence are to accurately calibrate the pH measurement system with robust buffer solutions, to accurately set the slope, and to verify that the measurement system is functioning properly. The purpose of the Control Sequence is to quantitatively determine the magnitude of the residual liquid junction potential bias for a particular set of electrodes which must be applied in the rainwater measurement sequence to obtain more reliable and intercomparable results. 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 other applications as inaccuracies may ensue.

General Directions

Record the solution temperature to within 1 °C. Record 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. 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/186Ic, 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.^B DO NOT CONTINUE until the conditions for calibration and Nernstian response have been satisfied. 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., SRM 2694-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., SRM 2694-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 measurements of rainwater.)

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.
- 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, and
 - 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) Standard Reference Material 2694, 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.