NBS SPECIAL PUBLICATION **260-106**

U.S. DEPARTMENT OF COMMERCE/National Bureau of Standards

Standard Reference Materials:

Methods and Procedures Used at the National Bureau of Standards to Prepare, Analyze and Certify SRM 2694, Simulated Rainwater, and Recommendations for Use

William F. Koch, Editor

*T*he National Bureau of Standards[1] was established by an act of Congress on March 3, 1901. The Bureau's overall goal is to strengthen and advance the nation's science and technology and facilitate their effective application for public benefit. To this end, the Bureau conducts research and provides: (1) a basis for the nation's physical measurement system, (2) scientific and technological services for industry and government, (3) a technical basis for equity in trade, and (4) technical services to promote public safety. The Bureau's technical work is performed by the National Measurement Laboratory, the National Engineering Laboratory, the Institute for Computer Sciences and Technology, and the Institute for Materials Science and Engineering.

The National Measurement Laboratory

Provides the national system of physical and chemical measurement; coordinates the system with measurement systems of other nations and furnishes essential services leading to accurate and uniform physical and chemical measurement throughout the Nation's scientific community, industry, and commerce; provides advisory and research services to other Government agencies; conducts physical and chemical research; develops, produces, and distributes Standard Reference Materials; and provides calibration services. The Laboratory consists of the following centers:

- Basic Standards[2]
- Radiation Research
- Chemical Physics
- Analytical Chemistry

The National Engineering Laboratory

Provides technology and technical services to the public and private sectors to address national needs and to solve national problems; conducts research in engineering and applied science in support of these efforts; builds and maintains competence in the necessary disciplines required to carry out this research and technical service; develops engineering data and measurement capabilities; provides engineering measurement traceability services; develops test methods and proposes engineering standards and code changes; develops and proposes new engineering practices; and develops and improves mechanisms to transfer results of its research to the ultimate user. The Laboratory consists of the following centers:

- Applied Mathematics
- Electronics and Electrical Engineering[2]
- Manufacturing Engineering
- Building Technology
- Fire Research
- Chemical Engineering[2]

The Institute for Computer Sciences and Technology

Conducts research and provides scientific and technical services to aid Federal agencies in the selection, acquisition, application, and use of computer technology to improve effectiveness and economy in Government operations in accordance with Public Law 89-306 (40 U.S.C. 759), relevant Executive Orders, and other directives; carries out this mission by managing the Federal Information Processing Standards Program, developing Federal ADP standards guidelines, and managing Federal participation in ADP voluntary standardization activities; provides scientific and technological advisory services and assistance to Federal agencies; and provides the technical foundation for computer-related policies of the Federal Government. The Institute consists of the following centers:

- Programming Science and Technology
- Computer Systems Engineering

The Institute for Materials Science and Engineering

Conducts research and provides measurements, data, standards, reference materials, quantitative understanding and other technical information fundamental to the processing, structure, properties and performance of materials; addresses the scientific basis for new advanced materials technologies; plans research around cross-country scientific themes such as nondestructive evaluation and phase diagram development; oversees Bureau-wide technical programs in nuclear reactor radiation research and nondestructive evaluation; and broadly disseminates generic technical information resulting from its programs. The Institute consists of the following Divisions:

- Ceramics
- Fracture and Deformation[3]
- Polymers
- Metallurgy
- Reactor Radiation

Standard Reference Materials:

Methods and Procedures Used at the National Bureau of Standards to Prepare, Analyze and Certify SRM 2694, Simulated Rainwater, and Recommendations for Use

William F. Koch, Editor

Center for Analytical Chemistry
National Bureau of Standards
Gaithersburg, Maryland 20899

Preface

Standard Reference Materials (SRM's) as defined by the National Bureau of Standards (NBS) are well-characterized materials, produced in quantity and certified for one or more physical or chemical properties. They are used to assure the accuracy and compatibility of measurements throughout the Nation. SRM's are widely used as primary standards in many diverse fields in science, industry, and technology, both within the United States and throughout the world. They are also used extensively in the fields of environmental and clinical analysis. In many applications, traceability of quality control and measurement processes to the national measurement system is carried out through the mechanism and use of SRM's. For many of the Nation's scientists and technologists it is therefore of more than passing interest to know the details of the measurements made at NBS in arriving at the certified values of the SRM's produced. An NBS series of papers, of which this publication is a member, called the NBS Special Publication - 260 Series, is reserved for this purpose.

The 260 Series is dedicated to the dissemination of information on different phases of the preparation, measurement, certification, and use of NBS SRM's. In general, much more detail will be found in these papers than is generally allowed, or desirable, in scientific journal articles. This enables the user to assess the validity and accuracy of the measurement processes employed, to judge the statistical analysis, and to learn details of techniques and methods utilized for work entailing the greatest care and accuracy. These papers also should provide sufficient additional information not found on the certificate so that new applications in diverse fields not foreseen at the time the SRM was originally issued will be sought and found.

Inquiries concerning the technical content of this paper should be directed to the author(s). Other questions concerned with the availability, delivery, price, and so forth, will receive prompt attention from:

Office of National Reference Materials
National Bureau of Standards
Gaithersburg, MD 20899

Stanley D. Rasberry, Chief
Office of Standard Reference Materials

Catalog of NBS Standard Reference Materials (1984-85 edition), Catherine H. Hudson, ed., NBS Spec. Publ. 260 (February 1984). $5.50* SN003-003-02558-5.

Michaelis, R. E., and Wyman, L. L. Standard Reference Materials: Preparation of White Cast Iron Spectrochemical Standards. NBS Misc. Publ. 260-1 (June 1964). COM74-11061**

Michaelis, R. E., Wyman, L. L., and Flitsch, R., Standard Reference Materials: Preparation of NBS Copper-Base Spectrochemical Standards. NBS Misc. Publ. 260-2 (October 1964). COM74-11063**

Michaelis, R. E., Yakowitz, H., and Moore, G. A., Standard Reference Materials: Metallographic Characterization of an NBS Spectrometric Low-Alloy Steel Standard. NBS Misc. Publ. 260-3 (October 1964). COM74-11060**

Hague, J. L. Mears, T. W., and Michaelis, R. E., Standard Reference Materials: Sources of Information, NBS Misc. Publ. 260-4 (February 1965). COM74-11059

Alvarez, R., and Flitsch R., Standard Reference Materials: Accuracy of Solution X-Ray Spectrometric Analysis of Copper-Base Alloys. NBS Misc. Publ. 260-5 (March 1965). PB168068**

Shultz, J. I., Standard Reference Materials: Methods for the Chemical Analysis of White Cast Iron Standards, NBS Misc. Publ. 260-6 (July 1965). COM74-11068**

Bell, R. K., Standard Reference Materials: Methods for the Chemical Analysis of NBS Copper-Base Spectrochemical Standards. NBS Misc. Publ. 260-7 (October 1965). COM74-11067**

Richmond, M.S., Standard Reference Materials: Analysis of Uranium Concentrates at the National Bureau of Standards. NBS Misc. Publ. 260-8 (December 1965). COM74-11066**

Anspach, S. C., Cavallo, L. M. Garfinkel, S. B. Hutchinson, J. M. R., and Smith, C. N., Standard Reference Materials: Half Lives of Materials Used in the Preparation of Standard Reference Materials of Nineteen Radioactive Nuclides Issued by the National Bureau of Standards NBS Misc. Publ. 260-9 (November 1965). COM74-11065**

Yakowitz, H., Vieth, D. L., Heinrich, K. F. J., and Michaelis, R. E., Standard Reference Materials: Homogeneity Characterization of NBS Spectrometric Standards II: Cartridge Brass and Low-Alloy Steel, NBS Misc. Publ. 260-10 (December (1965). COM74-11064**

Napolitano, A., and Hawkins, E. G., Standard Reference Materials: Viscosity of Standard Lead-Silica Glass, NBS Misc. Publ. 260-11 (November 1966). NBS Misc. Publ. 260-11**

Yakowitz, H., Vieth, D. L., and Michaelis, R. E., Standard Reference Materials: Homogeneity Characterization of NBS Spectrometric Standards III: White Cast Iron and Stainless Steel Powder Compact, NBS Misc. Publ. 260-12 (September 1966). NBS Misc. Publ. 260-12**

Spijkerman, J. L., Snediker, D. K., Ruegg, F. C., and DeVoe, J. R., Standard Reference Materials: Mossbauer Spectroscopy Standard for the Chemical Shift of Iron Compounds, NBS Misc. Publ. 260-13 (July 1967). NBS Misc. Publ. 260-13**

Menis, O., and Sterling, J. T., Standard Reference Materials: Determination of Oxygen in Ferrous Materials - SRM 1090, 1091, and 1092, NBS Misc. Publ. 260-14 (September 1966). NBS Misc. Publ. 260-14**

Passaglia, E., and Shouse, P. J., Standard Reference Materials: Recommended Method of Use of Standard Light-Sensitive Paper for Calibrating Carbon Arcs Used in Testing Textiles for Colorfastness to Light, NBS Misc. Publ. 260-15 (June 1967). (Replaced by NBS Spec. Publ. 260-41.)

Yakowitz, H., Michaelis, R. E., and Vieth, D. L., Standard Reference Materials: Homogeneity Characterization of NBS Spectrometric Standards IV: Preparation and Microprobe Characterization of W-20% MO Alloy Fabricated by Powder Metallurgical Methods, NBS Spec. Publ. 260-16 (January 1969). COM74-11062**

Catanzaro, E. J., Champion, C. E., Garner, E. L., Marinenko, G., Sappenfield, K. M., and Shields, W. R., Standard Reference Materials: Boric Acid; Isotopic and Assay Standard Reference Materials, NBS Spec. Publ. 260-17 (February 1970). Out of Print.

Geller, S. B., Mantek, P. A., and Cleveland, N. G., Standard Reference Materials: Calibration of NBS Secondary Standard Magnetic Tape (Computer Amplitude Reference) Using the Reference Tape Amplitude Measurement "Process A," NBS Spec. Publ. 260-18 (November 1969). (See NBS Spec. Publ. 260-29.)

Paule, R. C., and Mandel, J., Standard Reference Materials: Analysis of Interlaboratory Measurements on the Vapor Pressure of Gold (Certification of Standard Reference Material 745). NBS Spec. Publ. 260-19 (January 1970). PB190071**

Paule, R. C., and Mandel, J., Standard Reference Materials: Analysis of Interlaboratory Measurements on the Vapor Pressures of Cadmium and Silver, NBS Spec. Publ. 260-21 (January 1971). COM74-11359**

Yakowitz, H., Fiori, C. E., and Michaelis, R. E., Standard Reference Materials: Homogeneity Characterization of Fe-3 Si Alloy, NBS Spec. Publ. 260-22 (February 1971). COM74-11357**

Napolitano, A., and Hawkins, E. G., Standard Reference Materials: Viscosity of a Standard Borosilicate Glass, NBS Spec. Publ. 260-23 (December 1970). COM71-00157**

Sappenfield, K. M., Marineko, G., and Hague, J. L., Standard Reference Materials: Comparison of Redox Standards, NBS Spec. Publ. 260-24 (January 1972). COM72-50058**

Hicho, G. E., Yakowitz, H., Rasberry, S. D., and Michaelis, R. E., Standard Reference Materials: A Standard Reference Material Containing Nominally Four Percent Austenite, NBS Spec. Publ. 260-25 (February 1971). COM74-11356**

Martin, J. F., Standard Reference Materials: National Bureau of Standards-US Steel Corporation Joint Program for Determining Oxygen and Nitrogen in Steel, NBS Spec. Publ. 260-26 (February 1971). 85 cents* PB 81176620

Garner, E. L., Machlan, L. A., and Shields, W. R., Standard Reference Materials: Uranium Isotopic Standard Reference Materials, NBS Spec. Publ. 260-27 (April 1971). COM74-11358**

Heinrich, K. F. J., Myklebust, R. L., Rasberry, S. D., and Michaelis, R. E., Standard Reference Materials: Preparation and Evaluation of SRM's 481 and 482 Gold-Silver and Gold-Copper Alloys for Microanalysis, NBS Spec. Publ. 260-28 (August 1971). COM71-50365**

Geller, S. B., Standard Reference Materials: Calibration of NBS Secondary Standard Magnetic Tape (Computer Amplitude Reference) Using the Reference Tape Amplitude Measurement "Process A-Model 2," NBS Spec. Publ. 260-29 (June 1971). COM71-50282

Gorozhanina, R. S., Freedman, A. Y., and Shaievitch, A. B. (translated by M. C. Selby), Standard Reference Materials: Standard Samples Issued in the USSR (A Translation from the Russian). NBS Spec. Publ. 260-30 (June 1971). COM71-50283**

Hust, J. G., and Sparks, L. L., Standard Reference Materials: Thermal Conductivity of Electrolytic Iron SRM 734 from 4 to 300 K, NBS Spec. Publ. 260-31 (November 1971). COM71-50563**

Mavrodineanu, R., and Lazar, J. W., Standard Reference Materials: Standard Quartz Cuvettes, for High Accuracy Spectrophotometry, NBS Spec. Publ. 260-32 (December 1973). 55 cents* SN003-003-01213-1

Wagner, H. L., Standard Reference Materials: Comparison of Original and Supplemental SRM 705, Narrow Molecular Weight Distribution Polystyrene, NBS Spec. Publ. 260-33 (May 1972). COM72-50526**

Sparks, L. L., and Hust, J. G., Standard Reference Materials: Thermoelectric Voltage, NBS Spec. Publ. 260-34, (April 1972). COM72-50371**

Sparks, L. L., and Hust, J. G., Standard Reference Materials: Thermal Conductivity of Austenitic Stainless Steel, SRM 735 from 5 to 280 K, NBS Spec. Publ. 260-35 (April 1972.) 35 cents* COM72-50368**

Cali, J. P., Mandel, J., Moore, L. J., and Young, D. S., Standard Reference Materials: A Referee Method for the Determination of Calcium in Serum, NBS SRM 915, NBS Spec. Publ. 260-36 (May 1972). COM72-50527**

Shultz, J. I. Bell., R. K. Rains, T. C., and Menis, O., Standard Reference Materials: Methods of Analysis of NBS Clay Standards, NBS Spec. Publ. 260-37 (June 1972). COM72-50692**

Richmond, J. C., and Hsia, J. J., Standard Reference Materials: Preparation and Calibration of Standards of Spectral Specular Reflectance, NBS Spec. Publ. 260-38 (May 1972). COM72-50528**

Clark, A. F., Denson, V.A., Hust, J. G., and Powell, R. L., Standard Reference Materials: The Eddy Current Decay Method for Resistivity Characterization of High-Purity Metals, NBS Spec. Publ. 260-39 (May 1972). COM72-50529**

McAdie, H. G., Garn, P.D., and Menis, O., Standard Reference Materials: Selection of Thermal Analysis Temperature Standards Through a Cooperative Study (SRM 758, 759, 760), NBS Spec. Publ. 260-40 (August 1972.) COM72-50776**

Wood, L. A., and Shouse, P. J., Standard Reference Materials: Use of Standard Light-Sensitive Paper for Calibrating Carbon Arcs Used in Testing Textiles for Colorfastness to Light, NBS Spec. Publ. 260-41 (August 1972) COM72-50775**

Wagner, H. L. and Verdier, P. H., eds., Standard Reference Materials: The Characterization of Linear Polyethylene, SRM 1475, NBS Spec. Publ. 260-42 (September 1972). COM72-50944**

Yakowitz, H., Ruff, A. W., and Michaelis, R. E., Standard Reference Materials: Preparation and Homogeneity Characterization of an Austenitic Iron-Chromium-Nickel Alloy, NBS Spec. Publ. 260-43 (November 1972). COM73-50760**

Schooley, J. F., Soulen, R. J., Jr., and Evans, G. A., Jr., Standard Reference Materials: Preparation and Use of Superconductive Fixed Point Devices, SRM 767, NBS Spec. Publ. 260-44 (December 1972). COM73-50037**

Greifer, B., Maienthal, E. J., Rains, T. C., and Rasberry, S. D., Standard Reference Materials: Powdered Lead-Based Paint, SRM 1579, NBS Spec. Publ. 260-45 (March 1973). COM73-50226**

Hust, J. G., and Giarratano, P. J., Standard Reference Materials: Thermal Conductivity and Electrical Resistivity Standard Reference Materials: Austenitic Stainless Steel, SRM's 735 and 798, from 4 to 1200 K, NBS Spec. Publ. 260-46 (March 1975). SN003-003-01278-5*

Hust, J. G., Standard Reference Materials: Electrical Resistivity of Electrolytic Iron, SRM 797, and Austenitic Stainless Steel, SRM 798, from 5 to 280 K, NBS Spec. Publ. 260-47 (February 1974). COM74-50176**

Mangum, B. W., and Wise, J. A., Standard Reference Materials: Description and Use of Precision Thermometers for the Clinical Laboratory, SRM 933 and SRM 934, NBS Spec. Publ. 260-48 (May 1974). 60 cents* SN003-003-01278-5

Carpenter, B. S., and Reimer, G. M., Standard Reference Materials: Calibrated Glass Standards for Fission Track Use, NBS Spec. Publ. 260-49 (November 1974). COM74-51185

Hust, J. G., and Giarratano, P. J., Standard Reference Materials: Thermal Conductivity and Electrical Resistivity Standard Reference Materials: Electrolytic Iron, SRM's 734 and 797 from 4 to 1000 K, NBS Spec. Publ. 260-50 (June 1975). $1.00* SN003-003-01425-7

Mavrodineanu, R., and Baldwin, J. R., Standard Reference Materials: Glass Filters As a Standard Reference Material for Spectrophotometry; Selection; Preparation; Certification; Use-SRM 930, NBS Spec. Publ. 260-51 (November 1975). $1.90* SN003-003-01481-8

Hust, J. G., and Giarratano, P. J., Standard Reference Materials: Thermal Conductivity and Electrical Resistivity Standard Reference Materials 730 and 799, from 4 to 3000 K, NBS Spec. Publ. 260-52 (September 1975). $1.05* SN003-003-01464-8

Durst, R. A., Standard Reference Materials: Standardization of pH Measurements, NBS Spec. Publ. 260-53 (December 1975, Revised). $1.05 SN003-003-01551-2

Burke, R. W., and Mavrodineanu, R., Standard Reference Materials: Certification and Use of Acidic Potassium Dichromate Solutions as an Ultraviolet Absorbance Standard, NBS Spec. Publ. 260-54 (August 1977). $3.00* SN003-003-01828-7

Ditmars, D. A., Cezairliyan, A., Ishihara, S., and Douglas, T. B., Standard Reference Materials: Enthalpy and Heat Capacity; Molybdenum SRM 781, from 273 to 2800 K, NBS Spec. Publ. 260-55 (September 1977). $2.20* SN003-003-01836-8

Powell, R. L., Sparks, L. L., and Hust, J. G., Standard Reference Materials: Standard Thermocouple Materials, Pt.67: SRM 1967, NBS Spec. Publ. 260-56 (February 1978). $2.20* SN003-003-018864

Cali, J. P. and Plebanski, T., Guide to United States Reference Materials, NBS Spec. Publ. 260-57 (February 1978). $2.20* PB 277173

Barnes, J. D., and Martin, G. M., Standard Reference Materials: Polyester Film for Oxygen Gas Transmission Measurements SRM 1470, NBS Spec. Publ. 260-58 (June 1979) $2.00* SN003-003-02077

Chang, T., and Kahn, A. H. Standard Reference Materials: Electron Paramagnetic Resonance Intensity Standard; SRM 2601, NBS Spec. Publ. 260-59 (August 1978) $2.30* SN003-003-01975-5

Velapoldi, R. A., Paule, R. C., Schaffer, R., Mandel, J., and Moody, J. R., Standard Reference Materials: A Reference Method for the Determination of Sodium in Serum, NBS Spec. Publ. 260-60 (August 1978). $3.00* SN003-003 01978-0

Verdier, P. H., and Wagner. H. L., Standard Reference Materials: The Characterization of Linear Polyethylene (SRM 1482, 1483, 1484), NBS Spec. Publ. 260-61 (December 1978). $1.70* SN003-003-02006-1

Soulen, R. J., and Dove, R. B., Standard Reference Materials: Temperature Reference Standard for Use Below 0.5 K (SRM 768). NBS Spec. Publ. 260-62 (April 1979). $2.30* SN003-003-02047-8

Velapoldi, R. A., Paule, R. C., Schaffer, R. Mandel, J., Machlan, L. A., and Gramlich, J. W., Standard Reference Materials: A Reference Method for the Determination of Potassium in Serum. NBS Spec. Publ. 260-63 (May 1979). $3.75* SN003-003-02068

Velapoldi, R. A., and Mielenz, K. D., Standard Reference Materials: A Fluorescence Standard Reference Material Quinine Sulfate Dihydrate (SRM 936), NBS Spec. Publ. 260-64 (January 1980). $4.25* SN003-003-02148-2

Marinenko, R. B., Heinrich, K. F. J., and Ruegg, F. C., Standard Reference Materials: Micro-Homogeneity Studies of NBS Standard Reference Materials, NBS Research Materials, and Other Related Samples. NBS Spec. Publ. 260-65 (September 1979). $3.50* SN003-003-02114-1

Venable, W. H., Jr., and Eckerle, K. L., Standard Reference Materials: Didymium Glass Filters for Calibrating the Wavelength Scale of Spectrophotometers (SRM 2009, 2010, 2013). NBS Spec. Publ. 260-66 (October 1979). $3.50* SN003-003-02127-0

Velapoldi, R. A., Paule, R. C., Schaffer, R., Mandel, J., Murphy, T. J., and Gramlich, J. W., Standard Reference Materials: A Reference Method for the Determination of Chloride in Serum, NBS Spec. Publ. 260-67 (November 1979). $3.75* SN003-003-02136-9

Mavrodineanu, R. and Baldwin, J. R., Standard Reference Materials: Metal-On-Quartz Filters as a Standard Reference Material for Spectrophotometry-SRM 2031, NBS Spec. Publ. 260-68 (April 1980). $4.25* SN003-003-02167-9

Velapoldi, R. A., Paule, R. C., Schaffer, R., Mandel, J., Machlan, L. A., Garner, E. L., and Rains, T. C., Standard Reference Materials: A Reference Method for the Determination of Lithium in Serum, NBS Spec. Publ. 260-69 (July 1980). $4.25* SN003-003-02214-4

Marinenko, R. B., Biancaniello, F., Boyer, P. A., Ruff, A. W., DeRobertis, L., Standard Reference Materials: Preparation and Characterization of an Iron-Chromium-Nickel Alloy for Microanalysis, NBS Spec. Publ. 260-70 (May 1981). $2.50* SN003-003-02328-1

Seward, R. W., and Mavrodineanu, R., Standard Reference Materials: Summary of the Clinical Laboratory Standards Issued by the National Bureau of Standards, NBS Spec. Publ. 260-71 (November 1981). $6.50* SN003-003-02381-7

Reeder, D.J., Coxon, B., Enagonio, D., Christensen, R. G., Schaffer, R., Howell, B. F., Paule, R. C., Mandel, J., Standard Reference Materials: SRM 900, Antiepilepsy Drug Level Assay Standard, NBS Spec. Publ. 260-72 (June 1981). $4.25* SN003-003-02329-9

Interrante, C. G., and Hicho, G. E., Standard Reference Materials: A Standard Reference Material Containing Nominally Fifteen Percent Austenite (SRM 486), NBS Spec. Publ. 260-73 (January 1982). $2.75* SN003-003-02386-8

Marinenko, R. B., Standard Reference Materials: Preparation and Characterization of K-411 and K-414 Mineral Glasses for Microanalysis: SRM 470. NBS Spec. Publ. 260-74 (April 1982). $3.50 SN003-003-023-95-7

Weidner, V. R., and Hsia, J. J., Standard Reference Materials: Preparation and Calibration of First Surface Aluminum Mirror Specular Reflectance Standards (SRM 2003a), NBS Spec. Publ. 260-75 (May 1982). $3.75 SN003-003-023-99-0

Hicho, G. E. and Eaton, E. E., Standard Reference Materials: A Standard Reference Material Containing Nominally Five Percent Austenite (SRM 485a), NBS Spec. Publ. 260-76 (August 1982). $3.50 SN003-003-024-33-3

Furukawa, G. T., Riddle, J. L., Bigge, W. G., and Pfieffer, E. R., Standard Reference Materials: Application of Some Metal SRM's as Thermometric Fixed Points, NBS Spec. Publ. 260-77 (August 1982). $6.00 SN003-003-024-34-1

Hicho, G. E. and Eaton, E. E., Standard Reference Materials: Standard Reference Material Containing Nominally Thirty Percent Austenite (SRM 487), NBS Spec. Publ. 260-78 (September 1982). $3.75* SN003-003-02435-0

Richmond, J. C., Hsia, J. J. Weidner, V. R., and Wilmering, D. B., Standard Reference Materials: Second Surface Mirror Standards of Specular Spectral Reflectance (SRM's 2023, 2024, 2025), NBS Spec. Publ. 260-79 (October 1982). $4.50* SN003-003-02447-3

Schaffer, R., Mandel, J., Sun, T., Cohen, A., and Hertz, H. S., Standard Reference Materials: Evaluation by an ID/MS Method of the AACC Reference Method for Serum Glucose, NBS Spec. Publ. 260-80 (October 1982). $4.75* SN003-003-02443-1

Burke, R. W., and Mavrodineanu, R. (NBS retired), Standard Reference Materials: Accuracy in Analytical Spectrophotometry, NBS Spec. Publ. 260-81 (April 1983). $6.00* SN003-003-024-8

Weidner, V. R., Standard Reference Materials: White Opal Glass Diffuse Spectral Reflectance Standards for the Visible Spectrum (SRM's 2015 and 2016). NBS Spec. Publ. 260-82 (April 1983). $3.75* SN003-003-02489-9**

Bowers, G. N., Jr., Alvarez, R., Cali, J. P. (NBS retired), Eberhardt, K. R., Reeder, D. J., Schaffer, R., Uriano, G. A., Standard Reference Materials: The Measurement of the Catalytic (Activity) Concentration of Seven Enzymes in NBS Human Serum SRM 909, NBS Spec. Publ. 260-83 (June 1983). $4.50* SN003-003-024 99-6

Gills, T. E., Seward, R. W., Collins, R. J., and Webster, W. C., Standard Reference Materials: Sampling, Materials Handling, Processing, and Packaging of NBS Sulfur in Coal Standard Reference Materials, 2682, 2683, 2684, and 2685, NBS Spec. Publ. 260-84 (August 1983). $4.50* SN003-003-02520-8

Swyt, D. A., Standard Reference Materials: A Look at Techniques for the Dimensional Calibration of Standard Microscopic Particles, NBS Spec. Publ. 260-85 (September 1983). $5.50* SN003-003-02521-6

Hicho, G. E. and Eaton, E. E., Standard Reference Materials: A Standard Reference Material Containing Two and One-Half Percent Austenite, SRM 488, NBS Spec. Publ. 260-86 (December 1983). $1.75* SN003-003-02541-1

Mangum, B. W., Standard Reference Materials: SRM 1969: Rubidium Triple-Point - A Temperature Reference Standard Near 39.30 °C, NBS Spec. Publ. 260-87 (December 1983). $2.25* SN003-003-02544-5

Gladney, E. S., Burns, C. E., Perrin, D. R., Roelandts, I., and Gills, T. E., Standard Reference Materials: 1982 Compilation of Elemental Concentration Data for NBS Biological, Geological, and Environmental Standard Reference Materials, Spec. Publ. 260-88 (March 1984). $7.00* SN003-003-02565-8

Hust, J. G., Standard Reference Materials: A Fine-Grained, Isotropic Graphite for Use as NBS Thermophysical Property RM's from 5 to 2500 K, NBS Spec. Publ. 260-89 (September 1984). $4.50* SN003-003-02608-5

Hust, J. G., and Langford, A. B., Standard Reference Materials: Update of Thermal Conductivity and Electrical Resistivity of Electrolytic Iron, Tungsten, and Stainless Steel, NBS Spec. Publ. 260-90 (September 1984). $3.00* SN003-003-02609-3

Goodrich, L. F., Vecchia, D. F., Pittman, E. S., Ekin, J. W., and Clark, A. F., Standard Reference Materials: Critical Current Measurements on an NbTi Superconducting Wire Standard Reference Material, NBS Spec. Publ. 260-91 (September 1984). $2.75* SN003-003-02614-0

Carpenter, B. S., Standard Reference Materials: Calibrated Glass Standards for Fission Track Use (Supplement to NBS Spec. Publ. 260-49). NBS Spec. Publ. 260-92 (September 1984). $1.50* SN003-003-02610-7

Ehrstein, J., Preparation and Certification of Standard Reference Materials for Calibration of Spreading Resistance Probes, NBS Spec. Publ. 260-93 (January 1985). $2.25* SN003-003-02633-6

Gills, T. E., Koch, W. F., Stolz, J. W., Kelly, W. R., Paulsen, P. J., Colbert, J. C., Kirklin, D. R., Pei, P.T.S., Weeks, S., Lindstrom, R. M., Fleming, R. F., Greenberg, R. R., and Paule, R. C., Methods and Procedures Used at the National Bureau of Standards to Certify Sulfur in Coal SRM's for Sulfur Content, Calorific Value, Ash Content, NBS Spec. Publ. 260-94 (December 1984). $2.25* SN003-003-02629-8

Mulholland, G. W., Hartman, A. W., Hembree, G. G., Marx, E., and Lettieri, T. R., Standard Reference Materials: Development of a 1 m Diameter Particle Size Standard, SRM 1690, NBS Spec. Publ. 260-95 (May 1985). SN003-003-02665-4

Carpenter, B. S., Gramlich, J. W., Greenberg, R. R., and Machlan, L. A., Standard Reference Materials: Uranium-235 Isotopic Abundance Standard Reference Materials for Gamma Spectrometry Measurements, NBS Spec. Publ. 260-96 (In Preparation).

Mavrodineanu, R. and Gills, T. E., Standard Reference Materials: Summary of the Coal, Ore, Mineral, Rock, and Refractory Standards Issued by the National Bureau of Standards, NBS Spec. Publ. 260-97 (September 1985).

Hust, J. G., Standard Reference Materials: Glass Fiberboard SRM for Thermal Resistance, NBS Spec. Publ. 260-98 (August 1985). SN003-003-02674-3

Callanan, J. E., Sullivan, S. A., and Vecchia, D. F., Standard Reference Materials: Feasibility Study for the Development of Standards Using Differential Scanning Calorimetry, NBS Spec. Publ. 260-99 (August 1985). SN003-003-02675-1

Taylor, J. K., Standard Reference Materials: Handbook for SRM Users, NBS Spec. Publ. 260-100 (September 1985).

Mangum, B. W., Standard Reference Materials: SRM 1970, Succinonitrile Triple-Point Standard: A Temperature Reference Standard Near 58.08 °C, NBS Spec. Publ. 260-101 (March 1986).

Weidner, V. R., Mavrodineanu, R., Mielenz, K. D., Velapoldi, R. A., Eckerle, K. L., and Adams, B., Standard Reference Materials: Holmium Oxide Solution Wavelength Standard from 240- 650 nm, SRM 2034, NBS Spec. Publ. 260-102 (In Press).

Hust, J. G., Standard Reference Materials: Glass Fiberblanket SRM for Thermal Resistance, NBS Spec. Publ. 260-103 (September 1985). SN003-003-02687-5

Mavrodineanu, R. and Alvarez, R., Standard Reference Materials: Summary of the Biological and Botanical Standards Issued by the National Bureau of Standards, NBS Spec. Publ. 260-104 (November 1985).

Mavrodineanu, R. and Rasberry, S.D., Standard Reference Materials: Summary of the Environmental Research, Analysis, and Control Standards Issued by the National Bureau of Standards, NBS Spec. Publ. 260-105 (March 1986).

Koch, W. F., ed., Standard Reference Materials: Methods and Procedures Used at the National Bureau of Standards to Prepare, Analyze and Certify SRM 2694, Simulated Rainwater, and Recommendations for Use, NBS Spec. Publ. 260-106.

* Send order with remittance to Superintendent of Documents, US Government Printing Office Washington, DC 20402. Remittance from foreign countries should include an additional one-fourth of the purchase price for postage.

** May be ordered from: National Technical Information Services (NTIS). Springfield Virginia 22161.

Abstract

This report describes the development, preparation, analysis and certification of Standard Reference Material, SRM 2694, Simulated Rainwater, intended to aid in the analysis of acidic rainfall. Details of the formulation and preparation of the two levels of solutions (2694-I and 2694-II) are given, as well as those of the precursor to the SRM, namely Research Material, RM 8409, Simulated Rainwater. The analytical techniques used to measure the twelve components in the solutions are described in detail. The data used in the statistical evaluation of the results are summarized and the recommended values for pH, specific conductance, acidity, fluoride, chloride, nitrate, sulfate, sodium, potassium, ammonium, calcium, and magnesium are tabulated. The instability of ammonium ion in acidic solutions is discussed. Recommendations for the use of SRM 2694, particularly with regard to the measurement of pH, are given.

Key words: acid rain; acidity; ammonium; analytical chemistry; conductivity; measurement; pH; precipitation; rainwater; Standard Reference Material; statistics; sulfate.

Foreword

Wet deposition is monitored by various laboratories and agencies as part of national and international networks to record accurately the composition of rainfall. These efforts are intended to determine the extent of the problem of "acid rain", and to establish spatial and temporal trends. Discrepancies in data often occur due to differences in instruments and techniques. These discrepancies limit the conclusions which may be drawn from the data. To establish a common basis for chemical measurements in rainwater, a multi-year research effort in the Inorganic Analytical Research Division, Center for Analytical Chemistry has been established. This effort has resulted in the issuance of initially a Research Material, RM 8409, Simulated Rainwater, and then a Standard Reference Material (SRM) 2694, Simulated Rainwater. This publication consists of a series of reports describing in detail the production, analysis, and certification of SRM 2694.

William F. Koch

Disclaimer

In order to describe adequately materials and experimental procedures discussed in this work, it was occasionally necessary to identify commercial products by manufacturer's name or label. In no instance does such identification imply endorsement by NBS of the particular product or equipment as being best available for that purpose.

Table of Contents

Part I

Preparation and Certification of Reference Materials for Rainwater Analysis

William F. Koch, George Marinenko, and Lisa A. Holland
Center for Analytical Chemistry

and

Robert C. Paule
National Measurement Laboratory
National Bureau of Standards
Gaithersburg, Maryland 20899

Introduction

The initial stages of the evolution of this SRM are described in detail in a previous article [1]. In that article, the early formulations of multi-component solutions are given, and the problems with their stablity are discussed. The stability problems inherent in these early formulations stem from both the complexity of the solutions and the use of glass ampoules as storage containers. The progression to polyethylene bottles and to simplified solutions, from which the transition and heavy metals were eliminated, resulted in solutions of greater stability and overall applicability to the measurements of pH, acidity, conductance, nitrate, and sulfate. These components are most critical to acid rain studies. As will be discussed later, not all the problems with stability, especially with respect to nitrate and ammonium have been solved. Research is continuing in this area. Associated difficulties with the measurement of pH and acidity are treated in other articles [2,3,4].

The pressing need of the scientific community for a common reference material for rainwater and the desire by us to field test such a material led to the production and distribution of a Research Material, RM 8409, Simulated Rainwater. RMs are distinguished from SRMs according to the definitions of the Office of Standard Reference Materials, National Bureau of Standards, [5]. In brief, RMs are high quality materials whose composition have been established by a single technique for each component. The composition of SRMs is certified after much more extensive testing involving at least two independent techniques for each component, or analysis by a definitive method. Often an RM uncovers unforeseen problems, as was the situation in this case. This problem involved the long-term stability of the ammonium ion. The extent of the instability and its ramifications will be addressed below. The primary focus of this paper will be the preparation, analysis, and certification of SRM 2694, beginning with a detailed discussion of RM 8409. Much of what is said about the RM is relevant to the SRM, as well.

The Preparation of RM 8409

The decision to prepare simulated rainwater, rather than collecting natural rainfall was based on the need to minimize contamination and unwanted components that would compromise the overall stability of the solutions. The

intent was to prepare two solutions of different concentrations of the various components, and to control the levels closely. Thus, simulated rainwater prepared by the dissolution of salts and acids in water was the best recourse.

The production of this simulated rainwater involved careful coordination of several operations, including bottle cleaning, formulations, dilution, mixing, and bottling.

Bottle Cleaning

Based on earlier research [1], low density polyethylene (LDPE) bottles (60-mL capacity) were chosen for this project. The bottles were cleaned using a rigorous procedure to minimize contamination. In brief, this cleaning procedure consisted of rinsing and soaking the bottles and caps for extended periods in filtered, distilled/deionized water. The bottles were then dried at 40 °C in a clean oven, and recapped until the filling operation was started. At all times, the bottles were kept away from areas with acid fumes. The exact procedure used to clean the bottles is given in Part III, Section 1.

Formulation and Target Values

Two levels of simulated rainwater containing the cations and anions commonly found in acid rain were formulated to span a useful analytical range of concentrations of all components. The target values for the two levels are shown in Table 1. It should be noted that the measurement of pH was the primary driving force behind the development of this reference material. Hence, the stability of the solutions with respect to pH was an over-riding constraint.

Unbuffered solutions at pH 4.5 or above are extremely susceptible to fluctuations in pH and acidity due to absorption and desorption of atmospheric carbon dioxide. These processes occur even through the walls of the polyethylene bottles. For this reason, although it would have been desirable to issue a solution of pH 5.0, RM 8409-I (as well as SRM 2694-I) was targeted at pH 4.3 as a precaution.

Mixing of Simulated Rainwater

Seven ACS-reagent grade salts and three high-purity acids [6] were used in the preparation of the two levels of simulated rainwater. For convenience in the mixing process, stock solutions of the salts and acids were prepared. Table 2 lists the chemicals and the concentrations of the stock solutions. Table 3 lists the weights of each of the stock solutions used in the final dilutions of the solutions.

A 20-liter polyethylene carboy that had been cleaned according to the same procedure used for the bottles, was used in the final dilution of the appropriate amount of each of the stock solutions. The dilution volume was only approximate. It was never intended to prepare these solutions to an exact concentration; rather, the concentrations of the analytes of interest would be determined by analysis. After diluting, the solutions were mixed thoroughly by vigorous shaking of the carboy and allowed to equilibrate for 48 hours before bottling. The bottles were filled, capped, and then sealed

Table 1. Target Values of RM 8409 and SRM 2694, Simulated Rainwater

	Level I	Level II
pH	4.3	3.6
Specific Conductance, μS/cm	25	130
Acidity, meq/L	0.05	0.28
Fluoride, mg/L	0.05	0.1
Chloride, mg/L	0.25	1.0
Nitrate, mg/L	0.5	7
Sulfate, mg/L	2.7	11
Sodium, mg/L	0.2	0.4
Potassium, mg/L	0.05	0.1
Ammonium, mg/L	0.1	1.0
Calcium, mg/L	0.01	0.05
Magnesium, mg/L	0.025	0.05

Table 2. Stock Solutions Used in the Preparation of RM 8409 and SRM 2694

Stock Solution	Chemical	Concentration
1	$NaNO_3$	1 mg salt/g solution
2	KNO_3	1 mg salt/g solution
3	$CaCl_2 \cdot 2H_2O$	1 mg salt/g solution
4	$MgSO_4 \cdot 7H_2O$	1 mg salt/g solution
5	NH_4Cl	1 mg salt/g solution
6	$(NH_4)_2SO_4$	1 mg salt/g solution
7	H_2SO_4	0.100 N (0.050 mol/L)
8	HNO_3	0.100 N (0.100 mol/L)
9	HCl	0.050 N (0.050 mol/L)
10	NaF	1 mg salt/g solution

Table 3. The Weights of the Stock Solutions Used in the
Preparation of RM 8409

Stock Solution	8409-I (Final Volume, 20 L)	8409-II (Final Volume, 20 L)
1	9.8 grams	19.6 grams
2	2.6 grams	5.2 grams
3	1.1 grams	3.7 grams
4	4.1 grams	8.2 grams
5	6.0 grams	0 grams
6	0 grams	73.3 grams
7	10.0 grams	30.0 grams
8	0.2 grams	20.0 grams
9	0 grams	10.0 grams
10	2.3 grams	4.7 grams

with white plastic shrink-seals. Periodic checks of the pH of the solutions
were made during the filling process to track the homogeneity. Approximately
300 bottles of each level were filled, and labeled RM 8409-I and RM 8409-II.

Analysis of RM 8409

The techniques used in the analysis of RM 8409 were potentiometry,
conductimetry, coulometry, ion chromatography, atomic absorption spectro-
metry, and flame emission spectrometry. Note that for an RM, only a single
technique is required for each analyte or parameter. A brief overview of the
methods follows. The methods are described in more detail as they were
applied to the analysis of SRM 2694 in Part II of the publication.

The pH of the solutions was determined using a combination glass/
reference electrode and pH meter of commercial manufacture. The pH measure-
ment system was calibrated with two standard buffer solutions, prepared from
SRMs 185f potassium hydrogen phthalate, and 186Ic/186IIc potassium dihydrogen
phosphate/disodium hydrogen phosphate. To minimize the bias due to residual
liquid junction potentials, all pH measurements were normalized to a dilute
solution of sulfuric acid, SA84. The pH of SA84 was determined using the
procedure and apparatus used in the certification of the NBS pH buffers in
cells without liquid junction and with hydrogen electrodes. The pH value of
SA84 so determined was verified by calculations based on the coulometric
determination of hydrogen ion and the ion chromatographic determination of
sulfate ion. Activity coefficient corrections were applied. For solutions
of sulfuric acid of this concentration the activity coefficient is 0.926.
The pH value of SA84 is 3.77 with an uncertainty of 0.01.

The acidity of RM 8409 was determined by coulometric titration through the electrogeneration of hydroxide ion according to procedures developed and verified in this laboratory. The equivalence point was determined, using a combination glass/reference electrode, by location of the inflection point. The samples were de-aerated using argon gas to remove dissolved carbon dioxide. It has been established that carbon dioxide, if not expurgated, will bias the acidity value.

The aqueous conductance of RM 8409, expressed as specific conductance, was measured using a dip-type cell with a cell constant of 0.0997 cm^{-1}. The cell constant was determined using a 0.001 demal potassium chloride solution. All measurements were made in a thermostated bath at 25.0 °C.

The anions, sulfate, nitrate, chloride, and fluoride, were determined by ion chromatography. Three different procedures were used based on two instruments, three different separator columns, different eluents, and either packed-bed resin suppression or hollow-fiber suppression. Similar results were obtained by all procedures.

Ammonium ion was determined using an ammonia sensing ion selective electrode. The procedure used was that described in "Methods for Chemical Analysis of Water and Wastes," EPA-600/4-79-020, March 1979, Method 350.3.

Sodium, potassium, and calcium were determined by flame emission spectrometry with repetitive optical scanning. Magnesium was determined by flame atomic absorption spectrometry. Dilutions from each level were prepared and analyzed. The recovery of each analyte was checked by the single standard addition method.

The results of the characterization of RM 8409 are shown in Tables 4 and 5. The uncertainties are expressed as the standard deviation of a single measurement and include only the random components of error. The Report of Investigation for RM 8409 is given in Part III, Section II of this publication. Note that although values for ammonia and ammonium ion are listed in Table 4, no values appear in the Report of Investigation. This is discussed in detail in the next section.

Stability of RM 8409

The problem with the stability of ammonium ion was first noticed upon re-analysis of RM 8409 eight months after its preparation. The concentration of ammonium in RM 8409-I had decreased from 0.085 mg/L to 0.025 mg/L. Re-analysis of other samples of simulated rainwater which were part of a long-term stability study of pH and conductivity, indicated that similar decreases in ammonium ion had occurred. The decrease was significant when the initial concentration of ammonium was below 0.2 mg/L and the pH was above 4.0 (see Table 6). The cause of this decrease is not known at this time, but it is suspected to be biological activity. The loss of ammonium does not appear to have significantly affected any other components. A solution to this problem involving the sterilization of the "Simulated Rainwater" is currently under investigation. Preliminary studies indicate that chloroform tends to retard the loss of ammonium ion, but does not completely eliminate the degradation.

Table 4. Summary of Values for RM 8409-I

	Mean	Std. Dev.[1]	n[2]
pH	4.32	0.03	10
Specific Conductance, μS/cm at 25.0 °C	25.5	0.2	6
Acidity, meq/L	0.055	0.002	10
Fluoride, mg/L	0.058	0.001	10
Chloride, mg/L	0.230	0.003	8
Nitrate, mg/L	0.535	0.004	8
Sulfate, mg/L	2.62	0.01	8
Sodium, mg/L	0.208	0.006	5
Potassium, mg/L	0.058	0.003	5
Ammonium, mg/L	0.085	0.006	7
Calcium, mg/L	0.027	0.004	5
Magnesium, mg/L	0.026	0.001	5

[1]Standard deviation of a single measurement.
[2]n is the number of independent measurements.

Table 5. Summary of Values for RM 8409-II

	Mean	Std. Dev.[1]	n[2]
pH	3.61	0.02	8
Specific Conductance, µS/cm at 25.0 °C	128.3	0.4	6
Acidity, meq/L	0.280	0.005	6
Fluoride, mg/L	0.102	0.002	8
Chloride, mg/L	1.00	0.02	15
Nitrate, mg/L	7.18	0.10	8
Sulfate, mg/L	10.47	0.05	8
Sodium, mg/L	0.410	0.004	5
Potassium, mg/L	0.112	0.002	5
Ammonium, mg/L	1.074	0.026	7
Calcium, mg/L	0.054	0.005	5
Magnesium, mg/L	0.050	0.006	5

[1] Standard deviation of a single measurement.
[2] n is the number of independent measurements.

Table 6. Stability of Ammonium Ion in Simulated Rainwater

			Ammonium Ion, mg/L	
Sample	Preparation Date	pH	Initial	Feb. 20, 1985
RM 8409-I	June 1984	4.3	0.085	0.025
RM 8409-II	June 1984	3.6	1.07	1.07
DSPRM V-1	Feb. 1983	4.5	0.14	0.09
DSPRM V-2	Feb. 1983	3.5	1.11	1.08
DSPRM V-3	Feb. 1983	4.0	0.42	0.42

The recovery after 6 months was approximately 90%. All other components were unaffected by the addition of chloroform to the sample. Sterilization by gamma-ray irradiation (Co-60) resulted in 100% recovery of ammonium ion after 6 months. However, there were some losses of nitrate (approximately 10%) presumably due to radiolysis. It is planned to further investigate this procedure to ascertain whether the radiolysis affects a large set of samples in a uniform manner.

There have been isolated incidences of visible fungal growth in a few bottles of RM 8409, returned to NBS by the Illinois State Water Survey. When analyzed, these returned samples showed elevated sodium and chloride concentrations, decreased ammonium and nitrate concentrations, higher pH, and an unidentified anion, which eluted just before sulfate on the ion chromatograph. At first it was suspected that the cause may have been improperly rinsed bottles which still contained traces of sodium carbonate. This hypothesis has been disproven by extensive testing in which some samples were deliberately spiked with sodium carbonate and incubated for 1 month at 37 °C. Such treatment did not affect the chloride concentration, nor did it accelerate bacterial degradation of the sample, nor did it give the new anion peak. Furthermore, documentation of the bottle-cleaning procedure for RM 8409 indicates that sodium carbonate was not used in the process.

Upon visual examination of twenty sets of RM 8409 on October 15, 1985, it was noticed that some of the bottles caps had become loose, some to the extent that when the bottles were squeezed they would leak solution, although there was no apparent bacterial/fungal growth. Eight out of the twenty sets were analyzed by ion chromatography. The bottles with the loose caps exhibited the increase in Na^+ and Cl^-, and the appearance of the new anion peak, as had been observed with the samples returned from Illinois State Water Survey. Note that all samples had been securely tightened when prepared and had been "sealed" with the white shrink bands. We conclude that the contamination problem is due to bottles caps backing-off from their sealed positions over time, thereby permitting losses of solution and/or gain of contamination. This effect would be enhanced if the samples are shipped in the unpressurized cargo hold of an airplane.

The re-analysis of samples of RM 8409 (from bottles whose caps were securely tightened) indicated that the solutions are very stable for most components for 18 months, (see Table 7), the notable exception being ammonium ion in level I. The pH of level I also seems to have changed slightly downward. All other components tested in this re-analysis are within the uncertainty of the measurements.

The Preparation of SRM 2694

Having established the need for a simulated rainwater reference material, the decision was made to prepare new sets of solutions at a scaled-up production level and to certify these new sets as a Standard Reference Material, SRM 2694. The same philosophy that guided the production of RM 8409 was in force for SRM 2694. Two levels of solutions were to be prepared, similar in all respects to the RM. The target values were identical (see Table 2) and the bottles were cleaned according to the same instructions used for the RM (see Part III, section I).

Table 7. Re-analysis of Selected Components in RM 8409
18 Months After Preparation

	8409-I		8409-II	
	After 18 Months	Initial	After 18 Months	Initial
pH	4.27	4.32	3.60	3.61
Chloride, mg/L	0.23	0.230	1.0	1.00
Nitrate, mg/L	0.51	0.535	7.2	7.18
Sulfate, mg/L	2.66	2.62	10.6	10.5
Sodium, mg/L	0.21	0.208	0.42	0.410
Potassium, mg/L	0.056	0.058	0.10	0.112
Ammonium, mg/L	0.017	0.085	1.08	1.07

Mixing of SRM 2694

Seven ACS-reagent grade salts and three high-purity acids [6] were used in the preparation of the two levels of simulated rainwater. For convenience in the mixing process, stock solutions of the salts and acids were prepared in identical fashion as for RM 8409 (see Table 2). Table 8 lists the weights of each of the stock solutions used in the final dilutions of the solutions.

Table 8. The Weights of the Stock Solutions Used in the
Preparation of SRM 2694

Stock Solution	2694-I (Final Volume, 170 L)	2694-II (Final Volume, 150 L)
1	83.43 grams	147.27 grams
2	22.06 grams	38.74 grams
3	9.61 grams	27.66 grams
4	34.88 grams	61.60 grams
5	50.97 grams	0 grams
6	0 grams	550.05 grams
7	85.00 grams	225.04 grams
8	1.78 grams	149.98 grams
9	0 grams	75.00 grams
10	19.89 grams	35.24 grams

A 200-liter polyethylene, cylindrical tank, which had been cleaned according to the same procedure used for the bottles, was used in the final dilution of the appropriate amounts of each of the stock solutions. Graduations at 10-liter increments were made on the outside of the tank as it was being filled during the cleaning process. These marks served only as an indication of the volume, and were not intended to calibrate the volume accurately. A stirring motor with a teflon paddle was used to thoroughly mix the solutions. Figure 1 shows a picture of the apparatus in operation.

Approximately 170 liters of 2694-I and approximately 150 liters of 2694-II were prepared in February 1985, according to the following procedure. The calculated amounts of stock solutions #1 through #9, (see table 8), were added to 100 liters of filtered, distilled/deionized water in the tank. The resulting solution was mixed thoroughly. Then the calculated amount of solution #10 (sodium fluoride) was slowly added. It was necessary to delay the input of sodium fluoride to prevent the possible precipitation of calcium fluoride, which is extremely difficult to redissolve. Filtered distilled/ deionized water was then added to bring the total volume to the pre-established mark. The solution was thoroughly homogenized by intermittent vigorous stirring over a 24-hour period. Note that although care was taken to add exact amounts of each component and to dilute with the correct amount of water, there was no convenient way to accurately assess the final volume. Hence, the weights and volumes could not be used as an analytical measure of the concentrations of the various components. This was left to the analytical chemists and their myriad of techniques.

Bottling

Before the bottling commenced, a sample of each level was analyzed by ion chromatography and potentiometry to verify that the target values had been met. The bottling of each level was completed in a single day. The bottles were filled manually, capped immediately, and placed sequentially in numbered cartons. Concurrent with the bottling operation, a homogeneity test was run. One out of every 120 bottles was pulled from the line and tested for specific conductance. The results, shown in Tables 9 and 10, demonstrate that the two solutions are homogeneous.

The Analysis of Simulated Rainwater

After establishing the homogeneity of the solutions by the measurement of conductivity, the statistical design for the sampling and analysis of the other components was configured. Each component was to be determined in triplicate in each of three bottles (selected from the beginning, middle and end of the bottling operation) by each technique. Because of experimental exigencies of some techniques, this analysis design was not strictly adhered to in every case, but was followed whenever possible.

The techniques used in the analysis of SRM 2694 were ion chromatography (IC), conductivity, potentiometry, coulometry, isotope dilution mass spectrometry (IDMS), spectrophotometry, laser enhanced ionization flame spectrometry (LEIS), flame emission spectrometry (FES), inductively coupled plasma (ICP), and flame atomic absorption spectrometry (FAAS). Details of the analytical procedures for each technique are given in Part II of this publication. A brief overview of the methods will be given here.

Figure 1. Apparatus used in the preparation and dispensing of SRM 2694

Table 9. Homogeneity Test, Specific Conductance of SRM 2694-I
         in Units of Microsiemens Per Centimeter at 25.0 °C

Bottle Number	Run #1	Run #2
101a	25.43	25.52
101b	25.48	25.50
102a	25.45	25.44
102b	25.43	25.47
103a	25.48	25.50
103b	25.47	25.44
104a	25.44	25.47
104b	25.46	25.50
105a	25.45	25.44
105b	25.45	25.47
106a	25.44	25.48
106b	25.50	25.48
107a	25.48	25.46
107b	25.44	25.50
108a	25.46	25.48
108b	25.45	25.45
109a	25.49	25.48
109b	25.45	25.48
110a	25.47	25.44
110b	25.46	25.46

Mean   25.47 µS/cm at 25.0 °C
Std. Dev. of a
   Single Measurement   0.02

Table 10. Homogeneity Test, Specific Conductance of SRM 2694-II in Units
          of Microsiemens Per Centimeter at 25.0 °C

Bottle Number	Run #1	Run #2
1a	130.1	130.3
1b	129.4	130.2
2a	129.8	130.0
2b	129.8	129.6
3a	130.2	129.8
3b	130.1	129.7
4a	130.1	130.0
4b	130.3	130.2
5a	129.4	129.8
5b	130.3	130.2
6a	129.6	129.9
6b	130.0	130.7
7a	130.2	130.8
7b	130.4	129.9
8a	130.1	129.9
8b	130.4	130.8
9a	129.9	129.7
9b	130.1	130.1

Mean   130.1 µS/cm at 25.0 °C
Std. Dev. of a
   Single Measurement   0.3

Ion chromatography was used to determine the concentrations of fluoride, chloride, nitrate, sulfate, sodium, potassium, and ammonium. Dual channel, dual column IC with hollow fiber chemical suppressor systems was employed. For each level and each component, three calibration points (peak height versus concentration) which bracketed closely the concentrations of the individual components were established. Chloride, nitrate, and sulfate were determined sequentially under one set of chromatographic conditions. A different set of conditions, involving an extremely weak carbonate eluent, was required to resolve the fluoride peak from the negative water-dip to allow the accurate determination of the fluoride concentrations. The cations were determined using a hydrochloric acid eluent.

The specific conductance was measured using a dip-type conductance cell of nominal cell constant 0.1 cm^{-1} and an A.C. conductivity bridge operating at 1 kHz. Measurements for certification were made at 25.0 °C by thermostating the solutions in a water-jacketed beaker, the outer chamber of which contained circulating constant temperature water to maintain the temperature at 25.0 °C. The exact cell constant of the cell was determined using 0.001 demal KCl, which has a specific conductance of 146.93 microsiemens per centimeter [μS/cm]. Measurements were also made at temperatures ranging from 20 °C to 28 °C to establish the temperature coefficient for the specific conductance of these solutions. The temperature coefficient for both levels was determined to be 1.5 percent per °C at 25.0 °C.

Potentiometry was used to measure pH, fluoride, ammonium, and chloride. Measurements of pH were made with a combination glass electrode according to the procedure established at NBS. All measurements were corrected for residual liquid junction potential bias by normalizing to a dilute solution of sulfuric acid, whose pH had been determined accurately in a hydrogen cell without liquid junction. This cell is of the type used in the certification of the NBS pH buffers. Fluoride was measured with a fluoride ion-selective electrode after addition of an ionic strength adjustment buffer. Standards which bracketed the concentrations of the rainwater samples were analyzed. Ammonium ion was determined using an ammonia electrode. The method involves addition of concentrated base to the sample thereby liberating ammonia which diffuses through the semipermeable membrane of the electrode and is sensed by an internal glass pH electrode. Chloride was also determined potentiometrically using a chloride ion-selective electrode. However, the concentrations of chloride in the simulated rainwater are well below the linear range of response. Thus they are prone to a large uncertainty. The chloride measurements serve only as an indication of concentration and were not used in the final statistical analysis. This method and its values are presented for information only.

The acidity of SRM 2694-II was determined by coulometric reduction of hydrogen ion in a weighed sample, from which CO_2 had been removed by purging with argon [3,4]. Titrations were carried out to the neutrality point, determined potentiometrically.

Thermal ionization isotope dilution mass spectrometry was used to determine the total sulfur in the simulated rainwater. This value was then converted to sulfate concentration. Briefly, the method involves the reduction of sulfate to sulfide, distillation of sulfide and collection in a basic arsenic [III] solution, followed by mass spectrometric identification and quantitation of AsS^+ isotopes [7,8].

Spectrophotometry was used for the determination of nitrate. The procedure was based on the color reaction produced by the interaction of nitrate ion and the organic reagent, brucine. Careful attention to experimental procedures and frequent calibration with nitrate standards were required to obtain satisfactory results by this method.

Laser-enhanced ionization flame spectrometry, a new analytical tool in the Inorganic Analytical Research Division, was utilized for the determination of sodium, potassium, calcium, and magnesium. Wavelength scans near the analysis lines were performed to check for spectral background and interfering lines. Minor corrections were applied to the magnesium determination to correct for sodium interference. Magnesium concentration was also determined by flame atomic absorption spectrometry.

Inductively coupled plasma spectrometry was used to measure the calcium concentration in the samples, and flame emission spectrometry was used to determine sodium and potassium. The recovery of each analyte was checked by the single standard addition method.

In addition, the density of the solutions was determined to be 0.997 g/mL at 23 °C, essentially identical to pure water at this temperature.

Results and Statistical Analysis

The average values from each measurement technique are shown in Table 11. Values in parentheses represent the standard deviation of a single measurement. Values in braces are the number of analyses performed. We have used established techniques to calculate weighted averages for the SRM certificate values. The statistical weighting is based on the observed variabilities of the various data sets for each analyte. The procedures for deriving the weighted averages and their uncertainties have been described in a previous article [9]. Table 12 contains the certified values and uncertainties for SRM 2694.

The uncertainties associated with fluoride, nitrate, sodium, potassium, calcium, and magnesium are two standard deviations of the certified values. The uncertainties in the certified values for pH, acidity, and specific conductance are based on scientific judgment and experience, rather than on true statistical evaluations because there were no practical second methods of analysis for these components. Definitive methods were used for the measurements of pH, acidity, and specific conductance.

The uncertainties tabulated for sulfate are also based on scientific judgment even though there were two independent methods of analysis. For this analyte, the agreements both within and between the methods of analysis were so close that the statistical evaluations of the uncertainties were not believed to be realistic. The uncertainties for these latter four components [pH, acidity, specific conductance, and sulfate] are believed to be roughly equivalent to two standard deviations of the certified values.

Table 11. Summary of Data Used in the Initial
Certification of SRM 2694

Component Technique	2694-I[1]	2694-II[1]
1. pH		
A. Potentiometry	4.297(.010){7}	3.591(.007){8}
2. Specific Conductance (μS/cm @ 25 °C)		
A. Conductimetry	25.47(.02){40}	130.1(.3){36}
3. Acidity, meq/L		
A. Coulometry	0.0501(.0015){6}	0.2835(.0045){6}
4. Fluoride, mg/L		
A. IC	0.055(.001){12}	0.095(.001){11}
B. Potentiometry	0.0532(.0015){8}	0.102(.003){8}
5. Chloride, mg/L		
A. IC	0.242(.007){9}	1.003(.032){9}
B. Potentiometry	0.29(.05){8}	0.87(.19){8}
6. Nitrate, mg/L		
A. IC	0.513(.007){9}	7.141(.044){9}
B. Spectrophotometry	0.49(.02){9}	6.98(.05){9}
7. Sulfate, mg/L		
A. IC	2.688(.018){9}	10.83(.06){12}
B. IDMS	2.697(.012){5}	10.81(.03){6}
8. Sodium, mg/L		
A. IC	0.204(.004){12}	0.412(.002){12}
B. LEIS	0.1974(.0030){22}	0.411(.006){22}
C. FES	0.212(.004{5}	0.432(.006){5}
9. Potassium, mg/L		
A. IC	0.053(.008){8}	0.107(.010){12}
B. LEIS	0.0478(.0015){12}	0.1023(.0031){16}
C. FES	0.055(.001){6}	0.111(.001){6}
10. Ammonium, mg/L		
A. IC		1.064(.005){12}
B. Potentiometry	0.1031(.0039){6}	1.034(.010){7}
11. Calcium, mg/L		
A. LEIS	0.0126(.0004){12}	0.0436(.0005){12}
B. ICP	0.015(.002){6}	0.054(.003){7}
12. Magnesium, mg/L		
A. LEIS	0.0231(.0003){14}	0.0492(.0005){13}
B. FAAS	0.025(.001){6}	0.052(.006){6}

[1]Values in parentheses represent the standard deviation of a single
measurement. Values in braces are the number of determinations.

Table 12. Certified Values for SRM 2694 (September 19, 1985)

Component	2694-I[1]	2694-II[1]
pH @ 25 °C	4.30 ± 0.02	3.59 ± 0.02
Specific Conductance (μS/cm @ 25 °C)	26 ± 2	130 ± 2
Acidity, meq/L	0.050 ± 0.002	0.284 ± 0.005
Fluoride, mg/L	0.054 ± 0.002	0.098 ± 0.007
Chloride, mg/L	(0.24)[2]	(1.0)[2]
Nitrate, mg/L	0.501 ± 0.026	7.06 ± 0.15
Sulfate, mg/L	2.69 ± 0.03	10.8 ± 0.1
Sodium, mg/L	0.205 ± 0.009	0.419 ± 0.015
Potassium, mg/L	0.052 ± 0.007	0.106 ± 0.008
Ammonium, mg/L		(1.0)[2]
Calcium, mg/L	0.014 ± 0.003	0.049 ± 0.011
Magnesium, mg/L	0.024 ± 0.002	0.051 ± 0.003

[1] The estimated uncertainties are 2 standard deviations of the certified values, except in the cases of pH, acidity, conductance, and sulfate which are based on scientific judgment and are roughly equivalent to 2 standard deviations of the certified value.

[2] The values for chloride and ammonium are not certified, but are listed for information only.

The values for chloride and ammonium are listed for information only. Chloride was not certified because the potentiometric method had insufficient precision and accuracy at these levels to corroborate the ion chromatographic data. Until a second independent technique verifies the IC measurements, chloride will not be certified. Ammonium ion was not certified because of very real concerns about the stability of this ion in these solutions, based on the experience with RM 8409, and on preliminary stability studies of SRM 2694.

Re-Analysis of SRM 2694

As part of our continuing quality assurance program, SRM 2694 was subjected to re-analysis of select components approximately one year after its preparation. The procedures used in this analysis were similar to those described in brief above, and in detail in Part II of this document. Specific conductance was measured using a dip-type conductance cell, thermostated at 25 °C. The pH values of the solutions were determined potentiometrically with a combination glass electrode. The control sample used in this case was an internally generated standard of dilute, sulfuric acid, the pH of which had been determined via the Harned cell. The anions, chloride, nitrate, and sulfate, were determined by ion chromatography. Fluoride was determined potentiometrically using a fluoride ion-selective electrode. The cations, sodium, ammonium and potassium, were determined by ion chromatography.

The results of this re-analysis are summarized in Table 13. It is apparent that some components have changed to the extent of being outside of certification. The pH of 2694-I appears to have shifted slightly lower. It is recommended to change the pH value to 4.27 to 0.03. Sulfate has increased in both 2694-I and 2694-II, approximately 3-5 micrograms per bottle. This is possibly due to leaching of sulfur from the bottle or from diffusion of sulfur dioxide through the bottle. It is recommended to revise the certified values of sulfate to 2.75 ± 0.05 mg/L for 2694-I, and to 10.9 ± 0.2 mg/L.

Nitrate in 2694-I is particularly worrisome. The mean value listed in Table 13 does not fully indicate the extent of the problem. Of the nine bottles analyzed in this recheck, one of the bottles exhibited a marked decrease in nitrate content of about 10%. Two independent laboratories who had purchased SRM 2694 also reported greatly reduced concentrations of nitrate in 2694-I. It is believed that, similar to the problems with ammonium, bacterial or fungal activity is at fault. Because of this instability it is recommended that the value for nitrate in 2694-I be removed from Certification.

The Certificate of Analysis has been revised to reflect these changes as recommended above and is included in Section IV in Part III.

Table 13. Summary of the 12-Month Re-Analysis of SRM 2694

Component	2694-I[1]	2694-II[1]
pH @ 25 °C	4.258 (0.004)	3.595 (0.002)
Specific Conductance (5 @ 25 °C)	26.1 (0.3)	129 (2)
Fluoride, mg/L	0.053 (0.003)	0.009 (0.002)
Chloride, mg/L	0.238 (0.003)	1.02 (0.0)[1]
Nitrate, mg/L	0.510 (0.023)	7.22 (0.01)
Sulfate, mg/L	2.76 (0.001)	10.93 (0.02)
Sodium, mg/L	0.202 (0.001)	0.414 (0.002)
Ammonium, mg/L	----	1.064 (0.001)
Potassium, mg/L	0.052 (0.001)	0.112 (0.003)

[1] Values listed in parentheses represents the standard deviation of a single measurement.

Precautions and Recommendations for Use

It must be noted that the solutions of SRM 2694, being very dilute and unbuffered, are very susceptible to contamination, which can cause gross changes in the certified values. 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. It has been reported to us that a sample of RM 8409 which had been opened, recapped, and stored in a refrigerator lost virtually all of its nitrate content, but gained a significant amount of nitrite.

SRM 2694 should be stored in an area free from acid and/or ammonia vapors. These vapors can permeate the polyethylene bottles and contaminate the samples. A set of samples placed in our laboratory refrigerator which also contained a polyethylene bottle of concentrated ammonium hydroxide showed a substantial increase in ammonium ion concentration. Refrigeration of SRM 2694 is not necessary. However, the solutions should not be exposed to extreme heat (i.e., temperatures above 35 °C) as this will accelerate transpiration of water vapor from the bottles. The bottles of SRM 2694 have been sealed in aluminized bags to retard transpiration and should remain within the sealed bags until just before use. The search for a better container has been initiated.

If conductance and pH are to be measured on the same sample, then conductance should be measured first. Otherwise, leakage of concentrated KCl from the pH reference electrode will affect the conductance reading. The measurement of pH should be performed according to the guidelines set forth in an attachment to the Certificate of Analysis of SRM 2694, appended to this report (Part III). Adherence to this procedure will 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. Other precautions specific to the individual techniques used in the analysis of rainwater are detailed in Part II of this publication.

Acknowledgements

References

1. Koch, W.F., Marinenko, G., and Wu, Y.C., "The Development of Reference Materials for Acid Rain Research," Environment International 10, 117-121 (1984).

2. Koch W.F. and Marinenko, G., "Simulated Precipitation Reference Materials: Measurement of pH and Acidity," Sampling and Analysis of Rain, ASTM STP 823, S.A. Campbell, Ed., American Society for Testing and Materials, 10-17 (1983).

3. Marinenko, G. and Koch, W.F., "A Critical Review of Measurement Practices for the Determination of pH and Acidity of Atmospheric Precipitation," Environment International 10, 315-319 (1984).

4. Marinenko, G. and Koch, W.F., "Evaluation of Methods Used for the Determination of Acidity in Acid Rain Samples," National Bureau of Standards [U.S.], NBSIR 85-3114, March 1985, 16 pp.

5. NBS Standard Reference Materials Catalog 1984-1985, C.H. Hudson, Ed., National Bureau of Standards [U.S.], Special Publication 260, p. 2, (February 1984).

6. Moody, J.R. and Beary, E.S., "Purified Reagents for Trace Metal Analysis," Talanta 29, 1003-1010, (1982).

7. Paulsen, P.J. and Kelly, W.R., "Determination of Sulfur by Isotope Dilution Thermal Ionization Mass Spectrometry as AsS+ Ions," Anal. Chem. 56, 707-713 (1984).

8. Kelly, W.R. and Paulsen, P.J., "Determination of Sulfur in NBS Coals by Isotope Dilution Thermal Ionization Mass Spectrometry," in Methods and Procedures used at the National Bureau of Standards to Certify Sulfur in Coal SRMs for Sulfur Content, Calorific Value, Ash Content, T. E. Gills, Ed., National Bureau Standards (U.S.), Special Publication 260-94, pp 7-13, (December 1984).

9. Paule, R.C. and Mandel, J., "Consensus Values and Weighting Factors", J. Res. Natl. Bur. Stand. 87, 377-385 (1982).

Determination of Nitrate by Spectrophotometry

M.V. Smith and R.W. Burke
Center for Analytical Chemistry
National Bureau of Standards
Gaithersburg, Maryland 20899

Introduction

The concentrations of nitrate ions in the two levels of SRM 2694, Simulated Rainwater, were determined by a spectrophotometric method based on the color reaction produced by NO_3^- and the organic reagent brucine. Color development is carried out in a sulfuric acid medium in a boiling water bath. Although many variables affect the reproducibility of the method, careful control of reaction conditions and the utilization of proper technique for transferring the viscous acid solutions to cuvettes for spectrophotometric measurement provide a procedure that is adequate for the analysis of these kinds of water samples. Some analytical points that merit special attention in order to obtain precise and accurate nitrate results are outlined below.

The specific brucine procedure used for the analysis of the Simulated Rainwater samples was basically that developed by Jenkins and Medsker [1]. This procedure is a modification of the older Standard Methods Procedure [2] that provided the following improvements: (1) improved precision by closer control of reaction conditions, (2) eliminated variable chloride interference by "masking" with a high concentration of added chloride, and (3) improved linearity of calibration plots by reducing the sulfuric acid concentration used for color development. Additionally, Jenkins and Medsker cautioned about the non-suitability of certain lots of brucine for nitrate determination and described a useful test for checking for this possibility. Two other points not specifically mentioned in their paper, but which could be useful to analysts using this procedure, concern (1) a somewhat novel design for the water bath and (2) a recommended technique for transferring the sample solutions to and from the spectrophotometer cuvettes.

The water bath used for these measurements was fabricated from a 190 mm x 100 mm crystallizing dish that was fitted with a 190 mm diameter porcelain cover plate. This plate originally had been the crucible support in a desiccator. This plate contained seven 40 mm diameter holes that were equally spaced around its periphery. Rubber O-rings were used to suspend 25 mm x 150 mm test tubes in the bath. During color development, the bath was maintained at 100 °C with a hot plate and stirred constantly with a motor-driven stirrer that passed through a hole that had been drilled in the center of the plate. The level of water in the stirred bath was maintained at the level of liquid in the test tubes by adjustment of the O-rings. To further improve heat transfer, the solutions in the individual tubes were stirred with glass rods every five minutes throughout the course of the one hour color development step.

Our experience in transferring solution to the cuvettes has been that the best way to avoid producing bubbles and schlieren in viscous solutions is, once the solutions are thoroughly mixed, subsequent agitation of the solutions should be kept at a minimum. The best way to do this is to effect all transfers of solutions to and from the measuring curvettes with disposable Pasteur-type pipettes. In these operations, the tip of the pipette is always kept below the surface of the liquid and in contact with a non-polished wall of the curvette. Solution is introduced or removed by gentle compression or release of the rubber manipulating bulb.

Application of the above method and precautions to the determination of nitrate in NBS SRM 2694 Simulated Rainwater produced the data given in Table 1. It remains to be shown if the precision of the brucine procedure can be improved significantly over that obtained here by still closer control of the experimental conditions.

Table 1. Nitrate Ion Concentration of SRM 2694, Simulated Rainwater

- - - - - Level I - - - - -		- - - - - Level II - - - - -	
Bottle No.	NO_3^-, mg/L	Bottle No.	NO_3^-, mg/L
174	0.51	763	6.98
	0.48		6.93
	0.51		7.01
976	0.49	961	7.01
	0.50		7.08
	0.46		6.98
1948	0.48	1927	6.90
	0.45		7.00
	0.50		6.97
Average	0.49	Average	6.98
Std. Dev. (1s)	0.02	Std. Dev. (1s)	0.05

References

1. Jenkins, D. and Medsker, L.L., Anal. Chem. 36, 610-612 (1964).

2. Standard Methods for the Examination of Water and Sewage, 11th Ed., p. 175, American Public Health Association, Inc., New York, 1960.

Determination of Fluoride, Chloride, Nitrate, Sulfate, Ammonium,
Sodium, and Potassium by Ion Chromatography, and Specific
Conductance by Conductimetry

William F. Koch, Han Kai, and Melissa Knoerdel
Center for Analytical Chemistry
National Bureau of Standards
Gaithersburg, Maryland 20899

Introduction

SRM 2694, Simulated Rainwater, consists of two levels of aqueous
solutions, and is intended to be representative of the major components in
acidic wet deposition. The solutions were prepared, and bottled in 60-mL,
clean, polyethylene bottles in February 1985. They are labeled as SRM 2694-I
and SRM 2694-II. During the bottling operation, one out of every 120 bottles
was pulled from the line in order to monitor the homogeneity of the lot
through the measurement of specific conductance. After establishing the
homogeneity by this approach, the statistical design for all other components
involved the determination of each component in triplicate in each of three
bottles (selected from the beginning, middle and end of the bottling
operation) by each technique.

Sample Preparation

The bottle should be shaken well before sampling. Care must to taken
when sampling so as to not contaminate the solution.

Specific Conductance

The specific conductance of each solution was measured using a dip-type
conductance cell (Beckman) of nominal cell constant 0.1/cm, and an A.C. con-
ductivity bridge (Altex RC-20). All measurements were compensated for capac-
itance. Measurements were made using the 1 kHz mode. Measurements for
certification were made at 25.0 °C, thermostating the solutions in a water-
jacketed beaker, the outer chamber of which had constant temperature water
circulating through it to maintain the temperature. The exact cell constant
of the cell was determined using 0.001 demal KCl, (which has a specific con-
ductance of 146.93 microsiemens per centimeter (μS/cm) at 25.0 °C) and found
to be 0.09955 μS/cm with a standard deviation of 0.0012, (n=6). The results
of the measurements of SRM 2694 are tabulated in Tables 1 and 2. An uncer-
tainty of 5% and 1% should be combined with the tabulated standard deviation
for levels I and II, respectively, to take into account systematic sources of
uncertainty. RM 8409 was run as a control.

In addition to the measurements made at 25.0 °C, measurements were made
at temperatures ranging from 20 to 28 °C to establish the temperature coeffi-
cient for the specific conductance of these solutions. The temperature
coefficient for both levels has been determined to be 1.5% per °C at 25.0 °C.

Table 1.   Specific Conductance of SRM 2694-I in Units of
           Microsiemens Per Centimeter at 25 °C

Bottle Number	Run #1	Run #2
101a	25.43	25.52
101b	25.48	25.50
102a	25.45	25.44
102b	25.43	25.47
103a	25.48	25.50
103b	25.47	25.44
104a	25.44	25.47
104b	25.46	25.50
105a	25.45	25.44
105b	25.45	25.47
106a	25.44	25.48
106b	25.50	25.48
107a	25.48	25.46
107b	25.44	25.50
108a	25.46	25.48
108b	25.45	25.45
109a	25.49	25.48
109b	25.45	25.48
110a	25.47	25.44
110b	25.46	25.46

Mean   25.47 μS/cm at 25.0 °C

Std. Dev.   0.02

RM 8409-I   26.07
                  26.14
                  26.22
Mean   26.14 μS/cm

Previous Value 25 μS/cm

Table 2. Specific Conductance of SRM 2694-II in Units of
Microsiemens Per Centimeter at 25.0 °C

Bottle Number	Run #1	Run #2
1a	130.1	130.3
1b	129.4	130.2
2a	129.8	130.0
2b	129.8	129.6
3a	130.2	129.8
3b	130.1	129.7
4a	130.1	130.0
4b	130.3	130.2
5a	129.4	129.8
5b	130.3	130.2
6a	129.6	129.9
6b	130.0	130.7
7a	130.2	130.8
7b	130.4	129.9
8a	130.1	129.9
8b	130.4	130.8
9a	129.9	129.7
9b	130.1	130.1

Mean   130.1 µS/cm at 25.0 °C

Std. Dev.   0.3

RM 8409-II   127.8
                   128.0

Mean   127.9 µS/cm

Previous Value   128 µS/cm

Ion Chromatography, Anions

The anions were determined by ion chromatography with chemical suppression. The instrument used was the Dionex Model 2020i. Standards used to calibrate the instrument were made by dilution of stock solutions which had been freshly prepared from: reagent-grade potassium sulfate, sodium nitrate, and sodium fluoride, and from SRM 999, potassium chloride. All four salts had been previously compared with coulometrically standardized high purity acids and found to be stoichiometric and pure to better than 99.5%. For each level and each component, three calibration points (peak height vs. concentration) were established which bracketed closely the concentration of the individual components. The three-point calibration sequence was run after every third injection of the rainwater samples. In order to determine accurately all four anions, two different sets of chromatographic conditions were required.

For sulfate, nitrate, and chloride, an AS3 anion separator column (Dionex) was used, without a guard column. The eluent was an admixture of 3.5 mmol/L $NaHCO_3$ and 2.3 mmol/L Na_2CO_3, flowing at 2.5 mL/min with a system pressure of 320 psi. A 50 microliter sample loop was used for samples and standards. Chemical suppression of the eluent conductivity was effected with a hollow fiber suppressor, using 0.0125 mol/L H_2SO_4 as the regenerant, flowing at 2.8 mL/min. (The background conductance was 22.5 microsiemens, and was electronically offset to 0.00). The full scale range used was 3 microsiemens.

For fluoride, an AS4A anion separator column (Dionex) was used, without a guard column. The eluent was 0.1 mmol/L Na_2CO_3, flowing at 2 mL/min with a system pressure of 560 psi. A 50 microliter sample loop was used for samples and standards. Chemical suppression of the eluent conductivity was effected with a hollow fiber suppressor, using 0.0125 mol/L H_2SO_4 as the regenerant, flowing at 2.8 mL/min. (The background conductance was 4.45 microsiemens, and was electronically offset to 0.00). The full scale range used was 1 microsiemens for Level I and 3 microsiemens for Level II. After every three samples, the column had to be stripped of the other anions with 4.8 mmol/L Na_2CO_3, and then re-equilibrated with the weak eluent.

The results of the anion determinations are shown in Tables 3 and 4. Rm 8409 was run as the control. The following systematic uncertainties should be combined with the tabulated standard deviations of the individual result to arrive at the total uncertainty of the measurement: sulfate, 1%; nitrate, 1%; chloride, 1%; and fluoride, 3%.

Ion Chromatography, Cations

The cations, sodium, ammonium, and potassium, were determined by ion chromatography with chemical suppression. The instrument used was the Dionex Model 2020i. The standard solutions used to calibrate the instrument were made by dilution of stock solutions, which had been freshly prepared from: high-purity sodium chloride, reagent grade ammonium chloride, and SRM 999 potassium chloride. The estimated purity of the commercial salts is better than 99%. For each level and each cation, three calibration points (peak height vs. concentration) were established which bracketed closely the concentration of the individual species in the rainwater samples. The calibration sequence was run after every third injection of rainwater.

The following chromatographic conditions were used for this analysis. A CS1 cation separator column (Dionex) without guard column was used. The eluent was 6.25 mmol/L HCl flowing at 2.3 mL/min with a system pressure of 520 psi. A 100 microliter sample loop was used for samples and standards. Reduction of the eluent conductance was achieved using a cation fiber suppressor with 0.04 mol/L tetramethylammonium hydroxide as the regenerant flowing at 2.6 mL/min. (The background conductance was 5.10 microsiemens and was electronically offset to 0.00). The full scale range for the conductivity meter was set at 1 microsiemens for Level I and 3 microsiemens for Level II.

Table 3. Determination of Anions by IC in SRM 2694-I

- - - - - - - - - - μg/g - - - - - - - - - - - -

Bottle	Sulfate	Nitrate	Chloride	Fluoride
172	2.697	0.508	0.249	0.055
	2.720	0.526	0.237	0.055
	2.686	0.517	0.249	0.055
1946	2.662	0.513	0.239	0.054
	2.705	0.518	0.239	0.055
	2.689	0.504	0.253	0.055
982	2.681	0.508	0.244	0.055
	2.676	0.514	0.236	0.055
	2.674	0.508	0.232	0.056
2XXX				0.056
				0.055
				0.055
Mean	2.688	0.513	0.242	0.055
Std. Dev.	0.018	0.007	0.007	0.001
RM 8409-I	2.627	0.523	0.249	0.057
	2.630	0.531	0.235	0.057
	2.603	0.541	0.230	0.055
	2.665	0.527	0.231	
	2.618	0.538	0.235	
	2.615	0.535	0.240	
Mean	2.626	0.532	0.237	0.056
Std. Dev.	0.021	0.007	0.007	0.001
Previous Value	2.62	0.535	0.230	0.058

Table 4. Determination of Anions by IC in SRM 2694-II

- - - - - - - - - - μg/g - - - - - - - - - - -

Bottle	Sulfate	Nitrate	Chloride	Fluoride
975	10.85	7.125	0.978	0.093
	10.84	7.126	1.009	0.096
	10.82	7.136	1.013	0.095
	10.89	7.198	1.031	
177	10.87	7.141	1.009	0.093
	10.81	7.155	1.025	0.096
	10.81	7.127	1.004	
	10.91	7.120	0.915	
1935	10.84	7.133	1.015	0.097
	10.76	7.075	1.001	0.094
	10.71	7.068	0.999	0.096
	10.88	7.194	1.037	
2XXX				0.094
				0.094
				0.099
Mean	10.83	7.141	1.003	0.095
Std. Dev.	0.06	0.044	0.032	0.001
RM 8409-II	10.57	7.296	1.013	0.095
	10.50	7.262	1.003	0.099
	10.51	7.248	1.004	0.095
	10.48	7.212	1.000	0.100
				0.098
				0.097
				0.100
				0.096
Mean	10.52	7.254	1.005	0.0098
Std. Dev.	0.04	0.035	0.006	0.002
Previous Value	10.5	7.18	1.00	0.102

The results of the cation determinations are shown in Tables 5 and 6. RM 8409 was run as the control. A systematic uncertainty of 2% should be combined with the tabulated standard deviation of the individual result to arrive at the total uncertainty for this analysis. The ammonium content in Level I has been shown to be unstable in previous work and hence is not included in this report. The potassium concentrations in these solutions are near the detection limit for ion chromatography under this set of conditions.

Table 5. Determination of Cations by IC in SRM 2694-I

Bottle	Sodium	Ammonium*	Potassium
1930	0.205		0.056
	0.209		0.057
	0.206		0.055
	0.208		0.034
170	0.203		0.063
	0.206		0.057
	0.204		
	0.203		
970	0.207		0.053
	0.201		0.057
	0.205		
	0.193		
Mean	0.204		0.053
Std. Dev.	0.004		0.008
RM 8409-I	0.205		0.053
	0.202		0.054
	0.201		0.025
Mean	0.203		0.044
Std. Dev.	0.002		0.016
Previous Value	0.208		0.058

*Ammonium ion at this concentration is not stable. Hence, no data are given.

Table 6. Determination of Cations by IC in SRM 2694-II

| | | - - - - - - - µg/g - - - - - - - - - | |
Bottle	Sodium	Ammonium*	Potassium
1939	0.412	1.069	1.109
	0.412	1.071	0.126
	0.414	1.062	0.104
	0.413	1.065	0.104
179	0.413	1.063	0.116
	0.412	1.058	0.085
	0.407	1.072	0.110
	0.413	1.067	0.106
973	0.413	1.064	0.113
	0.412	1.058	0.104
	0.412	1.066	0.102
	0.413	1.057	0.102
Mean	0.412	1.064	0.107
Std. Dev.	0.002	0.005	0.010
RM 8409-II	0.412	1.066	0.114
	0.414	1.049	0.088
	0.415	1.069	0.125
	0.416	1.068	0.111
Mean	0.414	1.063	0.110
Std. Dev.	0.002	0.009	0.015
Previous Value	0.410	1.07	0.112

Laser-Enhanced Ionization Spectrometry in Flame for the Analysis
of Simulated Rainwater

G.C. Turk
Inorganic Analytical Research Division
National Bureau of Standards
Gaithersburg, Maryland 20899

and

Mo De-Ming
Institute of Geochemistry
Academia Sinica, Guiyang
People's Republic of China

Introduction

Laser-enhanced ionization (LEI) is a new method of atomic flame
spectroscopy which has been developed at the National Bureau of Standards for
the detection of trace metals (1,2). The method is based upon the enhanced
rate of collisional ionization of the analyte atom which occurs in a flame
when a tunable dye laser is used to populate selectively an excited state of
that atom. This enhanced ionization can be electrically detected directly in
the flame by using electrodes to conduct a current through the flame and
measuring the increase in current which occurs as a result of LEI. The
non-optical nature of this type of detection is unique among the methods of
flame spectroscopy. The high efficiency of ionization and detection result
in excellent sensitivity, with many detection limits in the 10 parts-per-
trillion range. Because of the high degree of sensitivity, LEI spectroscopy
is suitable for the analysis of rain water.

The tunable dye lasers (Molectron Model DL-16) utilized in this work
were optically pumped by a Nd:YAG laser (Quanta-Ray, Model DCR-1) operated at
10 pulses-per-second in either the second or third harmonic. For tunable
ultraviolet laser radiation, the output of the dye laser was frequency
doubled using a servo tracking frequency doubling system (INRAD Model 5-12).
A Fizeau interferometric wavemeter (Lasertechnics Model 100) was utilized to
set the laser wavelengths at the appropriate analysis lines.

An air-acetylene flame was used with a 5 cm single-slot burner. A
potential of -1200 V was applied to a water cooled cathode (3), which was
aligned 16 mm above the burner head. The burner head was used as the anode.
The LEI signal consists of pulses of increased flame current which are inte-
grated by a gated integrator (Princeton Applied Research Model 165),
digitized, and input to a 16-bit microcomputer on a pulse by pulse basis.

The synthetic rainwater SRM samples were aspirated directly into the
flame from their original containers, without any sample preparation. Final
dilutions of standards were prepared by weighing more concentrated standards
into polypropylene volumetric flasks. Glass volumetric flasks or pipettes
are a source of unpredictable contamination at the lower concentration

levels. Acidity levels of the final dilutions of the standard solutions were kept quite low in an effort to better match levels in the rainwater sample. Typically, the final standards contained on the order of 0.002% (v/v) HCl. For each element determined, a sample spiked with standard was prepared by weighing approximately 1 g of an appropriate standard into approximately 10 g of the synthetic rainwater, in a clean dry plastic vessel. Blank solutions of acidified distilled-deionized water were also prepared.

Before each determination, the wavelength of the laser was scanned over the region of the analysis line in order to check for any spectral interferences. In the case of Mg, a slight interference was observed, as is shown in figure 1. The Mg line at 285.213 nm is slightly affected by the nearby and much larger signal from Na at 285.281 nm. Despite the low transition probability of this Na line, high LEI sensitivity results from the population of a Na excited state which is very close to the ionization potential of Na. However, the interference was small enough so that a reliable correction could be made by using Na standards at the concentrations found in the rainwater to measure the false Na signal at the Mg wavelength.
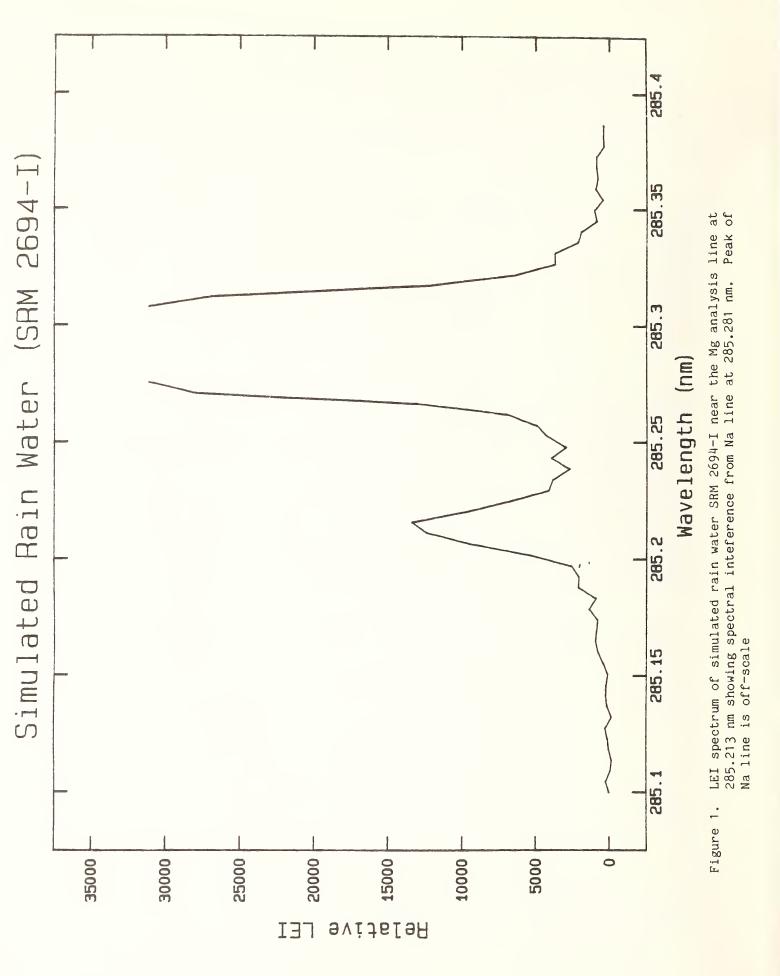
The analytical measurements were taken with the laser fixed at the peak centers of the analytical lines. Table 1 lists the lines utilized in this work, together with the laser dyes used. For Ca, we utilized a stepwise excitation scheme. This is a double resonance procedure, which requires the use of two independently tunable dye lasers, spatially and temporarly coincident at the flame. The first laser at 422.673 nm excites the Ca atoms in the flame from the ground state to a level at 23652 cm^{-1} and the second laser at 585.745 nm further excites the atom from this level to one at 40720 cm^{-1}. The proximity of this upper level to the ionization potential at 49306 cm^{-1} results in a high rate of ionization and consequently high sensitivity. This was the first use of stepwise excitation for Ca, and a limit of detection of 0.03 ng/mL was measured using averages of 30 laser shots and a signal to blank-noise level of 3. When only the first step laser was used a detection limit of 15 ng/mL was recorded.

Table 1. Wavelengths and Laser Dyes Used for the Analysis of Synthetic Rainwater Using Laser-Enhanced Ionization Spectrometry

Element	Wavelength(s) (nm)	Energy Levels (cm^{-1})	Dyes
Ca	422.643	0-23652	1.5 mM Stilbene 422
	585.745*	23652-40720	0.9 mM Rhodamine 610
K	321.715	0-31075	1.5 mM Rhodamine 640 + 0.08 mM Nile Blue A**
Mg	285.213	0-35051	0.3 mM Rhodamine 6G**
Na	588.995	0-16973	0.9 mM Rhodamine 610

* Stepwise Excitation
**Frequency Doubled

Figure 1. LEI spectrum of simulated rain water SRM 2694-I near the Mg analysis line at 285.213 nm showing spectral interference from Na line at 285.281 nm. Peak of Na line is off-scale

Each instrumental reading consisted of the average of 100 signal pulses. For each individual determination, the instrument was calibrated directly before and after each sample reading, using the average result of the standard readings for calibration. These individual results are reported in Table 2, along with the mean and standard deviations of the replicate determinations. No significant blank problems were encountered.

The spiked solutions were analyzed and recoveries calculated to check for multiplicative intereferences. In the case of Ca, recoveries of 124% for the level I sample, and 143% for the level II sample were initially measured. We found however that we could remove this enhancement by adding Na to the standard solutions at concentrations approximately matching that of the synthetic rainwater samples. Enhancements were also observed for Mg, where recoveries of 112% and 104.8% were measured for levels I and II. We were unable to remove this interference experimentally, and have applied a correction factor to the final result, as shown in Table 2. The standard deviation of the mean final result for Mg includes the uncertainty propagated through the measurement of the recovery factor.

References

1. Travis, J.C., Turk, G.C., and Green, R.B., Anal. Chem. 54, 1006A (1982).

2. Travis, J.C., Turk, G.C., DeVoe, J.R., Schenck, P.K., and Van Dijk, C.A., Prog. Anal. Atomic Spectrosc. 7, 199 (1984).

3. Turk, G.C., Anal. Chem. 53, 1187 (1981).

Table 2. LEIS Results for SRM 2694

Element	Level	Bottle Identification	Run Date	Results (ng/mL)	Mean	S	S of Mean
Ca	I	GCTA	4/23	12.9, 12.7, 12.6, 12.5			
		GCTB	4/23	13.0, 12.6, 13.0, 12.9	12.6	0.36	0.10
		GCTC	4/23	12.1, 11.9, 12.2, 12.4			
	II	GCTD	4/23	44.4, 43.9, 42.8, 43.9	43.6	0.45	0.13
		GCTE	4/23	43.3, 43.5, 43.2, 43.7			
		GCTF	4/23	43.5, 43.3, 44.2, 43.9			
K	I	GCTA	4/16	48.6, 47.9, 48.1 46.8			
		GCTB	4/16	47.3, 48.7, 48.3, 45.5	47.8	1.5	0.43
		GCTC	4/16	51.3, 47.5, 46.3, 46.9			
	II	GCTD	4/18	100.3, 103.5, 102.4, 102.1			
		GCTE	4/18	103.4, 105.4, 96.6, 105.7	102.3	3.14	0.79
		GCTF	4/18	105.2, 101.2, 102.9, 95.7			
		#981	4/18	100.4, 103.6, 107.3, 100.3			
Mg	I	GCTA	4/25	27.4, 25.8, 24.9, 25.0			
		GCTB	4/25	27.0, 25.1, 25.6, 25.1	25.32	0.84	0.22
		GCTC	4/24	26.6, 26.9, 25.8, 25.9	(uncorrected)		
			4/25	25.5, 24.9			
				Correction Factor	÷1.12		0.012
				Corrected Value	23.05		0.32
	II	GCTD	4/25	52.1, 50.9			
		GCTE	4/25	51.9, 51.6, 52.0, 52.6	51.58	0.73	0.20
		GCTF	4/25	51.7, 52.4, 51.3, 49.9	(uncorrected)		
			4/26	50.7, 51.6, 51.9			
				Correction Factor	÷1.048		0.01
				Corrected Value	49.22		0.51
Na	I	#166	3/28	196.3, 201.2			
			3/29	194.3, 197.7, 200.1, 198.0			
		#1952	3/28	195.8, 200.0			
			3/29	200.6, 195.7, 195.1, 190.5	197.4	2.95	0.63
		#964	3/28	194.8, 195.6			
			3/29	196.7, 201.3, 192.5, 198.0			
		GCTG	4/26	198.2, 198.1, 201.5, 200.0			
	II	#1929	3/28	412.6, 413.4			
			3/29	407.1, 413.8, 408.9, 401.2			
		#167	3/28	416.7, 417.9			
			3/29	404.9, 412.6, 406.1, 404.5	411.2	5.63	1.20
			4/26	409.0, 415.8			
		#481	3/28	409.4, 424.1			
			3/29	407.2, 403.0, 413.0, 417.8			
		GCTE	4/26	412.0, 415.3			

34

Trace Elements in Simulated Rainwater by Atomic Absorption,
Flame Emission and Inductively Coupled Plasma Spectrometry

T.C. Rains, T.A. Butler, T.A. Rush, and D.M. Mo
Center for Analytical Chemistry
National Bureau of Standards
Gaithersburg, MD   20899

Introduction

Atomic absorption, flame emission, and inductively coupled plasma atomic emission spectrometry are unique analytical techniques for the determination of 60 metallic elements. The absorption of radiant energy by ground state atoms in the gaseous state is the basis of atomic absorption (AAS). When radiation of proper wavelength passes through a vapor containing ground state atoms, some of this radiation will be absorbed by excitation of particulate atoms (1). The magnitude of the absorption signal is directly related to the number of these ground state atoms found in the optical path. Ground state atoms necessary for the measurements are produced from the sample material by vaporization of the material introduced into an appropriate excitation source followed by dissociation of the molecular species into neutral atoms.

Historically a flame was the original means of producing atomic vapor for AAS. The flame is still the basic source for the vast majority of the AAS measurements; however, if additional sensitivity is needed, electro-thermal atomization is generally used which provides one to three orders of sensitivity over flame atomization techniques (2,3).

Atomic emission spectrometry has been used to determine every element in the periodic table in a wide variety of materials. Over the years there have been various excitation sources (arc, spark, chemical flames, electrical flames, and gas discharges) used as a means of producing atoms. The early use of a flame as an excitation source for analytical emission spectrometry dates back to Herschel (4) who identified alkali metals by flame excitation. Since this original work by Herschel, many advancements have been made. The use of a high resolution monochromator and relatively high temperature flames have greatly improved the sensitivity and specificity. With the introduction of wavelength modulation, a new dimension was introduced which alleviated many spectral interferences encountered in flame systems (5). Another and rather novel way of heating the atomic reservoir is through induction heating. The resulting induction coupled plasma (ICP) has not had its roots in spectroscopy, but sprang from a branch of technology which is based on the discovery of electromagnetic induction by Faraday in 1831. With the higher gas kinetic temperature of the ICP, it is less susceptible to chemical inter-ferences (6). Its precision is comparable to flame sources, but has a greater dynamic range (three to five decades) with improved sensitivity over the flame excitation source.

Experimental

Reagents

All standard stock solutions were prepared by dissolving high purity metals or salts in acids prepared at NBS using sub-boiling distillation (7). Working standard solutions were prepared as needed by serial dilution from the stock solution.

Instrumentation

The instrumental systems used in this study consist of a Perkin-Elmer Model 5000 AAS, an NBS designed and built flame emission spectrometer (FES) (5), and a Perkin-Elmer Model 6000 ICP. Experimental conditions are listed in Table 1.

Table 1. Experimental Conditions for AAS, FES, and ICPAES

Element	Wavelength, nm	Mode	Special Conditions
Ca	422.7	FES	Air/$N_2O(1:1)$-C_2H_2 Flame
	393.3	ICP	
K	766.5	FES	Air-C_2H_2 Flame
Mg	285.2	AAS	Air-C_2H_2 Flame
Na	589.0	FES	Air-C_2H_2 Flame

Calibration of Instrumentation

A five point calibration curve was used to calibrate each instrument. The working standards were prepared by serial dilution of aqueous stock solutions as described by Deans and Rains (8). These were acidified with HNO_3 to one percent to match the acid concentration in the sample solutions. Standard addition procedures were used to check for the presence of matrix suppression or enhancement and to correct for these interferences when they were present (2).

Procedure

Duplicate test portions of each sample were transferred to volumetric flasks. To one of the volumetric flasks, a known concentration of the analyte was added and the flask diluted to calibration volume. The solutions were mixed and immediately transferred to clean plastic bottles.

The instrument was turned on and the excitation source (flame or plasma) was allowed to stabilize. The five point calibration curve was setup and then repeated to assure that instrumental conditions had stabilized. The emission or absorption values of the unknown and the spiked unknown were

measured. Then a low standard concentration was repeated, followed by the unknowns and a higher standard concentration. The concentration of the unknown solutions were calculated using the bracketing technique. If complete recovery of the spiked sample was not attained, correction was made using the single addition method (2).

Results

The results of the determination of Ca, K, Mg, and Na in SRM 2694, Simulated Rainwater are given in Tables 2 and 3.

References

1. Dean, J.A. and Rains, T.C., Eds., Flame Emission and Atomic Absorption Spectrometry, Vol. 1, Theory, Marcel Dekker, New York, 1969.

2. Dean, J.A. and Rains, T.C., Eds., Flame Emission and Atomic Absorption Spectrometry, Vol. 3, Elements and Matrices, Marcel Dekker, New York, 1975.

3. Cantle, J.E., Ed., Atomic Absorption Spectrometry, Elsevier Scientific, New York, 1982.

4. Herschel, J.F.W., Trans. R. Soc. Edin. 9, 445 (1823).

5. Snelleman, W., Rains, T.C., Yee, K.W., Cook, H.P., and Menis, O., Anal. Chem. 42, 394 (1970).

6. Fassel, V.A. and Kniseley, R.M., Anal. Chem. 46, 1117A (1974).

7. Keuhner, E.C., Alvarez, R., Paulson, P.S., and Murphy, T.J., Anal. Chem. 44, 2050 (1972).

8. Dean, J.A. and Rains, T.C., Eds., Flame Emission and Atomic Absorption Spectrometry, Vol. 2, Components and Techniques, Marcel Dekker, New York 1971.

Table 2. Determination of Ca, Mg, Na, and K in SRM 2694

Identification Number		Laboratory Number	Ca[a]	Mg[b]	Na[c]	K[c]
			— — — — — — μg/mL — — — — — —			
2694-I	182	202		0.023		
	1936	203		0.025	0.207	
	974	204		0.023	0.210	
	980	210			0.215	
	1938	211			0.215	
	164	212			0.215	
	269401	217	0.013	0.025		0.055
			0.013			0.056
	269401	218	0.018	0.026		0.054
			0.017			0.055
	269401	219	0.015	0.026		0.056
			0.015			0.056
		Average =	0.015	0.025	0.212	0.055
		Std. Dev. (1s)	0.002	0.001	0.004	0.0008
2694-II	1937	205	0.057	0.050	0.430	
	963	206	0.055	0.050	0.435	
			0.054	0.053		
	175	207	0.054	0.053	0.440	
	1931	213	0.050		0.435	0.110
			0.050			0.112
	979	214		0.053		0.109
						0.111
	169	213	0.057	0.055	0.430	0.112
						0.110
		216				
		Average =	0.054	0.052	0.432	0.111
		Std. Dev. (1s)	0.003	0.002	0.006	0.001

[a] Inductively Coupled Plasma
[b] Flame Atomic Absorption
[c] Flame Emission Spectrometry

Table 3. Recheck of Ca and Na in SRM 2694

Identification Number		Laboratory Number	Ca[a]	Ca[b]	Na[a]
			- - -	μg/mL	- - - -
2694-I	972	274			.203
	1933	275			.202
	180	276			.202
		Average =			.202
		Std. Dev. (1s)			.001
2694-II	969	277	.0518	.0508	.434
	165	278			.434
	1925	279	.0543	.0552	.434
	979	214	.0466	.0477	
		Average =	.0509	.0512	.434
		Std. Dev. (1s)	.0039	.0037	.002

[a]Flame Emission Spectrometry
[b]Direct Current Plasma

Determination of Ammonium Ion, Fluoride, Chloride and pH by Potentiometry and Total Acidity by Coulometry

George Marinenko and Melissa Knoerdel
Center for Analytical Chemistry
National Bureau of Standards

Direct potentiometric methods, using ion selective electrodes (ISE), were used for the determination of NH_4^+, F^-, Cl^-, and pH in Simulated Rainwater Standard Reference Material (SRM) 2694-I and 2694-II. Determination of acidity was accomplished by coulometric titration.

Ammonium Ion

Ammonium ion was determined using a Corning ammonia membrane electrode. The determination requires that the sample be made strongly alkaline by the addition of 10 mol/L NaOH. Ammonium ion is thus converted to molecular ammonia gas, which in turn diffuses through a semipermeable membrane of the ammonia electrode and is detected by the internal pH sensing glass electrode. The emf developed by this electrode is the logarithmic function of the concentration (activity) of NH_4^+ in the original sample. Two NH_4Cl solutions, accurately prepared from reagent grade NH_4Cl, were used as standards for the electrode response calibration. In addition, for control purposes, Research Materials RM 8409-I and RM 8409-II, were analyzed along with SRM 2694. The results of all these measurements are summarized in Table 1.

Each measurement was performed on a freshly taken sample of a standard solution or on a new sample bottle of SRM 2694 or RM 8409. The determined concentrations of NH_4^+ in SRM 2694-I and SRM 2694-II are 0.103 ± 0.005 and 1.03 ± 0.02 mg NH_4^+/kg solution, where the uncertainty figures represent one standard deviation. The above two values are in line with the target values for preparation of the two solutions (0.1 and 1.0 mg NH_4^+/kg solution).

The concentration of NH_4^+ found in RM 8409-II is slightly lower then it was at the time of preparation of the material (1.04 vs 1.07 mg NH_4^+/kg solution), however this difference is well within the uncertainties of the two values. On the other hand RM 8409-I yielded significantly lower results than the NH_4^+ concentration at the time of preparation (0.051 mg NH_4^+/kg solution vs 0.085 mg NH_4^+/kg solution). Such lowering of NH_4^+ concentration with time has been further documented and is now under investigation in our laboratory. It is postulated that consumption of what by microgranisms and transformation of NH_4^+ is taking place.

In view of all the evidence that ammonium ion is gradually lost from these solutions it was recommended that ammonium ion concentration be given only as an "information number at the time of certification" and not as a certified number. In fact the users of these solutions are cautioned about almost inevitable losses of NH_4^+.

Table 1. Concentration of NH_4^+ in SRM 2694, Measured with ISE
(Concentration Reported in mg NH_4^+/kg Solution)

Standard Solution GMXXXIII-29-3 (Calc. NH_4^+ Conc. = 0.0676 mg/kg sol'n)	Standard Solution GMXXXIII-29-2 (Calc. NH_4^+ Conc. = 1.357 mg/kg sol'n)
0.072	1.366
0.064	1.349
0.067	1.331
0.067	1.365
0.074	1.304
0.073	1.359
0.074	1.320
0.061	1.315
0.063	1.359
0.063	
0.068	1.341
s = 0.005	s = 0.024

SRM 2694-I	SRM 2694-II	RM 8409-I	RM 8409-II
0.1062	1.043		
0.1040	1.043	0.043	1.060
0.1027	1.043	0.058	1.009
0.1079	1.017		
0.1010	1.030	0.051	1.035
0.0969	1.034	s = 0.011	s = 0.036
	1.027		
0.1031	1.034		
s = 0.0039	s = 0.010		

The recommended "information numbers" are as follows:

SRM 2694-I   0.1 mg NH_4^+/kg solution

SRM 2694-II   1.0 mg NH_4^+/kg solution.

No uncertainty figure is warranted for this parameter.

Fluoride Ion

Fluoride was determined potentiometrically using a Corning fluoride ion electrode. The procedure entails addition of ionic strength adjustor solution (TISAB II) to both the standard and to the unknown, followed by measurement of the emf. The emf produced is the log function of the concentration of fluoride ion.

Two standard solutions (0.228 and 0.0546 µg F⁻/g solution) were prepared from reagent grade NaF, and used for calibration of the electrode response. Research materials RM 8409-I and RM 8409-II were also incorporated into the experimental scheme as controls. The results of fluoride ion measurements are summarized in Table 2. Each measurement corresponds to a new aliquot of standard solution or a new bottle of SRM 2694 or RM 8409. The concentrations of the two standard solutions was such that the concentrations of the unknowns fell between them, thus requiring only interpolation.

Table 2. Concentration of F⁻ in SRM 2694, Measured with ISE
(Concentration Reported in mg F⁻/kg Solution)

Standard Solution GMXXXIII-37-2 (Calc. Conc. F⁻ = 0.228 mg/kg sol'n)	Standard Solution GMXXXIII-37-3 (Calc. Conc. F⁻ = 0.0546 mg/kg sol'n)
0.244	0.0523
0.229	0.0526
0.223	0.0570
0.214	0.0546
	0.0573
0.228	0.0548
s = 0.013	s = 0.0024

SRM 2694-I	SRM 2694-II	RM 8409-I	RM 8409-II
0.0551	0.1082	0.0559	0.1069
0.0538	0.1023		0.1052
0.0544	0.0972		0.1129
0.0525	0.0991		0.1083
0.0518	0.1013		s = 0.0040
0.0507	0.1017		
0.0529	0.1035		
0.0544	0.1034		
0.0532	0.1023		
s = 0.0015	s = 0.0033		

Only one measurement of RM 8409-I was made. However, the measured value, 0.0559 mg F/kg solution, is in good agreement with the previous value 0.058 mg F/kg solution. The mean value of the three RM 8409-II samples is 0.1083 s = 0.0040 mg F/kg solution, which is also in good agreement with the value reported earlier for this material, 0.102 µg F/kg solution.

The concentrations of fluoride ion measured in SRM 2694-I and 2694-II are 0.0532 (s = 0.0015) and 0.1021 (s = 0.0033) mg F⁻/kg solution respectively, and are consistent with the preparation target values 0.05 and 0.10 mg F/kg solution.

The reported random error (standard deviation of a single determination) represents not only the experimental random error of measurement, but also any possible bottle-to-bottle variations.

Any possible systematic errors (biases), such as inaccuracy of concentration of standard solutions, weight of solution etc., are much smaller than the experimentally encountered random errors. It is therefore recommended that the largest encountered experimental error be used as the uncertainty. Specifically for standard solution GMXXXIII-37-2, this error is 5%. Thus the recommended values for fluoride ion concentration in SRM 2694 are:

SRM 2694-I $[F^-]$ = 0.053 ± 0.003 mg F^-/kg solution

SRM 2694-II $[F^-]$ = 0.102 ± 0.005 mg F^-/kg solution

Chloride Ion

Chloride ion was also determined potentiometrically using a Corning chloride ISE. Calibration of the ISE response was done with standard chloride solutions prepared from SRM 918 KCl. The two standard solutions of interest are solution GMXXXIII-53-4, 1.53 mg Cl^-/kg sol'n, and solution GMXXXIII 53-5, 0.24 mg Cl^-/kg sol'n. These two concentrations bracket the chloride ion concentrations in the two SRM 2694 solutions. The results of chloride determinations are summarized in Table 3.

It should be pointed out that these measurements are being made at the threshold of measurable concentrations of chloride ions by this particular ISE method. The solid membrane employed in this electrode is AgCl. Since the solubility product constant, K_{sp}, for AgCl is 10^{-10}, the equilibrium chloride ion concentration, due to solubility of AgCl, is 10^{-5} mol/L. The two standard solutions, which bracket the concentrations of our "unknowns", are 5×10^{-5} and 7×10^{-6} mol/L, the latter value being less than that produced by solubility of AgCl. Hence the electrode response is much less than theoretical (23 mV rather than 59 mV per decade), and the system requires an extremely long equilibration time.

In this concentration range any possible systematic error contribution is overshadowed by the random errors of measurement due to the above discussed difficulty with the system.

The recommended values for chloride ion concentration are as follows:

SRM 2694-I 0.29 ± 0.07 mg Cl^-/kg solution

SRM 2694-II 0.9 ± 0.2 mg Cl^-/kg solution

where the uncertainties are based on the largest experimental standard deviation for standard solution GMXXXIII-53-4.

Acidity

Acidity of SRM 2694 was determined by coulometric reduction of hydrogen ion in a weighed sample, from which CO_2 was removed by purging with argon. Approximately 60 g of sample were used for each titration, to which 5 mL of saturated KCl were added. Sixty grams of deaerated, distilled water with

Table 3. Concentration of Cl⁻ in SRM 2694, Measured with ISE
(Concentration Reported in mg Cl⁻/kg Solution)

Standard Solution GMXXXIII-53-5 (Calc. Cl⁻ conc. = 0.24 mg Cl⁻/kg sol'n)	Standard Solution GMXXXIII-53-4 (Calc. Cl⁻ conc. = 1.53 mg Cl⁻/kg sol'n)
0.21	1.28
0.25	1.95
0.27	1.44
0.22	
0.24	1.56
s = 0.03	s = 0.35

SRM 2694-I	SRM 2694-II
0.24	1.02
0.23	0.96
0.30	1.24
0.25	0.84
0.27	0.74
0.34	0.77
0.30	0.71
0.36	0.66
0.29	0.87
s = 0.05	s = 0.19

addition of 5 mL of the saturated KCl were titrated to pH = 7 as a blank.
All sample titers were corrected for this blank. The results are summarized
in Table 4.

Table 4. Coulometrically Determined Concentration of H⁺ in SRM 2694

SRM 2694-I meq H⁺/kg sol'n	SRM 2694-II meq H⁺/kg sol'n
0.0501	0.2834
0.0501	0.2831
0.0497	0.2910
0.0529	0.2840
0.0484	0.2822
0.0493	0.2771
0.0501	0.2835
s = 0.0015	s = 0.0045

All possible known systematic errors are below 0.1%. The recommended acidity values are:

SRM 2694-I   0.050 ± 0.002 meq/kg solution

SRM 2694-II 0.284 ± 0.005 meq/kg solution

pH

Measurements of pH were made using a Corning semimicro combination electrode, reserved strictly for "acid rain" pH work. The pH meter was calibrated with pH 6.86 phosphate buffer (SRM 186Ic/186IIc) and the appropriate slope adjustment was made using pH 4.00 potassium acid phthalate buffer (SRM 185f). Each pH measurement was made on a fresh portion of standard solution or fresh bottle of SRM 2694. Measurements of pH of SRM 2694 were alternated with pH measurements of strong acid pH reference solution SA-84, for which pa_H was determined in a hydrogen cell without liquid junction and found to be 3.775. All measured pH's were normalized to SA-84. The normalized results are summarized in Table 5.

Table 5. pH of SRM 2694, Measured with a Corning Semimicro
Combination Electrode

	pH		
	SRM 2694-I	SRM 2694-II	RM-8409-II
	4.316	3.580	3.603
	4.305	3.605	3.595
	4.296	3.595	
	4.296	3.586	
	4.288	3.588	
	4.289	3.593	
	4.292	3.593	
		3.590	
	4.297	3.591	3.599
	s = 0.010	s = 0.007	s = 0.006

Two measurements on two different portions of RM 8409-II were made as an internal check. Using the coulometrically determined hydrogen ion concentrations and the activity coefficients of Harned and Owen, the calculated pH values are as follows: SRM 2694-I pH(calc.) = 4.306; SRM 2694-II pH(calc.) = 3.555. For the corresponding solutions the measured values are: 4.30 ± 0.01 and 3.59 ± 0.01 respectively, where the uncertainty figure represents one standard deviation. The mean value obtained for RM 8409-II pH(meas) = 3.60 ± 0.01 is in excellent agreement with the earlier reported value of 3.61 ± 0.01. No bias exceeding the random error of measurement is anticipated.

Determination of Sulfur in NBS SRM 2694
(Simulated Rainwater) by Thermal Ionization
Mass Spectrometry

W.R. Kelly
Center for Analytical Chemistry
National Bureau of Standards
Gaithersburg, Md   20899

Introduction

Sulfur was determined in NBS SRM 2694 by isotope dilution thermal ionization mass spectrometry. In this procedure the sample is spiked with a known amount of isotopically enriched ^{34}S and the altered $^{34}S/^{32}S$ ratio is determined by measuring the thermally produced AsS^{+} molecular ions. SRM 2694-I and 2694-II were found to contain 2.70 and 10.8 µg $SO_4^{=}/g$ by this technique. The total uncertainty for these determinations was 3% and 2% relative. This technique is capable of measuring sulfur in a variety of matrices with relative measurement precisions of 0.1% (1s). The total chemical blank for the procedure averages 0.3 µg sulfur and is independent of sample size or type. Additional information is given in papers by Paulsen and Kelly [1] and Kelly and Paulsen (2).

Experimental Procedure

Sample Preparation and Dissolution

Duplicate samples were taken from each of three bottles of both the low level (2694-I) and high level (2694-II) of the SRM. Each set of samples consisted of 3 spike samples and a blank. Approximately 10g samples were removed from each bottle using a Fortuna polypropylene-polyethylene disposable syringe and added to modified Carius tubes. Approximately 30 µg of ^{34}S enriched spike was added by weight to each tube followed by 5g of NBS HNO_3. The ^{34}S spike was an aqueous solution of Na_2SO_4 in dilute NBS HCl. The acids used in these procedures were produced at NBS by sub-boiling distillation [3]. The tubes were cooled immediately to -78 °C in a CO_2-CCl_4-$CHCl_3$ slush and sealed with a gas-oxygen torch. The sealed tubes were placed in steel shells equipped with a threaded cap. The shells were closed and placed in an oven at 240 °C for 15-20 hours. This process insures equilibration of spike and sample sulfur. After the steel shells were cooled to room temperature, the Carius tubes were removed and placed behind an explosion shield. The neck of the tube was heated with a torch until a small vent blew open and released the internal pressure. Each tube was scored 5 cm below the shoulder and fire opened. The samples were transferred to 50 mL beakers, covered with watch glasses, placed on a hot plate under a glass dome (3L volume) which was continuously purged with dry N_2 (2L/min), and evaporated to dryness. Two mL of HCl were added to rinse the side of each beaker and the samples were heated to dryness. The last step was repeated twice using 1 mL of HCl each

time. The repeated additions of HCl destroy all nitrates which would interfere with the reduction step. The dried sample was dissolved in 5 mL HCl and transferred to the reduction flask.

Reduction of Sulfate to H_2S and Precipitation as As_2S_3

The sulfur in each sample was reduced to H_2S using hypophosphorous acid as the reducing agent. A master reducing solution was made from a mixture of ACS Reagent Grade H_3PO_2 (61 mL), HCl (205 mL), and HI (125 mL) [1].

Fifteen mL of the master solution was added to each reduction flask and refluxed at 120 °C for 45 min. After the solution cooled to room tempera-ture, the dissolved samples were added and refluxed for 45 min. The H_2S formed was flushed from the flask and passed through a 5 mL distilled water trap and was then trapped in a 15 mL centrifuge tube containing 1 mL aqueous ammonia solution and 1000 μg As^{+3}. During the collection step, the NH_3-As^{+3} solution was cooled in an ice bath to retard the loss of NH_3. The trapped S was precipitated as As_2S_3 by the dropwise addition of HCl to the solution. The precipitate was centrifuged for 10 min to insure that all particles of As_2S_3 were removed from the solution. The supernate, which contained a large amount of dissolved NH_4Cl, was removed with a pipet. The As_2S_3 was washed 5 times with 5 mL portions of distilled water. The washed As_2S_3 was dissolved in an As-NH_3 solution to a S concentration of 100 μg S/mL and an As/S atom ratio of 2. This solution was used for the ratio measurement by mass spectrometry.

Mass Spectrometry

Sample loading was performed in a plastic box flushed with N_2 to prevent sulfur contamination from ambient air. About 1.5 μg S and about 100 μg sil-ica gel were added to a rhenium flat filament and AsS^+ ions were thermally ionized at 950 °C.

The zone refined rhenium filaments were outgassed at 1500 °C at 10^{-7} torr for 1/2 hour and stored overnight before use. The silica gel was pre-pared from high purity quartz that was fused with Na_2CO_3 and washed repeatedly with quartz distilled water. A mixture of silica gel and H_3PO_4 was prepared, which contained 20 mg silica gel/mL of 0.4M H_3PO_4. This mix-ture was neutralized with high purity NH_3. The H_3PO_4 was prepared from high purity P_2O_5 and quartz distilled water.

A detailed description of the sample loading and mass spectrometric measurement procedure is given below. The silica gel-H_3PO_4 solution is shaken vigorously to disperse the silica gel and 1 cm (5 μL) is drawn into a 5 cm length of intermedic tubing and placed in the center of the filament. A current of 0.9 A is passed through the filament until the silica gel is dry and then heated an additional 15 sec. A 3 cm length (equivalent to 1.5 μg S) of the sample solution is drawn into the tubing and added as single drops to the dried silica gel. After the first drop is added the filament current is adjusted to 1.5 A. The silica gel will break up and disperse within the sam-ple drop. The remainder of the sample is added without allowing the solution on the filament to evaporate to dryness between additions. After the sample is dry it is heated for 15 sec. The current is increased and the sample dried at approximately 700 °C for 5 sec. No fumes are observed during this final heating step. If excess H_3PO_4 is present and fumes of P_2O_5 are

observed, it causes decomposition of As_2S_3 and the loss of sulfur as H_2S. For this reason, the silica gel and H_3PO_4 were premixed (neutralized with NH_3) in a ratio designed to maximize both signal intensity and stability while avoiding excess amounts of H_3PO_4.

The sample is loaded into the mass spectrometer with a total exposure to room atmosphere of two minutes or less. Heating of the filament is started when the pressure drops below 2×10^{-7} torr. A liquid N_2 cold finger is used to reduce the pressure in the source. The filament is initially heated to 800 °C which typically gives a AsS^+ beam of .2 to .5 volts with a $10^{11}\Omega$ feedback resistor. At this temperature the signal is decaying rapidly. The filament temperature is increased to 950 °C in 50 °C increments at 5 min. intervals. The source is focused for maximum intensity after each temperature adjustment. The ion current at 950 °C is stable and normally in the 10V range. Larger ion currents can be obtained above 950 °C but they are unstable. The signal increases and then decays after each temperature increase. Data collection commences at 30 min. The major isotope is either on the 10V or 3V scale and decaying at a moderate rate (5%/min.). Three data sets are collected. Each data set consists of 6 integrations of the mass 107 current and 5 integrations of the mass 109 current using an integration time of 15 sec. Delay times of 14 sec and 10 sec are used for ratios of 20/1 and 1/1, respectively. Background signals and electronic offsets are read before each set. Typical precision for a single set is 0.05 percent (1s). During the 21 minutes of data collection, the observed decrease in the 107/109 ratio as a result of isotopic fractionation is less than 0.1 percent.

Results and Discussion

Isotope dilution is based upon the equilibration of a known amount of enriched isotope with the isotopes of the element being determined and the measurement of the isotopic ratio of the resulting mixture. Sulfur has four stable isotopes with the following abundances: ^{32}S 95 percent, ^{33}S 0.75 percent, ^{34}S 4.2 percent, and ^{36}S 0.02 percent. Using sulfur enriched in ^{34}S as the tracer, the most precise data are obtained by measuring the $^{32}S/^{34}S$ ratio. The measured ratio in the mixture is given by the following equation:

$$\frac{^{32}S}{^{34}S}\Bigg|_m = \frac{(^{32}S)_{sample} + (^{32}S)_{tracer}}{(^{34}S)_{sample} + (^{34}S)_{tracer}} \tag{1}$$

Equation (1) can be rearranged to give the following:

$$(^{32}S)_{sample} = (^{34}S)_{tracer} \frac{\dfrac{^{32}S}{^{34}S}\Big|_t - \dfrac{^{32}S}{^{34}S}\Big|_m}{\dfrac{^{32}S}{^{34}S}\Big|_m \cdot \dfrac{^{32}S}{^{34}S}\Big|_s - 1} \tag{2}$$

It is obvious from equation (2), that to determine the moles of ^{32}S in the sample, only ratios need be measured and, therefore, the accuracy of an isotope dilution determination is independent of chemical yields provided blanks are relatively small. The concentration of sulfur in a sample is given by the following relation:

$$\mu g \text{ of } S/g = \frac{(^{32}S)_s(\text{at.wt})}{(^{32}A)(\text{wt})_s} \times 10^6 \qquad (3)$$

where the numerator equals the moles of ^{32}S times the atomic weight of sulfur and the denominator equals the fractional abundance of ^{32}S (^{32}A) in the sample times the sample weight in grams.

For the vast majority of elements, the isotopic composition is invariant in nature. However, sulfur is one of the few elements which exhibits variability in nature as a result of isotopic fractionation during biological processing by certain types of bacteria [4]. Therefore, the isotopic composition of the sulfur in all samples was measured on unspiked samples to preclude bias from this effect which could be 1 percent or larger if average isotopic abundance values were assumed.

Calibration of ^{34}S Enriched Tracer

The accuracy of an isotope dilution determination can be no better than the accuracy of the tracer concentration. Therefore, considerable effort was made to insure that the ^{34}S enriched tracer solution was accurately calibrated. The ^{34}S tracer used in this study was obtained from Oak Ridge National Laboratory in the form of elemental sulfur. It was converted to sulfate in HNO_3-HCl and diluted to an approximate concentration of 300 μg total sulfur per gram of solution. The ^{34}S tracer was calibrated against gravimetrically prepared solutions of high purity K_2SO_4 and Na_2SO_4 plus three different lots of coulometrically assayed sulfuric acid solutions. All five of these solutions showed measurable differences in their sulfur isotopic compositions. An accurately weighed portion of a natural solution and ^{34}S enriched tracer solution were added to a Teflon beaker, mixed thoroughly, and added directly to the reduction flask. Blanks were determined concurrently with the calibration mixtures and resulted in corrections of less than 0.02 percent relative in all cases. Duplicate mixes from all five solutions yield a mean of 313.65 ± 0.44 (1s).

Results

The sulfur concentrations in the two SRM simulated rainwater samples are given in Tables 1 and 2. The observed ranges for 2694-I and 2694-II were 1% and 0.8% indicating homogeneity to this degree or better. The last column in these two tables gives the relative difference between replicates which is an indication of measurement precision and control of blank. In all cases the replicates differed by less than 0.7%. The standard deviation for a single determination was 0.44% for 2694-I and 0.30% for 2694-II.

The relative contributions to the total uncertainty are given for each SRM in Table 3. For the low level sulfur sample the chemical blank is the largest source of error. From column 3 it is evident that the measurement

Table 1. Sulfur Concentration in SRM 2694-I

OSRM Bottle Number	Sample Weight (g)	µg S/g	µg $SO_4^=$/g	Difference Between Replicates (%)
162	10.5878	0.9036	2.707	0.15
	10.6830	0.9047	2.711	
968	11.0484	0.9017	2.701	0.67
	10.5348	0.8956	2.683	
1922	10.6110	0.8964	2.686	0.19
	11.3851	0.8983	2.691	
	mean	0.9001	2.697	
	std. deviation	0.0038	0.012	
	Total Uncertainty	0.0293	0.088	

Table 2. Sulfur Concentration in SRM 2694-II.

OSRM Bottle Number	Sample Weight (g)	µg S/g	µg $SO_4^=$/g	Difference Between Replicates (%)
161	11.1504	3.608	10.809	0.03
	10.2794	3.607	10.806	
977	11.5753	3.624	10.857	----
	a--	---	----	
1933	10.6899	3.600	10.785	0.11
	9.2617	3.596	10.773	
	mean	3.607	10.81	
	Std. deviation	±0.011	±0.03	
	Total Uncertainty	±0.060	±0.18	

---

[a]Sample was lost.

Table 3. Components for Total Uncertainties in
SRM 2694 in Percent Relative

SRM	N	95% (ts) based on N determinations	95% (ts) for spike	Blank	[a]Total Uncertainty
2694-I	6	1.09	0.35	1.83	3. 27
2694-II	5	0.85	0.35	0.45	1. 65

[a]Linear sum of columns 3, 4, and 5.

precisions for both samples are essentially equal. The total uncertainty was computed conservatively by adding the individual components linearly instead of in quadrature. It should be noted that the blank uncertainty is assumed to be equal to the magnitude of the blank for a given set of samples. This appears to be a very conservative assumption since the mean value for the four blanks measured in the four sets of samples was 0.15 ± 0.03 (1s). The mean value for the last 15 blanks measured was 0.203 ± 0.125 (1s).

References

1. Paulsen, P.J. and Kelly, W.R., Determination of Sulfur by Isotope Dilution Thermal Ionization Mass Spectrometry as AsS$^+$ Ions, Anal. Chem. 56, 708-713 (1984).

2. Kelly, W.R. and Paulsen, P.J., Precise Determination of Sulfur at High Concentrations by Isotope Dilution Thermal Ionization Mass Spectrometry, Talanta 31, 1063-1068 (1984).

3. Kuehner, E.C., Alvarez, R., Paulsen, P.J., and Murphy, T.J., Production and Analysis of High Purity Acids Purified by Sub-boiling Distillation Anal. Chem. 44, 2050-2056 (1972).

4. Krouse H.R., Sulfur Isotopes in our Environment, in Handbook of Environmental Isotope Geochemistry, P. Fritz and J. Ch. Fontes, eds., Elsevier, 435-471 (1980).

Bottle Cleaning Procedure for Rainwater SRM

Use high purity water, ASTM type II or better. Distilled/deionized water which has been filtered through a 0.2 micron filter is recommended for all washes and rinses, and MANDATORY for the final rinse sequence. Caps and bottles must be cleaned. Cleaning and drying must be done in a clean area, well removed from sources of acid fumes and other contaminants.

1. Remove the caps and rinse the bottles and caps 5x with distilled/deionized water.

2. For the bottles with distilled/deionized water, recap and allow to stand for 24 hours.

3. Remove the caps, empty the bottles, rinse 5x with distilled/deionized water.

4. Refill the bottles with distilled/deionized water, recap, and allow to stand for 24 hours.

5. Remove the caps, empty the bottles, and rinse 5x with filtered distilled/deionized water.

6. Shake out the excess water and allow the bottles and the caps to dry in a clean, dust-free area. A drying oven set at 40 °C may be used. (Higher temperatures melt the bottles.)

7. Be certain that the bottles are completely dry. Recap and place in large polyethylene bags to keep the bottles clean prior to filling. Store in a area free from acid fumes.

U. S. Department of Commerce
Malcolm Baldrige
Secretary

National Bureau of Standards
Ernest Ambler, Director

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

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 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.[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.

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 methods 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

Constituent Elements/ Parameters	Methods	2694-I	2694-II
pH @ 25 °C	c	4.30 ± 0.02	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	0.501 ± 0.026	7.06 ± 0.15
Sulfate, mg/L	a,e	2.69 ± 0.03	10.8 ± 0.1
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 SO_4, acidity, pH, and specific conductance which are based on scientific judgment and are roughly equivalent to 2 standard deviations of the certified value.

Techniques:

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

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.

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.

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 $\mu g/L$, 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 un-reliability 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 experi-mentally 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/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.[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 Materials 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.

A NOTE TO THE USER OF THIS SRM

Please take a moment to fill out and return this registration sheet. Frequently, we have difficulty contacting the actual users of SRMs, because the addresses to which we ship are often those of procurement agents. The information on this registration sheet will enable us to inform you, the user, directly of any changes in the Certificate, additions to the catalog, or other matters which may be of interest to you. Return of this sheet will also entitle you to a copy of a NBS Special Publication, describing the production, methods of analysis, and recommended uses of this SRM.

Thank you.

PLEASE TAKE A MOMENT TO REGISTER YOUR NEW
SRM 2694, SIMULATED RAINWATER

Date received: _____

Invoice No.: _____

Name: _____

Title: _____

Address: _____

_____

_____

_____

Phone: _____

Comments: _____

_____

_____

_____

_____

OFFICE OF STANDARD REFERENCE MATERIALS
ROOM B 316, CHEMISTRY BUILDING
NATIONAL BUREAU OF STANDARDS
GAITHERSBURG, MD 20899

ATTN: T. E. GILLS

U. S. Department of Commerce
Malcolm Baldrige
Secretary

National Bureau of Standards
Ernest Ambler, Director

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

Constituent Elements/ Parameters	Methods	2694-I	2694-II
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 SO_4, 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:

a. Ion Chromatography
b. Conductimetry
c. Potentiometry/Ion Selective Electrodes
d. Coulometry
e. Isotope Dilution Thermal Ionization Mass Spectrometry
f. Spectrophotometry
g. Laser Enhanced Ionization Spectrometry
h. Flame Emission Spectrometry
i. Inductively Coupled Plasma 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 $\mu g/L$, 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.

SRM 2694
Page 2

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/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.[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.)

SRM 2694
Page 3

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 no 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.

SRM 2694
Page 4

A NOTE TO THE USER OF THIS SRM

Please take a moment to fill out and return this registration sheet. Frequently, we have difficulty contacting the actual users of SRMs, because the addresses to which we ship are often those of procurement agents. The information on this registration sheet will enable us to inform you, the user, directly of any changes in the Certificate, additions to the catalog, or other matters which may be of interest to you. Return of this sheet will also entitle you to a copy of a NBS Special Publication, describing the production, methods of analysis, and recommended uses of this SRM.

Thank you.

PLEASE TAKE A MOMENT TO REGISTER YOUR NEW
SRM 2694, SIMULATED RAINWATER

Date received: _____

Invoice No.: _____

Name: _____

Title: _____

Address: _____

_____

_____

_____

Phone: _____

_____

Comments: _____

_____

_____

_____

_____

OFFICE OF STANDARD REFERENCE MATERIALS
ROOM B 316, CHEMISTRY BUILDING
NATIONAL BUREAU OF STANDARDS
GAITHERSBURG, MD 20899

ATTN: T. E. GILLS

SRM 2694
Page 5

66

U.S. DEPT. OF COMM. **BIBLIOGRAPHIC DATA SHEET** (See instructions)	1. PUBLICATION OR REPORT NO. NBS/SP-260/106	2. Performing Organ. Report No.	3. Publication Date July 1986

4. TITLE AND SUBTITLE

Methods and Procedures Used at the National Bureau of Standards to Prepare, Analyze and Certify SRM 2694, Simulated Rainwater, and Recommendations for Use

5. AUTHOR(S)

William F. Koch

6. PERFORMING ORGANIZATION (If joint or other than NBS, see instructions) **NATIONAL BUREAU OF STANDARDS DEPARTMENT OF COMMERCE** ~~WASHINGTON, D.C. 20234~~ GAITHERSBURG, MD 20899	7. Contract/Grant No.
	8. Type of Report & Period Covered Final

9. SPONSORING ORGANIZATION NAME AND COMPLETE ADDRESS (Street, City, State, ZIP)

Same as Item 6.

10. SUPPLEMENTARY NOTES

Library of Congress Catalog Card Number: 86-600562

☐ Document describes a computer program; SF-185, FIPS Software Summary, is attached.

11. ABSTRACT (A 200-word or less factual summary of most significant information. If document includes a significant bibliography or literature survey, mention it here) This report describes the development, preparation, analysis and certification of Standard Reference Material, SRM 2694, Simulated Rainwater, intended to aid in the analysis of acidic rainfall. Details of the formulation and preparation of the two levels of solutions (2694-I and 2694-II) are given, as well as those of the precursor to the SRM, namely Research Material, RM 8409, Simulated Rainwater. The analytical techniques used to measure the twelve components in the solutions are described in detail. The data used in the statistical evaluation of the results are summarized and the recommended values for pH, specific conductance, acidity, fluoride, chloride, nitrate, sulfate, sodium, potassium, ammonium, calcium, and magnesium are tabulated. The instability of ammonium ion in acidic solutions is discussed. Recommendations for the use of SRM 2694, particularly with regard to the measurement of pH, are given.

12. KEY WORDS (Six to twelve entries; alphabetical order; capitalize only proper names; and separate key words by semicolons)

acid rain; acidity; ammonium; analytical chemistry; conductivity; measurement; pH; precipitation; rainwater; Standard Reference Material; statistics; sulfate.

13. AVAILABILITY	14. NO. OF PRINTED PAGES
[X] Unlimited ☐ For Official Distribution. Do Not Release to NTIS [X] Order From Superintendent of Documents, U.S. Government Printing Office, Washington, D.C. 20402.	78
☐ Order From National Technical Information Service (NTIS), Springfield, VA. 22161	15. Price

NBS Technical Publications

Periodical

Journal of Research—The Journal of Research of the National Bureau of Standards reports NBS research and development in those disciplines of the physical and engineering sciences in which the Bureau is active. These include physics, chemistry, engineering, mathematics, and computer sciences. Papers cover a broad range of subjects, with major emphasis on measurement methodology and the basic technology underlying standardization. Also included from time to time are survey articles on topics closely related to the Bureau's technical and scientific programs. Issued six times a year.

Nonperiodicals

Monographs—Major contributions to the technical literature on various subjects related to the Bureau's scientific and technical activities.

Handbooks—Recommended codes of engineering and industrial practice (including safety codes) developed in cooperation with interested industries, professional organizations, and regulatory bodies.

Special Publications—Include proceedings of conferences sponsored by NBS, NBS annual reports, and other special publications appropriate to this grouping such as wall charts, pocket cards, and bibliographies.

Applied Mathematics Series—Mathematical tables, manuals, and studies of special interest to physicists, engineers, chemists, biologists, mathematicians, computer programmers, and others engaged in scientific and technical work.

National Standard Reference Data Series—Provides quantitative data on the physical and chemical properties of materials, compiled from the world's literature and critically evaluated. Developed under a worldwide program coordinated by NBS under the authority of the National Standard Data Act (Public Law 90-396).
NOTE: The Journal of Physical and Chemical Reference Data (JPCRD) is published quarterly for NBS by the American Chemical Society (ACS) and the American Institute of Physics (AIP). Subscriptions, reprints, and supplements are available from ACS, 1155 Sixteenth St., NW, Washington, DC 20056.

Building Science Series—Disseminates technical information developed at the Bureau on building materials, components, systems, and whole structures. The series presents research results, test methods, and performance criteria related to the structural and environmental functions and the durability and safety characteristics of building elements and systems.

Technical Notes—Studies or reports which are complete in themselves but restrictive in their treatment of a subject. Analogous to monographs but not so comprehensive in scope or definitive in treatment of the subject area. Often serve as a vehicle for final reports of work performed at NBS under the sponsorship of other government agencies.

Voluntary Product Standards—Developed under procedures published by the Department of Commerce in Part 10, Title 15, of the Code of Federal Regulations. The standards establish nationally recognized requirements for products, and provide all concerned interests with a basis for common understanding of the characteristics of the products. NBS administers this program as a supplement to the activities of the private sector standardizing organizations.

Consumer Information Series—Practical information, based on NBS research and experience, covering areas of interest to the consumer. Easily understandable language and illustrations provide useful background knowledge for shopping in today's technological marketplace.
Order the **above** *NBS publications from: Superintendent of Documents, Government Printing Office, Washington, DC 20402.*
Order the **following** *NBS publications—FIPS and NBSIR's—from the National Technical Information Service, Springfield, VA 22161.*

Federal Information Processing Standards Publications (FIPS PUB)—Publications in this series collectively constitute the Federal Information Processing Standards Register. The Register serves as the official source of information in the Federal Government regarding standards issued by NBS pursuant to the Federal Property and Administrative Services Act of 1949 as amended, Public Law 89-306 (79 Stat. 1127), and as implemented by Executive Order 11717 (38 FR 12315, dated May 11, 1973) and Part 6 of Title 15 CFR (Code of Federal Regulations).

NBS Interagency Reports (NBSIR)—A special series of interim or final reports on work performed by NBS for outside sponsors (both government and non-government). In general, initial distribution is handled by the sponsor; public distribution is by the National Technical Information Service, Springfield, VA 22161, in paper copy or microfiche form.