National Institute of Standards & Technology

Certificate of Analysis

Standard Reference Material® 189c

Potassium Tetroxalate Dihydrate pH Standard

This Standard Reference Material (SRM) is intended for use in preparing solutions for calibrating electrodes for pH measuring systems. SRM 189c Potassium Tetroxalate Dihydrate, $KH_3(C_2O_4)_2\ 2H_2O$, was prepared to ensure high purity and uniformity. However, this SRM is certified only as a pH standard, pH(S), not as a pure substance. A unit of SRM 189c consists of 65 g of potassium tetroxalate dihydrate.

Certified Values and Uncertainties: The certified pH(S) values provided in Table 1 correspond to log $(1/a_H)$, where a_H is the conventional activity of the hydrogen (hydronium) ion referred to the standard state ($p°$ = 1 atm = 101 325 Pa) on the scale of molality. The values were derived from electromotive force (emf) measurements of cells without liquid junction by the primary measurement (Harned cell) method [1].

The expanded uncertainty in the certified value, U, is calculated as $U = ku_c(y)$, where $u_c(y)$ is the combined standard uncertainty calculated according to the ISO/JCGM Guide [2]. The value of $u_c(y)$ is intended to represent the combined effect of the following uncertainty components associated with the primary measurement method and material homogeneity: the standard deviation of the pH(S) values after smoothing with respect to temperature as described in reference 3; standard electrode potentials, E^o; molality of HCl, b_{HCl}, used for determining E^o; measured cell potentials; correction to the standard pressure for H_2 gas; mean activity coefficient of HCl at b_{HCl}; gas constant; temperature; Faraday constant; the molality of added NaCl; the stability of the primary measurement; material homogeneity; and the uncertainty of the conventional calculation of log γ_{Cl} (Bates-Guggenheim convention [4]). Current expert opinion [1,5] has assessed the uncertainty attributable to the Bates-Guggenheim convention as 0.010 pH (95 % confidence level). The value of $u_c(y)$ has been multiplied by a coverage factor, k, obtained by the Student's t-distribution for effective degrees of freedom at the given temperature and a 95 % confidence level. A NIST certified value is a value for which NIST has the highest confidence in its accuracy in that all known or suspected sources of bias have been investigated or taken into account by NIST [6]. The certified pH(S) values and their expanded uncertainties are stated in Table 1.

Reference Values: To attain traceability to the NIST reference pH(S) values for SRM 189c when traceability to the SI is not necessary, the uncertainty of the Bates-Guggenheim convention is excluded from the uncertainty calculation. The respective pH(S) values in Table 2 are identical to those in Table 1, but they are listed to the number of decimal places corresponding to two significant figures for the corresponding expanded uncertainty, U_R:

$$U_R = k_R u_c \text{ (measurement)}$$

where k_R is the coverage factor corresponding to a level of confidence of 95 % for U_R. NIST reference values are noncertified values that are the best estimate of the true value; however, the values do not meet NIST criteria for certification and are provided with associated uncertainties that may not include all sources of uncertainty [6].

Traceability: The measurand is the pH of the specified buffer solution. The certified values in Table 1 are metrologically traceable to the International System of Units (SI) of amount-of-substance and mass and to the convention [4] used to define ionic activity, including its uncertainty [1,5]. The reference values in Table 2 are traceable to the SI units for amount-of-substance and mass and to this defining convention [4], taken as an exact value with no uncertainty (the uncertainty of the Bates-Guggenheim convention is excluded from the uncertainty calculation).

Expiration of Certification: The certification of **SRM 189c** is valid within the measurement uncertainty specified, until **05 May 2023**, provided the SRM is handled and stored in accordance with the instructions given in this certificate (see "Instructions for Storage and Use"). The certification is nullified if the SRM is damaged, contaminated, or otherwise modified.

Carlos A. Gonzalez, Chief
Chemical Sciences Division

Gaithersburg, MD 20899
Certificate Issue Date: 19 July 2018
Certificate Revision History on Last Page

Steven J. Choquette, Director
Office of Reference Materials

Maintenance of SRM Certification: NIST will monitor this SRM over the period of its certification. If substantive technical changes occur that affect the certification before the expiration of this certificate, NIST will notify the purchaser. Registration (see attached sheet or register online) will facilitate notification.

The experimental work leading to the certification of this material was performed by K.W. Pratt of the NIST Chemical Sciences Division.

Coordination of the technical measurements leading to the certification of SRM 189c was provided by K.W. Pratt.

Statistical consultation was provided by W.F. Guthrie of the NIST Statistical Engineering Division.

Support aspects involved with the issuance of this SRM were coordinated through the NIST Office of Reference Materials.

A solution of molality 0.05 mol/kg is recommended for the calibration of pH measuring systems. Values of pH(S), $u_c(y)$, and U of this solution as a function of Celsius temperature are given in Table 1. Values of U are given at the approximate 95 % level of confidence. The coverage factor, k, at each temperature is 1.96. The corresponding degrees of freedom, ν_{eff}, of $u_c(y)$ at each temperature is >1000.

Table 1. Certified pH(S) Values, Combined Standard Uncertainties, and Expanded Uncertainties for SRM 189c

Temperature[(a)] (°C)	pH(S)	$u_c(y)$[(b)]	U
5	1.666	0.0051	0.010
10	1.667	0.0051	0.010
15	1.669	0.0051	0.010
20	1.672	0.0051	0.010
25	1.677	0.0051	0.010
30	1.682	0.0051	0.010
37	1.690	0.0051	0.010
40	1.694	0.0051	0.010
45	1.700	0.0051	0.010
50	1.707	0.0051	0.010

(a) No value is certified at 0 °C owing to solubility restrictions of this compound [7].
(b) $u_c(y)$ is the combined standard uncertainty, which includes u_c for the measurement (see Table 2, below) and the standard uncertainty of the Bates-Guggenheim Convention (0.0050) [1,5].

Table 2. Reference pH(S) Values and Reference Uncertainty Information[(a)] for SRM 189c

Temperature[(b)] (°C)	pH(S)	u_c(measurement)	ν_{eff}	k_R	U_R
5	1.6657	0.00083	40	2.02	0.0017
10	1.6668	0.00079	35	2.03	0.0016
15	1.6691	0.00079	36	2.03	0.0016
20	1.6724	0.00080	36	2.03	0.0016
25	1.6766	0.00081	38	2.03	0.0016
30	1.6816	0.0011	137	1.98	0.0022
37	1.6897	0.0011	137	1.98	0.0022
40	1.6936	0.0011	138	1.98	0.0022
45	1.7003	0.0011	135	1.98	0.0022
50	1.7074	0.0011	138	1.98	0.0022

(a) u_c(measurement) and U_R each include all components associated with the measurement method and assessment of material homogeneity, but do not include the uncertainty of the Bates-Guggenheim Convention (0.0050) [1,5].
(b) No value is certified at 0 °C owing to solubility restrictions of this compound [7].

NOTICE AND WARNINGS TO USERS

Source of Material: The potassium tetroxalate dihydrate was obtained from a commercial company. The homogeneity of the material was assessed in the course of the certification of this SRM.

Calibrations with SRM 189c in pH Cells with Liquid Junction: The liquid junction potential of the common pH cell displays a greater variability in solutions of pH less than 2.5 than in solutions of pH between 2.5 and 11.5 [8]. Hence, the experimental pH in such cells for SRM 189c may differ by 0.02 to 0.05 from the values of pH(S) given in this Certificate of Analysis, owing to variations in liquid junction potential. This SRM is recommended for purposes of calibration and for confirmatory purposes in cells with liquid junction with this understanding.

INSTRUCTIONS FOR STORAGE AND USE

Storage: SRM 189c is stable when stored in its original container, with the cap tightly closed, in a dry environment and under normal laboratory temperatures.

Drying Instructions: Use as received. The salt must **not** be dried in an oven, nor in a desiccator, before use.

Preparation of the 0.05 mol/kg Solution: Quantities denoted by m_W and associated numerical factors in this paragraph include the effect of air buoyancy, i.e., they correspond to the balance indication in units of mass obtained in the laboratory (the "balance reading"). Weigh by difference approximately 12.1 g of SRM 189c, $m_{W,189c}$, to an accuracy of 1 mg, into a clean, dry, 1 L polyethylene bottle. Add a quantity of deionized or distilled water (resistivity greater than 17 MΩ·cm at delivery; electrical conductivity less than 0.06 µS/cm), equal to 78.4962 multiplied by $m_{W,189c}$, to an accuracy of 0.1 g. Shake until the solid has completely dissolved. Gravimetric preparation in this manner eliminates the need to weigh exactly predetermined masses of solid samples. The SRM material dissolves slowly. Shaking for 12 h or longer may be necessary to effect complete dissolution.

The corresponding apparent mass in air yielding a molality equal to 0.050 000 mol kg^{-1} is 12.7395 g $KH_3(C_2O_4)_2 \cdot 2H_2O$ per 1000.0 g H_2O. As an alternative to the above procedure, solid SRM 189c may be added in this proportion to water (resistivity greater than 17 MΩ·cm at delivery; electrical conductivity less than 0.06 µS/cm), yielding an identical solution to that obtained above.

A minimum of 4 g of SRM 189c should be used to prepare SRM 189c pH(S) buffer solutions as described above, yielding approximately 314 g of solution. Use of a smaller mass of SRM 189c may increase the uncertainty of pH(S) of the prepared solution if the material is heterogeneous at that level.

Stability of Prepared Solution: Solutions are stable for at least one month. For the highest accuracy, prepare fresh solutions on a weekly basis.

REFERENCES

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[7] Baucke, F.G.K.; *Lower Temperature Limit of NBS (DIN) pH Standard Buffer Solution Potassium Tetroxalate*; Electrochim. Acta, Vol. 24, pp. 95–97 (1979).

[8] Bates, R.G.; Pinching, G.D.; Smith, E.R.; *pH Standards of High Acidity and High Alkalinity and the Practical Scale of pH*; J. Res. Nat. Bur. Stand., Vol. 45, pp. 418–429 (1950).

Certificate Revision History: 19 July 2018 (Change of expiration date; editorial changes); 04 September 2013 (Editorial changes); 26 January 2009 (Original certificate date).

Users of this SRM should ensure that the Certificate of Analysis in their possession is current. This can be accomplished by contacting the SRM Program: telephone (301) 975-2200; fax (301) 948-3730; e-mail srminfo@nist.gov; or via the Internet at https://www.nist.gov/srm.