U. S. Department of Commerce Malcolnt Baldrige Secretary National Burage of Standards Ernest Ambler, Director

National Bureau of Standards

Certificate

Standard Reference Material 2202

Potassium Chloride

(Standard for Ion-Selective Electrodes)

B. R. Staples

This Standard Reference Material (SRM) is intended primarily for use in the calibration of ion-selective electrodes for potassium and chloride ions. SRM 2202 consists of approximately 160g of ACS Potassium Chloride. It conforms to the American Chemical Society specifications for analytical reagent-grade material, but should not be considered entirely free from impurities such as occluded water and traces of bromide and heavy metals. Coulometric analysis of this material indicates 99.9 percent purity, and upon drying at 500 °C for 24 hours, 99.99 percent of the calculated chloride was found.

This material is certified for the activity coefficients at $25 \,^{\circ}$ C of the potassium and chloride ions at various concentrations and the related values, pK and pCl. These values are given in the table on the reverse page. The accuracies of the pK and pCl values are estimated to be \pm 0.01. The mean activity coefficient may be represented by the equation:

$$\log \gamma \pm = \frac{-|Z+Z-|AI|^{\frac{1}{2}}}{1+BI^{\frac{1}{2}}} + \beta I + CI^{2} + DI^{3}$$

where I is the ionic strength at 25 °C, Z+ the charge on the cation, Z- the charge on the anion, and A and B the Debye - Hückel constants. Both Z+ and Z- are 1 in the case of potassium chloride. The numerical values of the constants at 25 °C are:

A = 0.5108 B = 1.295 $\beta = 0.00007$ C = 0.003599

D=(-)0.0001954

These constants are valid to 4.8 molal (saturation). The amounts of interfering ions in this material (bromide, sodium, etc.) were each less than 0.01 wt. percent.

The overall direction and coordination of the technical measurements leading to certification were performed under the chairmanship of R.A. Durst.

The technical and support aspects involved in the preparation, certification, and issuance of this Standard Reference Material were coordinated through the Office of Standard Reference Materials by T.W. Mears.

Washington, DC 20234 March 30, 1984 (Revision of Certificate dated 2-22-71)

Stanley D. Rasberry, Chief Office of Standard Reference Materials

Certified values of activity, activity coefficients (y) pK and pCl at 25 °C

Molality (m)	Molarity (M)	Concentration* (g/l)		Mean Molal	Activity	γt	Activity	γ	pK	pCl
		K ⁺	CI =	- γ±	(cation)		(anion)			
0.001	0.000997	0.0390	0.0353	0.965	0.000965	0.965	0.000965	0.965	3.016	3.016
.01	.00997	.3898	.3535	.901	.00901	.901	.00901	.901	2.045	2.04
.1	.0994	3.887	3.524	.768	.0770	.770	.0766	.766	1.112	1.11
.2	.1983	7.754	7.030	.717	.144	.721	.143	.713	0.841	0.84
.3	.2967	11.602	10.519	.687	.208	.693	.204	.681	.682	.69
.5	.4916	19.223	17.429	.649	.330	.659	.320	.639	.482	.49
1.0	.9692	37.898	34.361	.604	.623	.623	.586	.586	.206	.23
1.5	1.4329	56.029	50.801	.584	.917	.611	.836	.558	.0376	.07
2.0	1.8827	73.617	66.747	.573	1.219	.609	1.077	.539	~	

^{*}To convert to parts per million (mg/l) multiply by 10⁻³.

The mean activity coefficient at temperatures from 15 to 45 °C and for any concentration up to 0.1 molal may be obtained by using the equation on the face of the certificate and these temperature-dependence expressions for its constants A, and B (Constants β , C and D are unimportant at 0.1 molal and below.)

A =
$$0.5108 + 8.4705 \times 10^{-4} (t-25) + 3.5498 \times 10^{-6} (t-25)^2$$

B = $1.295 (1.0 + 4.7218 \times 10^{-4} (t-25))$.

The values for pK and pCl may be calculated from $\log \gamma \pm u \sin g$ the procedure described by Bates, Staples, and Robinson [Anal. Chem. 42, 867 (1970)].

Preparation of Standard Solutions

To prepare a 1.0 molal solution, transfer 72.234 g of potassium chloride (weight in air) to a 1-liter volumetric flask. Dissolve and fill to the mark with distilled water at 25 °C. The distilled water should have a conductivity no greater than $2 \times 10^{-6} \,\Omega^{-1}$. The potassium chloride should be dried for 2 hours at 110 °C before use. Similarly, a 0.1 molal solution may be prepared by the transfer of 7.410 g of potassium chloride (weight in air) to a 1-liter volumetric flask, dissolving, and diluting to mark with distilled water at 25 °C. Appropriate dilution of either standard solution should be used to obtain standards in the concentration range of interest to the user.

Electrode Calibration

It is recommended that reference standards be used at a concentration similar to that of the sample to minimize liquid junction potential errors. Use of a bracketing technique will minimize errors due to non-Nernstian response of the electrodes. The use of two standard solutions that bracket the concentration of the sample solution increases the reliability of the measurement. Thus, if standard solutions of concentrations slightly higher and lower than the sample solution are used to calibrate the pH/millivolt meter, the error due to liquid junction potential will be small.