8/6/71

Certificate

Standard Reference Material 2202

Potassium Chloride

(Standard for Ion-Selective Electrodes)

B. R. Staples

This standard reference material is certified for calibration of ion-selective electrodes for potassium and chloride ions. 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 °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 ±0.01. The mean activity coefficient may be represented by the equation:

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

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:

$$A = 0.5108$$
$$B = 1.2951$$
$$\beta = 0.00007$$
$$C = 0.003599$$
$$D = -0.0001954$$

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, D. C. 20234
February 22, 1971

J. Paul Cali, Chief
Office of Standard Reference Materials

(over)

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

Molality (m)	Molarity (M)	Concentration* (g/l)		Mean Molal $\gamma_\pm$	Activity (Cation)	γ_+	Activity (Anion)	γ_-	pK	pCl
		K$^+$	Cl$^-$							
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	2.045
.1	.0994	3.887	3.524	.770	.0772	.772	.0768	.768	1.112	1.115
.2	.1983	7.754	7.030	.718	.145	.723	.143	.713	0.841	0.846
.3	.2967	11.602	10.519	.688	.208	.693	.204	.680	.682	.690
.5	.4916	19.223	17.429	.649	.330	.659	.320	.639	.482	.495
1.0	.9692	37.898	34.361	.604	.623	.623	.586	.586	.206	.232
1.5	1.4329	56.029	50.801	.584	.917	.611	.836	.558	.0276	.078
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 equation relating mean activity coefficient to temperature at fixed concentrations from 15 to 45 °C is:

$$\log \gamma_\pm = A + \frac{B}{T} + C \log T$$

where T is the temperature in kelvins. The constants may be calculated at any concentration up to 0.1 molal from the following equations:

$$A = 0.78705 + 17.485m + 46.65m^2 - 3989.2m^3$$
$$B = -33.877 - 567.88m - 23292.0m^2 + 1.9450 \times 10^5\,m^3$$
$$C = -0.27960 - 7.3494m - 136.48m^2 + 1290.8m^3$$

The values for pK and pCl may be calculated from $\log \gamma_\pm$ using 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.