

# National Bureau of Standards

## Certificate

### Standard Reference Material 2203

#### Potassium Fluoride

#### (Standard for Ion-Selective Electrodes)

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This Standard Reference Material, certified for the activity of fluoride ion in solutions of this salt, is made available for the standardization of fluoride ion-selective electrodes. The material is of analytical reagent-grade purity, but should not be considered entirely free of traces of chloride, fluosilicates and heavy metals. Potentiometric measurements on solutions of this material employing fluoride ion-selective electrodes in cells without liquid junction indicate this material to be homogeneous within the precision ( $\pm 0.003$  pF unit) of the measured potential of the fluoride ion-selective electrode. Chemical analysis of this material indicates a minimum assay of 99.5 percent KF after drying.

This material is certified for the activity coefficient of fluoride ion and the related value of pF ( $\equiv -\log a_{F^-}$ , where  $a_{F^-}$  is a conventional activity of fluoride ion) at 25 °C for solutions of potassium fluoride over the range of molalities  $m = 0.0001$  to  $m = 2.0$ . Certified values of  $a_{F^-}$  and pF(S) at selected molalities are found in the table on the reverse page. The pF(S) values given are estimated to be accurate to  $\pm 0.01$  pF unit.

The mean molal activity coefficient of potassium fluoride from  $m = 0.0001$  to  $m = 2.0$  may be represented at 25 °C by the equation:

$$\log \gamma_{\pm} = \frac{-Am^{1/2}}{1+Bm^{1/2}} + \beta m + Cm^2$$

where  $m$  is the molality. The numerical values of the constants appearing in this expression are, at 25 °C:

$$\begin{aligned} A &= 0.5108 \\ B &= 1.2880 \\ \beta &= 2.7843 \times 10^{-2} \\ C &= 4.6933 \times 10^{-3} \end{aligned}$$

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  
May 21, 1973

J. Paul Cali, Chief  
Office of Standard Reference Materials

Values of  $\gamma_{\pm}$  calculated from the relation given above represent the most reliably known experimental activity coefficient data to an uncertainty of no larger than  $\pm 0.005$  in the value of  $\gamma_{\pm}$  over the range of molalities indicated.

Certified Values of Ionic Activity ( $a_{F^-}$ ) Single Ion Activity

Coefficients ( $\gamma_{F^-}$ ) and Standard Values of

pF ( $\equiv -\log a_{F^-}$  for Fluoride Ion at 25 °C

(all referred to the molality scale)

Molality (m)	KF Molarity (c)	Fluoride Ion Concentration* (g/l)	Activity	Activity	pF (S)
			Coefficient $\gamma_{F^-} = \gamma_{K^+} = \gamma_{\pm}$	$a_{F^-} = a_{K^+} = a_{\pm}$	
0.0001	0.0000997	0.00189	0.988	0.0000988	4.00 <sub>5</sub>
0.0005	0.000499	0.00947	0.975	0.000487	3.31 <sub>2</sub>
0.001	0.000997	0.0189	0.965	0.000965	3.01 <sub>6</sub>
0.005	0.00498	0.0947	0.927	0.00464	2.33 <sub>4</sub>
0.01	0.00997	0.1893	0.902	0.00902	2.04 <sub>5</sub>
0.05	0.0498	0.9463	0.818	0.0409	1.38 <sub>8</sub>
0.1	0.0996	1.892	0.773	0.0773	1.11 <sub>2</sub>
0.2	0.1990	3.781	0.726	0.145	0.83 <sub>8</sub>
0.3	0.2982	5.665	0.699	0.210	0.67 <sub>8</sub>
0.5	0.4961	9.425	0.670	0.335	0.47 <sub>5</sub>
0.75	0.7424	14.104	0.652	0.489	0.31 <sub>1</sub>
1.0	0.9873	18.757	0.645	0.645	0.19 <sub>0</sub>
1.5	1.4729	27.983	0.646	0.969	+0.01 <sub>4</sub>
2.0	1.9523	37.091	0.658	1.316	-0.11 <sub>9</sub>

\*To convert to parts per million (mg/l) multiply by 10<sup>3</sup>

The equation relating the mean molal activity coefficient to molality may be used to calculate values of pF at concentrations other than those appearing in the table. The convention used here for the assignment of ionic activities in solutions of potassium fluoride is based on hydration theory and is described by Robinson, Duer and Bates [Anal. Chem. 43, 1862 (1971)]. For this particular 1:1 electrolyte, the convention leads to  $\gamma_{F^-} = \gamma_{K^+}$  in aqueous solution, and values of  $a_{F^-}$  are therefore obtained by the relation

$$a_{F^-} = m\gamma_{F^-} = m\gamma_{\pm}$$

Preparation of Standard Solutions

To prepare a 1.0 molal solution, transfer 57.363 g of potassium fluoride (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 fluoride is hygroscopic and should be dried in two consecutive stages; initially for a period of 2 hours at 110 °C, followed by drying at  $200 \pm 10$  °C for an additional 2 hours. After drying, normal precautions should be exercised to prevent pickup of moisture, i.e., minimal exposure to humid conditions prior to and during weighing.

Similarly, a 0.1 molal solution may be prepared by the transfer of 5.786 g of potassium fluoride (weight in air) to a 1-liter volumetric flask, dissolving, and diluting to the 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.

After preparation, standard solutions should be transferred to non-silicate storage containers, e.g., polyethylene bottles, to avoid fluosilicate formation and the resulting decrease in fluoride ion activity.

#### Electrode Calibration

In order to minimize residual liquid junction potential errors arising at the reference electrode junction, it is recommended that reference standards be used at concentrations similar to those of the samples. Also, the use of a bracketing technique, whereby two standard solutions bracket the concentration range of the samples, will increase the reliability of the measurements by minimizing errors due to non-Nernstian electrode response.