



# Fluoride Determination in Pickling Solution of Stainless Steel by Ion Selective Electrode

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**Abstract:** The Fluoride Ion Selective Electrode is an ion-selective sensor and will quickly and accurately measure fluoride ion activity rather than concentration in aqueous solutions. Fluoride ion activity depends on the solution total ionic strength and pH, and on fluoride complexing species. Adding an appropriate buffer provides a nearly uniform ionic strength background, adjust pH, and breaks up complexes so that, in effect, the electrode measures concentration. Pickling removes a thin surface layer from the stainless, using an acid solution, which is usually a hydrofluoric acid (HF) and nitric acid (HNO<sub>3</sub>), also called mixed acid. In this study, fluoride ion strength has been measured of pickling waste water from stainless steel by ion selective electrode. The results met the specification.

**Keywords:** Pickling Stainless Steel Solution, Fluoride, Ion Selective Electrode

## 1. Introduction

### *Acid Cleaning (Pickling):*

Stainless steel is composed of iron (Fe), nickel (Ni), chromium (Cr) and several other minor components. Stainless steel is not resistant to chemical or physical attack. The corrosion resistance of stainless steel depends on the formation of a 'passive surface film' composed of nickel and chromium oxides (Cr<sub>2</sub>O<sub>3</sub>&NiO). When stainless steel is newly made it is cleaned of oils and greases used in the fabrication process.

Pickling is the most common chemical procedure used to remove oxides and iron contamination. Besides removing the surface layer by controlled corrosion, pickling also selectively removes the least corrosion-resistant areas such as the chromium-depleted zones. Pickling normally involves using an inorganic acid mixture containing nitric acid (HNO<sub>3</sub>), hydrofluoric acid (HF) and, sometimes, also sulfuric acid (H<sub>2</sub>SO<sub>4</sub>). Owing to the obvious risk of pitting corrosion, chloride-containing agents such as hydrochloric acid (HCl) must be avoided [1]. Pickling solution also remove contaminants such as ferrous and ferric oxide particles.

Pickling involves metal removal and a charge or dulling in the visual brightness of the metal.

## 2. Materials

### 2.1. Apparatus

1. Magnetic stirrer, with TFE-coated stirring bar
2. Timer
3. Fluoride electrode and ion-selective meter: The following apparatus were used for this study: Fluoride selective electrode, solution dispenser and, Hanna 2215/ISE NH35 meter with 0.1 mV resolution. The Fluoride Ion-Selective Electrode has a solid-state monocrystalline membrane. The electrode is designed for the detection of fluoride ions (F<sup>-</sup>) in aqueous solutions and is suitable for use in both field any laboratory applications. Optimum pH range is 4 to 8, temperature range is 0 to 80°C. The fluoride ion-selective electrode measures quick and accurately

fluoride ion activity in aqueous solution [2].

## 2.2. Reagents

1. *Pickling (Acid Cleaning) Stainless Steel Solution*
2. *Stock fluoride solution:* Dissolve 221.0 mg anhydrous sodium fluoride (NaF, GFS reagent ACS, min 99.0%, CAS# 7681-49-4) in distilled water and diluted to 1000 mL; 1 mL=100 µg F<sup>-</sup> Table 1 [3].
3. *Sodium Fluoride (second sources for check standard).* Certified ACS Powder, 99-100%. Lot# 157879, CAS# 761-49-4. Fisher Chemical
4. *Total Ionic Strength Fluoride Buffer solution, pH=5.32:* This solution marketed commercially under the trade name TSIAB [4]. Sufficient buffer for 15-20 determinations can be prepared by mixing with stirring 57 mL of glacial acetic acid, 58 g of sodium chloride, 4 g of cyclohexylaminodinitrotetraacetic acid, and 500 mL of distilled water in a 1-L beaker. Cool the contents in a water or ice bath, and carefully add 6 M sodium hydroxide to a pH of 5.0 to 5.5. Dilute to 1 L with

water, and store in a plastic bottle [5] [11].

5. *Standard fluoride solution (working solution):* Dilute 100 mL stock fluoride solution to 1000 mL with distilled water; 1.00 mL= 10.0 µg F<sup>-</sup>
  6. *Serial Fluoride standards:* Into 100 mL volumetric flasks, put V mL) of 10 mg/L fluoride standard, quantitatively fill with D. I. water to obtained series standards, mg F<sup>-</sup>/L (Table2) [3] [8].
  7. *Deionized water,* on the day of use. Water was purified using a Millipore Milli-Q system via a pure water device marked Purelab Option-Q7BP.
- All fluoride standard solutions should be stored in high density polyethylene bottles at 4°C [6], [7].

Table 1. Preparation of fluoride standard stock solution.

Stock std.	0.11050	m NaF (g)	Na	22.9890
Volume	0.5000	V L	F	18.9980
Conc.	100	[F] mg/L	F/NaF	0.4525
Std.	10		NaF	41.9970

Table 2. Serial standards for calibration curve.

Volume of Working Standard Solution (mL)	Diluted to total volume (mL)	Standard F <sup>-</sup> Concentration (mg/L)
2.0	100	0.2
5.0	100	0.5
10.0	100	1.0
20.0	100	2.0
40.0	100	4.0

## 2.3. Installation- Electrode Check

Remove the protective end cot covering the electrode tip rubber insert covering the filling hole of the reference electrode. Fill the combination electrode with the 4 N KCl filling solution. Connect the electrodes to the proper terminals of the meter [9] [10].

Check the operation of the electrode as follows: measure 30.0 mL of buffer solution (pH=5.32) in a 100 mL graduated cylinder. Add DI water to bring to volume to 99.0 mL. Pour the solution into a 400 mL plastic or Teflon beaker. Set the beaker on a magnetic mixer, put in a stirring bar, and start the mixer. Stir a moderate. Stir both standards and samples at the same rate. Set the meter in the mV display mode. Immerse the electrode tip in the solution and turn on the meter. Using a new pipet tip add 1.0 mL of Standard Fluoride Solution (100 mg/L). Measurements should always be made going from a more dilute to a more concentrated solution. Allow 15 minutes for the meter reading to stabilize. A reading that holds for 3-4 minutes is considered stable. Record the meter reading as mV<sub>1</sub>. Add second 1.0 mL portion of Standard Fluoride Solution. When the reading stabilizes record it as mV<sub>2</sub>. Subtract mV<sub>2</sub> from mV<sub>1</sub> to get ΔE. Look up the mV difference on the Table 5 to get mg F<sup>-</sup>. Interpolate to get a 3 decimal reading. The recovery should be from 0.100 to 0.105 mg F<sup>-</sup> [8] [9] [12].

$$E_1 = 40.3 \text{ mV}, E_2 = 22.6 \text{ mV}.$$

$\Delta E = 40.3 - 22.6 = 17.7 \text{ mV}$  (From the Table 5, for 17 mV (0.107 mg F<sup>-</sup>), for 18 mV (0.099 mg F<sup>-</sup>))

$$\text{Interpolation: } 0.107 - \frac{17.7 - 17.0}{18.0 - 17.0} \times (0.107 - 0.099) = 0.101 \text{ mg F}^-$$

## 2.4. Sample Preparation and Analytical Procedure for Analysis

For accurate measurement, the standards and the samples should be at the same temperature. Add DI water to a 1 liter volumetric flask to within ½ inch from the mark. Accurately pipet 1.0 mL of Pickling -Acid Cleaning Solution into the volumetric flask. Add DI water to the mark and mix. Pipet a 10.0 mL of the sample solution into a Teflon beaker, add 30.0 mL of buffer solution, 60 mL of DI water. Set the beaker on the mixer, immerse the electrode, stir well and record the stable reading as mV<sub>1</sub>. Add 1.0 mL portion of Standard Fluoride Solution in excess. When the reading stabilizes (about 3-4 minutes) record the meter reading as mV<sub>2</sub>. Subtract mV<sub>2</sub> from mV<sub>1</sub>, to get ΔE. Look up the mV difference on the Table 6 to get mg F<sup>-</sup> [2, 9].

## 3. Result and Discussion

The fluoride electrode is a solid state electrode can be used with a standard calomel reference electrode and almost any modern pH meter having an expanded millivolt scale. For the best results, the instrument was calibrated every 1-2 hours. Two standard solutions have been used to bracket the concentration range of interest.

Before use, the fluoride ion-selective electrode has been

calibrated by measuring a series of known standard solutions. For a full calibration, 100 mL of solutions containing 0.2, 0.5, 1.0, 2.0, and 4.0 ppm F<sup>-</sup> must be prepared [9].

**Table 3.** Calibration Curve Data.

Flouride				
Stock Sol.	0.2226	m NaF (g)	Na	22.989
	1	V L	F	18.998
	100.72	[F <sup>-</sup> ] mg/L	F/NaF	0.4525
Standard	10.07			
Series Std	[F <sup>-</sup> ] mg/L	Log [F <sup>-</sup> ]	E /mV	
0.2	0.201	-0.6959	87.2	
0.5	0.504	-0.2979	61.3	
1	1.007	0.0031	48.2	
2	2.014	0.3041	28.5	
4	4.029	0.6052	11.9	
		RSQ:	R <sup>2</sup>	0.9971
		dE/dlog [F]:	m	-57.3217
		E for [F]=1:	b	46.4877

**Table 4.** Ion-Selective Electrode Measurements.

Identity	E / mV	[F <sup>-</sup> ] mg/L	DF	Corr [F <sup>-</sup> ]
2.0 mg/L indep.	28.6	2.051	1	2.051
0.2 mg/L indep.	87.0	0.196	1	0.196
Water	166.0	0.008	1	0.008
Pickling sample A	20.7	2.818	1	2.818
Pickling Sample B	20.6	2.829	1	2.829
Spiked	13.2	3.808	1	3.808
Spiked duplicate	13.2	3.808	1	3.808
Average results of sample: 2.824 mg F/L				
mL of Spiking Solution: 0.5 mL				
Concentration of Spiking Solution: 100 mg/L				
Sample volume: 10 mL,				
Spiked amount: 1.0 mg/L				
%R MS	98.4%			
%R MSD	98.4%			

**Calculations**

The volume of sample taken for measurement is 1.0/1000 x10.0= 0.010 mL, therefore the F<sup>-</sup> content of the original sample in mg/L is mg F-x 100,000. The equivalent weight of F<sup>-</sup> is 19.0 g or 19,000 mg. The F<sup>-</sup> normality of the original pickling sample is then:

$$\text{Normality of Fluoride} = \text{mg F}^- \frac{100,000}{19,000}$$

**Appendix**

**Table 6.** Millivolt Difference and mg F<sup>-</sup>.

mV Difference	mg F <sup>-</sup>	mV Difference	mg F <sup>-</sup>	mV Difference	mg F <sup>-</sup>
8	0.274	37	0.032	66	0.0083
9	0.239	38	0.030	67	0.0080
10	0.210	39	0.029	68	0.0076
11	0.187	40	0.027	69	0.0073
12	0.168	41	0.026	70	0.0070
13	0.152	42	0.024	71	0.0067
14	0.138	43	0.023	72	0.0065
15	0.124	44	0.022	73	0.0062

**Table 5.** Measurement data of fluoride by ISE.

	E <sub>1</sub> (mV <sub>1</sub> )	E <sub>2</sub> (mV <sub>2</sub> )	ΔE	mg F <sup>-</sup>	N of F <sup>-</sup>
Pickling sample	40.6	19.9	20.7	0.0815	0.43
Duplicate	40.4	19.8	20.6	0.0820	0.43

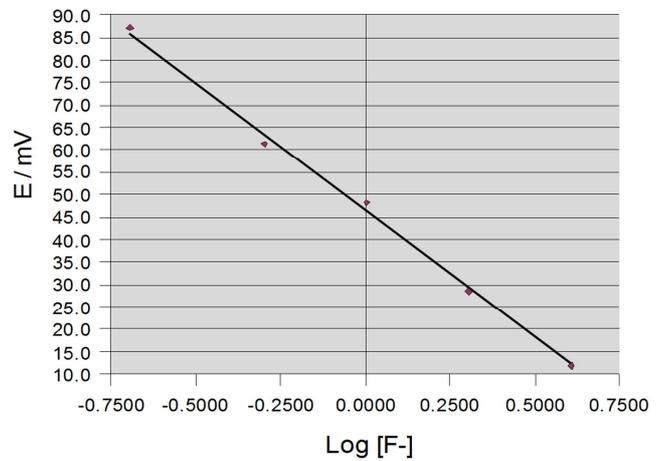
From the Table 5, for 20.0 mV [0.085 mg F<sup>-</sup>], for 21 mV [0.080 mg F<sup>-</sup>]

$$\text{Interpolation} = 0.085 - \frac{20.7-20.0}{21.0-20.0} \times (0.085-0.080) = 0.0815 \text{ mg F}^-$$

$$\text{Normality of F}^- = \frac{100,000}{19,000} = 0.43 \text{ N}$$

Spike Recovery Check (accuracy)

Calibration curve was obtained as E (mV) vs log [F<sup>-</sup>]. Where, [F<sup>-</sup>] is mg/L and log is base 10. Slope m is dE / dlog [F<sup>-</sup>], i.e. the usual y= mx + b, and intercept b is value of E for [F<sup>-</sup>]=1 mg/L, i.e. y intercept for x=0. Expect R<sup>2</sup> to be 0.999 or greater, 1.0000 obtained Table 4, and Figure 1.



**Figure 1.** Calibration curve of fluoride.

**4. Conclusions**

The Ion-Selective Electrode Method has been used for determining fluoride in the pickling (Acid Cleaning) Solution of Stainless Steel. The result have been displayed as ppm (mg/L), and mole/L in solution. The concentration of F<sup>-</sup> in Pickling (Acid Cleaning) Stainless Steel solution was 0.43 N. The specification range is 0.4 to 0.6.

The average spiked recovery of fluoride content in pickling solution was 98.4%, RPD was 0.39% Table 4.

mV Difference	mg F-	mV Difference	mg F-	mV Difference	mg F-
16	0.116	45	0.021	74	0.0060
17	0.107	46	0.020	75	0.0057
18	0.099	47	0.019	76	0.0055
19	0.092	48	0.018	77	0.0053
20	0.085	49	0.018	78	0.0051
21	0.080	50	0.017	79	0.0049
22	0.074	51	0.016	80	0.0047
23	0.070	52	0.015	81	0.0045
24	0.065	53	0.015	82	0.0043
25	0.061	54	0.014	83	0.0041
26	0.057	55	0.014	84	0.0040
27	0.054	56	0.013	85	0.0038
28	0.051	57	0.013	90	0.0031
29	0.048	58	0.012	100	0.0021
30	0.045	59	0.012	110	0.0014
31	0.043	60	0.011	120	0.00094
32	0.040	61	0.010	130	0.00064
33	0.038	62	0.010	140	0.00043
34	0.036	63	0.0094	150	0.00029
35	0.035	64	0.0090		
36	0.033	65	0.087		

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