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

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To cite this article:
Yusuf Yildiz, Angela Jan, Sapan Patel. Fluoride Determination in Pickling Solution of Stainless Steel by Ion Selective Electrode. World Journal of Applied Chemistry. Vol. 3, No. 1, 2018, pp. 28-31. doi: 10.11648/j.wjac.20180301.14

Received: February 23, 2018; Accepted: March 11, 2018; Published: April 9, 2018

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 (HNO₃), 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 (Cr₂O₃&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 (HNO₃), hydrofluoric acid (HF) and, sometimes, also sulfuric acid (H₂SO₄). 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⁻) 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 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 cyclohexylamininedinitriiotetraacetic 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

6. Serial Fluoride standards: Into 100 mL volumetric flasks, put V mL of 10 mg/L fluoride standard, quantitatively fill with DI water to obtain series standards, mg F/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.

| Volume (mL) | Conc. (mg/L) | Std. (mL) | Diluted to total volume (mL) | Standard F Concentration (mg/L) |
|------------|-------------|-----------|----------------------------|-------------------------------|
| 2.0        | 100         | 100       | 0.2                        | 0.11050                       |
| 5.0        | 100         | 100       | 0.5                        | 0.22100                       |
| 10.0       | 100         | 100       | 1.0                        | 0.44200                       |
| 20.0       | 100         | 100       | 2.0                        | 0.88400                       |
| 40.0       | 100         | 100       | 4.0                        | 1.76800                       |

Interpolation: 0.107 - \( \frac{17.7 - 17.0}{18.0 - 17.0} \times (0.107 - 0.099) = 0.101 \text{mg F}^{-1} \)

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 \( \frac{1}{2} \) 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 \( mV_1 \). Add 1.0 mL portion of Standard Fluoride Solution in excess. When the reading stabilizes (about 3-4 minutes) record the meter reading as \( mV_2 \). Subtract \( mV_2 \) from \( mV_1 \) to get \( \Delta E \). Look up the mV difference on the Table 6 to get mg F⁻¹ [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$^-$ must be prepared [9].

| Table 3. Calibration Curve Data. |
|----------------------------------|
| **Fluoride** | **Stock Sol.** | 0.2226 | **m NaF (g)** | Na | 22.989 |
| | 1 | V L | F | 18.998 |
| | 100.72 | [F$^-$] mg/L | F/NaF | 0.4525 |
| **Standard** | 10.07 |
| **Series Std** | [F$^-$] mg/L | Log [F$^-$] | 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$^2$ | 0.9971 |
| **E for [F$^-$]=1:** | b | -57.3217 |
| **Appendix** |

| Table 4. Ion-Selective Electrode Measurements. |
|-----------------------------------------------|
| **Identity** | E / mV | [F$^-$] mg/L | DF | Corr [F$^-$] |
| 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 |
| **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$^-$ content of the original sample in mg/L is mg F-x 100,000. The equivalent weight of F$^-$ is 19.0 g or 19,000 mg. The F$^-$ normality of the original pickling sample is then:

Normality of Fluoride = mg F / 19,000

**Appendix**

| Table 6. Millivolt Difference and mg F$^-$. |
|-------------------------------------------|
| **mV Difference** | **mg F$^-$** | **mV Difference** | **mg F$^-$** | **mV Difference** | **mg F$^-$** |
| 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 |

From the Table 5, for 20.0 mV [0.085 mg F$^-$], for 21 mV [0.080 mg F$^-$]

Interpolation = 0.085 - 0.080 x (0.085-0.080) = 0.0815 mg F$^-$

Normality of F$^-$ = 100,000 / 19,000 = 0.43 N

**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$^-$ 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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