

Potentiality of Fluoride Determination from Egyptian Phosphogypsum Using an Ion Selective Electrode

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Abstract: The determination of fluoride ions in phosphogypsum with ion selective electrode was studied. The operating conditions of fluoride determination have been experimentally optimized using a synthetic solution of fluoride ions which they are the pH, individual interfering ions concentrations and various kinds of TISABs in the presences of individual or multi-component of interfering ions as well as the equilibrium contact time. It has thus been found that the maximum recovery rate of fluoride determination is obtained at the optimum conditions which are 30 mL sample solution containing F⁻ mixed well with 10 mL of citrate buffer (TISAB-3) in a polyethylene beaker at room temperature. The contact time for masking the most interfering ions with citrate ions in this solution is 24 h prior the measurement of F⁻ ions and the equilibrium time is 15 min after immersing the electrode into the continuously stirred solution. The studied optimized conditions have successfully been applied for the generation of the calibration curve and the fluoride determination from phosphogypsum sample solution.

Keywords: Fluoride, Phosphogypsum, Ion-selective electrode, Total Ionic Strength Adjustment Buffer (TISAB).

I. Introduction

Fluoride is a fairly common element that does not occur in the elemental state in nature because of its high reactivity. It contains 0.06 – 0.09 % in the earth's crust⁽¹⁾. Generally, it exists in the form of a number of minerals like fluor spar, cryolite, and fluorapatite⁽²⁾. Furthermore, it exists in phosphogypsum (PG) that is the by-product of wet process phosphoric acid production. Phosphoric acid plants are really phosphogypsum plants because they make much more gypsum than phosphoric acid^(3, 4). The phosphogypsum is generally located in coastal areas close to phosphoric acid plants, where it occupies large land areas and cause serious environmental damage. The fluoride content of phosphogypsum is in the range of 0.35 to 1.35%⁽⁵⁾. Probably, fluoride ions were mostly in the form of HF and SiF₆²⁻ but the latter species might be partially hydrolyzed to SiF₄ which thus led to environmental concern⁽⁶⁾.

In the recent past, there had been an increasing interest in the determination of the fluoride content in many fields. The determination of fluoride concentrations is a great importance in various fields of science and technology. Fluoride determination is also of interest in the industry as a part of the chemical quality assurance of disposal waste. Fluorite (CaF₂) is used on a large scale to separate slag in steel-making. Fluoride has both positive and negative effects on individual health. Fluoride (F⁻) ions can be determined in its solution by a several methods such as potentiometry with ion-selective electrodes (ISE)⁽⁷⁻¹⁰⁾, flow injection analysis^(11, 12), gas chromatography⁽¹³⁾, ion chromatography⁽¹⁴⁾, capillary electrophoresis⁽¹⁵⁾, flame atomic absorption spectrometry⁽¹⁶⁾, and spectrophotometry⁽¹⁷⁻²¹⁾, as well as inductively coupled plasma-mass spectrometry^(22, 23). On the other hand, the most published methods were involved distillation⁽²⁴⁾, pyrohydrolysis⁽²⁵⁻²⁷⁾, alkaline fusion⁽²⁸⁻³⁰⁾ or decomposition⁽³¹⁾ followed by spectrophotometric or potentiometric measurement. Disadvantages of these methods are complicated and time-consuming, give an incomplete breakdown of the fluoride-containing components in coal and losses of fluoride during decomposition in a combustion, or lead to a loss of the element by volatilisation (alkaline fusion) if the fusion temperature is not closely and accurately controlled. In the meantime, ion-selective electrodes (ISE) had been widely used for determining fluoride where Frant and Ross⁽³³⁾ were first constructed a fluoride-ISE. On the other hand, some metal ions interfere with the fluoride determination by ion selective electrode due to the formation of stable complexes with fluoride ions. Hydroxide ions can interfere in fluoride determination because the fluoride and the hydroxide ions have the same valency and similar ion radius. On the other hand, Al³⁺, Fe³⁺ and Mg²⁺ are able to complex or precipitate with fluoride ions and these ions are able to reduce the free fluoride concentration in its solutions⁽³⁴⁾. As a result that, the fluoride ions must be separated from the coexisting ions by steam distillation prior the determination by ion selective electrodes^(35, 36). To overcome the effects of interfering ions without distillation, the suitable masking agents are added to the solution during the determination. These reagents are total ionic strength adjustment buffers (TISABs). In fluoride determination, TISAB solution serves to reduce interferences originating from

hydroxide ions by adjusting the pH and to prevent complex formation between H^+ and F^- in acidic solutions. In potentiometric measurements, the potential is dependent on activity rather than concentration. The ionic strength of all solutions should be kept constant, to assure proportionality of the activity and concentration. Besides providing a constant pH, TISABs regulate the ionic strength of the samples and standard solutions⁽³⁷⁻⁴¹⁾. Similarly, various complexing reagents have been used as TISABs, the most common being citrate⁽⁴²⁾, and 1,2-diaminocyclohexane-*N,N,N',N'*-tetraacetic acid (CDTA)⁽⁴³⁾. The total fluoride concentration in different sample solutions was then determined by ISE analysis without preliminary steam distillation using a tartrate- and tris(hydroxymethyl)methylamine (TRIS)-based total ionic strength adjustment buffer (TISAB) which reduced the interferences of most interfering ions such as, aluminum or boron^(44, 45).

Summing up, the method for fluoride determination from Egyptian phosphogypsum must be quite beneficially separated the fluoride ions prior the determination. The present study is mainly concerned with fluoride determination by ion selective electrode in the presence of interfering ions using the various kinds TISABs, which are masked or formed complexes with the interfering ions, as a result that the fluoride ions could be free in its solution. To realize the objective of this study, the parameters that influence the fluoride determination are investigated. These include the pH, individual interfering ions concentrations and various kinds of TISABs in the presences of individual or multi-components of interfering ions as well as the equilibrium contact time. The obtained optimized conditions have then been applied to construct the best calibration curve to determine the fluoride ions from the Egyptian phosphogypsum using ion selective electrode.

II. Materials And Methods

Materials characterization:

Phosphogypsum characteristics:

The studied phosphogypsum is a byproduct produced from the wet-acid production of phosphoric acid from rock phosphate at the El Nasr Co. for Intermediate Chemicals on Fayoum City, Egypt. It is a gray colored, damp, fine-grained powder, silt or silty-sand materials. It is mainly $CaSO_4 \cdot 2H_2O$ with small amounts of phosphate, sand, and clay. The working phosphogypsum sample is then analyzed after complete dissolution by alkali fusion using the suitable techniques.

Working sample dissolution:

The fluoride ions may be presented in phosphogypsum in the form of calcium fluoride or alkali fluorosilicate. The alkaline fusion could be used to dissolve the fluoride ions from the phosphogypsum sample according to the following equations:

To determine the total fluoride ions concentration in phosphogypsum, 0.2 g powder sample was treated or mixed well with 5.0 g of sodium hydroxide pellets in a platinum crucible. The crucible was put on a hot plate for evaporation to dryness, after that, it was covered and transferred into the muffle furnace for combustion. The temperature of the muffle furnace was set at 200 °C for approximately 16 h after which the temperature was increased to 550 °C for 3 h and then at 800 °C until the contents had fused. The crucible was cooled in air and transfer into Teflon beaker, 20 ml 6 M hydrochloric acid was added, then put on a hot plate in order to complete dissolution afterward it was completed to 100 ml distilled water in plastic measuring flask and the solution was transferred to 150 ml capped plastic bottle. The working sample solution was introduced to analyze using the standard methods.

Preparation of fluoride stock solutions:

A standard stock solution of 1000 mg/L F^- has been prepared by dissolving 2.219 g sodium fluoride (Analar grade, Merck) in 1000 ml distilled water after previously dried at 110 °C for two hours and then cooled in a desiccator overnight. This solution was actually used to determine the relevant factors of fluoride determination using the working ion selective electrode. Standard solutions of fluoride ions concentrations were obtained in a serial dilution through rigorous dilution of the standard stock solution ranging from 0.1 to 10 mg/L F^- to prepare the calibration curves for the spectrophotometric and the ion selective electrode methods. All fluoride solutions were stored in polyethylene containers.

Preparation of some interfering ions:

Several standard stock solutions of 1000 mg/L of possible ions have been prepared by dissolving suitable weights of their salts in 1000 ml distilled water e.g. Al^{3+} , Ca^{2+} , Fe^{3+} , etc. These ions are used for as standard solutions during the determination of fluoride ions. These ions have individually been introduced into

the synthetic aqueous fluoride solution in a suitable dilution to study the effect of their interferences on F⁻ determination using ion selective electrode.

Different types of TISABs:

The total ionic strength adjustment buffer (TISAB) is an important reagent for the determination of F⁻ ions using ion selective electrode to adjust the ionic strength, buffer of the pH and break up metal fluoride complexes. The preparation of several methods of TISAB solutions are described below:

TISAB-1 had been previously made by mixing well of sodium chloride (58.0 g), glacial acetic acid (57mL) and sodium citrate dihydrate (0.30 g) in 500 ml deionized water. The pH of this mixture was adjusted between 5.0 and 5.5 by dropwise adding 6 M NaOH. Cool, the solution to room temperature and adjust the final volume to one liter by adding distilled water⁽³³⁾.

TISAB-2 was prepared by dissolving sodium citrate dihydrate (147 g), potassium nitrate (10 g), glacial acetic acid (28.5 mL), and sodium chloride (29 g) in about 700 mL of distilled water and diluted to 1 L after adjusting the pH of the solution to 5.2 with 5 M NaOH⁽⁴³⁾.

TISAB-3 had also been obtained by the dissolution of citric acid (26 g) and sodium citrate dihydrate (300 g) in about 700 mL of distilled water, the pH was adjusted to 5.5 with sodium hydroxide solution, and the solution was diluted to 1 L with distilled water⁽⁴⁵⁾.

TISAB-4 was made by adding glacial acetic acid (57 mL) and sodium chloride (58 g) as well as 1, 2-cyclohexanedinitrilo-tetraacetic acid (CDTA) (4 g) in 500 mL distilled water. Adjust the solution pH to 5.5 with 5M NaOH. Transfer and complete the total solution to a 1L with distilled water. Transfer the solution to a clean polyethylene bottle⁽⁴⁶⁾.

All the prepared TISAB solutions are stored in an amber container, avoiding exposure to the light.

Fluoride ion selective electrode mechanism:

The used ion selective electrode is the combination of pH electrode and a single fluoride electrode. The sensing membrane in the fluoride ion electrode is single crystal lanthanum fluoride (LaF₃) which is widely used to measure the fluoride ions. The crystal is may be doped with europium to improve the conductivity. At each membrane-solution interface, the following equilibrium takes place:

The formation of LaF₂⁺ creates a charge at the membrane surface. The equilibrium will be shifted to the right for the solution with a smaller F⁻ concentration and the potential will become more positive relative to the other side of the membrane. It is this potential difference across the LaF₃ crystal membrane that is measured and related to F⁻ concentration. The fluoride electrode is extremely selective for F⁻ but can experience interference from OH⁻ above pH 8⁽⁴⁷⁾.

Work of ion-selective electrode is based on the fact that the linear relation between the electrical potential and the logarithm of activity (or effective concentration) of ions in the solution. This relationship is described by Nernst equation:

$$E = E^0 + \frac{2.303RT}{nF} \text{Log}(a)$$

where E is the measured electrode potential (mV), E⁰ is the standard electrode potential for the ion selective fluoride (mV), R is the gas constant (8.314 J/K/mol), T is the absolute temperature (K), a is the activity of the fluoride ion, n is the charge on the ion (-1 for fluoride), F is the Faraday constant (9.648 x 10⁴ Coulomb/mol), If all measurements are made at a room temperature (25°C), then the term 2.303 RT/nF for fluoride ion (where n = -1) is a constant and the Nernst equation is reduced to:

$$E = E^0 - 59.16 \log(a)$$

The Nernst equation is valid for very dilute solutions or for solutions which have constant ion strength. The activity is equivalent to the concentration in dilute solutions but becomes increasingly lower as the ion strength increases. The activity (a) represents the effective concentration while the total fluoride ion concentration may include some bound ions. The electrode responds only to free ions so it is important to avoid the formation of complexes that are meant to be measured. In this case, the complexation would lower the activity and therefore the electrode response.

The function of the ion-selective electrode is based on selective leakage of positively charged species from one phase to another, creating a difference in potential. Working principle is based on measuring the electrode potential (mV) depending on the concentration of tested ions in the solution. The reference electrode has a constant potential, and potential of ISE is changing by the concentration of certain ions.

Analytical procedures:

Before applying the fluoride ion selective electrode to the determine fluoride ion in the phosphogypsum sample solution, the analytical characteristics of the electrode were investigated. Several experimental parameters can affect the electrode response, namely the pH of the medium, individual interfering ions concentrations and various kinds of TISABs in the presences of individual or multi-components of interfering ions as well as the equilibrium contact time. The obtained optimized conditions have then been applied to measure the fluoride ions in the Egyptian phosphogypsum sample solution using ion selective electrode.

The quantitative analysis of phosphogypsum sample or its studied solution is then fulfilled for the determination of the impurities like Si^{4+} , Al^{3+} and PO_4^{3-} using Unicam UV2-100UV/Vis Spectrometer according to standard methods of analysis⁽⁴⁸⁾. The concentrations of the other elements have been determined through the Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES) technique using the proper standards.

Concerning the fluoride concentration in the phosphogypsum sample is firstly distillation and then spectrophotometrically determined by lanthanum/alizarin complexone at 620 nm⁽⁴⁸⁾ while the fluoride concentration in the studied solutions have all the time being measured by the combination fluoride ion selective electrode, Thermo Scientific Orion meter 920A, AC input 115 V instrument and comparing the final results with the spectrophotometric determination after distillation technique. The functioning of an ISE is based on the selectivity of the passage of charged species from one phase to another, leading to the creation of a potential difference. All experiments were repeated 3 times for each sample.

The normal calibration method was used for the fluoride ion selective electrode. The potential for each fluoride standard solution is measured and the calibration curve (E versus $\log[\text{F}^-]$) is constructed. The fluoride concentration in each sample is determined from the calibration curve. The parameters conditions of the fluoride determination are studied for the standards and applied on the phosphogypsum sample solution.

III. Results And Discussion

Phosphogypsum characterization:

The studied phosphogypsum has been completely analyzed using the above-mentioned procedures and the obtained results are shown in Table 1. From these results it is clearly evident that the major constitution of phosphogypsum contains Ca (28.31%), SO_3 (40.45%), SiO_2 (8.29%), Al_2O_3 (0.17%), Fe_2O_3 (0.31%), MgO (0.21%) and P_2O_5 (1.98%) as well as Na_2O (0.29%) while the concerning fluoride ions concentration in the studied sample is assaying 0.26% after distillation method. On the other hand, the prepared solution of the working phosphogypsum sample has also been completely analyzed and the obtained results are also given in Table 1. From the obtained data, it is revealed that the concentrations of some ions including calcium, sulfate, silicon, aluminum, iron, magnesium, phosphate and sodium ions are assaying 400.1, 950.2, 72.4, 2.3, 4.1, 2.5, 25.8 and 25000.8 mg/L respectively, beside that the concentration of the concerned fluoride ions in the studied solution after applying the distillation method is 5.2 mg/L which is used as a reference data for comparing the obtained result of fluoride determination using ISE in the applied solution.

Table (1): Chemical analysis of phosphogypsum sample and its working solution.

Parameter	PG sample (%)	Parameter	PG working solution (mg/L)
CaO	28.31	Ca^{2+}	400.1
SO_3	40.45	SO_4^{2-}	950.2
SiO_2	8.29	Si^{4+}	72.4
Al_2O_3	0.17	Al^{3+}	2.3
Fe_2O_3	0.31	Fe^{3+}	4.1
MgO	0.21	Mg^{2+}	2.5
P_2O_5	1.98	PO_4^{3-}	25.8
TiO_2	0.01	Ti^{4+}	-
Na_2O	0.29	Na^+	25000.8
K_2O	0.02	K^+	0.3
MnO	0.01	Mn^{4+}	-
F ⁻	0.26	F^-	5.2
Sr	0.09	Sr^{2+}	0.5
ΣREEs	0.05	ΣREEs	0.09
Loss on ignition (%)	19.71		

Optimization of fluoride determination parameters:

Effect of pH:

The pH of the solution plays a vital role in the fluoride determination by ISE technique. A series of experiments was carried out at different pH ranging from 1 to 10 using 30 mL solution volume at 25 °C and 50 rpm stirring speed for 15 min contact time in 100 ml polystyrene beakers. The potential measurement for sensing the ion selective electrode was thus studied at three different standard concentrations of fluoride ions varying from 1 to 5 and 10 mg/L. The combined fluoride electrode is rinsed by spraying with a jet of deionized water and gently dabbed dry with a soft tissue before measurement and then is immersed in the solution, and once the potential has stabilized and the measurement is taken. The corresponding electrode potentials for the three standard solutions at different pH range were actually recorded with the ion meter of the ion selective electrode after approximately 15 min inserting the electrode into the continuously stirred solution at 25 °C. From the obtained results (Table 2), it was found that the potential measurements for the three standard solutions are decreased with increasing the pH until pH 5. Therefore, the negative response is obtained for the fluoride ion selective electrode sensitivity at pH <5.0. This false response can be explained by fluoride ion combines with hydrogen ions (H⁺) producing equilibrium mixtures of HF and HF₂⁻ that cannot diffuse through the LaF₃ membrane of ISE. Thus, the fluoride ions will be low if the pH of the sample is lower than 5.0. However, the potential reading at pH 5.0–8.0 have relatively been constant due to the fluoride ions are not combined with hydrogen ions. The potential measurement is decreased at pH ≥ 8.5, thus, it have been the positive response to the sensitivity of the fluoride electrode due to the presence of hydroxide ions which could interfere with the fluoride determination. Whereas, the physical size of the hydroxyl ion (OH⁻) is about the same of the fluoride ion (F⁻) besides that the hydroxyl ions can migrate through the lanthanum fluoride membrane and produce a positive response. The false response can be also explained by the formation of a complex between the lanthanum in the electrode membrane and the hydroxide ions in the solution⁽⁴⁴⁾. Therefore, the ideal pH for fluoride determination by ISE is pH 5.5. To avoid the positive and negative interference of both OH⁻ and un-dissociated HF or HF₂⁻ respectively, pH 5.5 is must be achieved during the measurements using the TISAB solution.

Table (2): Effect of pH on the Potential (mV) reading of different standard F⁻ ions using ion selective electrode.

pH	Potential (mV)		
	1 mg/L	5 mg/L	10mg/L
1.0	190.3	-274.1	-309.2
2.0	-200.3	-286.6	-318.4
3.0	-210.5	-305.2	-334.9
4.0	-250.1	-325.8	-345.3
4.5	-280.5	-345.3	-361.7
5.0	-320.2	-360.4	-379.5
5.5	-337.8	-376.3	-393.9
6.0	-337.8	-376.9	-393.7
6.5	-338.6	-377.4	-393.5
7.0	-339.9	-377.7	-394.8
7.5	-338.2	-378.1	-394.1
8.0	-337.3	-379.6	-395.7
8.5	-339.3	-379.9	-395.5
9.0	-350.9	-397.8	-415.2
10.0	-370.5	-420.6	-435.9

Effect of some interfering ions:

The possible interference of the associated ions such as Ca²⁺, SO₄²⁻, PO₄³⁻, Al³⁺, Fe³⁺ and Mg²⁺, where these ions are presented in the phosphogypsum matrix solution and could lead to adverse effects on the fluoride determination using ion selective electrode. Thus, the effects of the studied interfering ions on the F⁻ determination with or without interfering ions were studied using a series of the individual synthetic interfering ions varying from 1 to 200 mg/L upon a 5 mg/L synthetic standard F⁻ in 30 mL solution volume at pH5.5 in 100 ml polystyrene beakers. The corresponding electrode potentials were actually recorded with the ion meter of the ion selective electrode after approximately 15 min inserting the electrode into the continuously stirred solution at 25 °C. The calibration of the ion meter was performed initially with a 1 mg/L F⁻ standard solution, then with a 10 mg/L F⁻ standard solution, and again with a 1 mg/L F⁻ standard solution to ensure the completeness of the calibration. From the obtained data in Table 3, it was found that the low concentrations of the studied interfering ions have been a positive and negative response on the meter reading of ion selective electrode. In the case of the sulfate and the phosphate anions, interferences show positive errors and the recoveries are over 100%. Taking into account the effect of ionic strength and activity, the recoveries rates should have been less than 100%. In case of the anion interferences, the ionic strength increases that lead to the ion loses some of its

effectiveness, and its activity coefficient decreases. This indicates that the possible reason could be the F⁻ electrode response to other anions when the concentration of anion interference is high enough⁽⁴⁹⁾. In case of the cation interferences, Al ions are showed the most serious influence on the determination of F ions. It is well known that Al ions readily form stable complexes with F ions. Therefore, the significant interference by Al ion is caused by the strong affinity of F ions for Al ions and the formation of an octahedral structure of Al-F with which one Al ion can combine up to a maximum of six F ions. Iron ions are also seemed to cause a negative error. The extent of the Fe interference is much less than that of Al, due to the stability constants for both Fe²⁺ and Fe³⁺ complexes with F is less than that of Al. While the Ca²⁺ and the Mg²⁺ show a positive error. The latter positive error could not be interpreted in terms of ionic strength and activity because the increase of the ionic strength causes a decrease in the activity, which should lead to a negative error. All the positive errors for these cations interferences seem to be caused by anion interference from the counter ion. This meant that Ca²⁺ and Mg²⁺ did not form strong fluoro-complexes like Al or Fe ions⁽⁴⁹⁾.

To overcome these problems, the TISAB must be added to each standard solution sample to avoid these interferences.

Table (3): Effect of some interfering ions concentrations on the determination efficiency of F ions.

Interfering ion (Salt)	Recovery percent (% R) of 5 mg/L F ⁻ ions							
	0	1 mg/L	10 mg/L	25 mg/L	50 mg/L	100 mg/L	150 mg/L	200 mg/L
Ca ²⁺ (CaCl ₂)	99.9	100.6	103.4	105.3	108.5	111.9	112.3	114.1
SO ₄ ²⁻ (Na ₂ SO ₄)	99.9	102.4	105.2	110.9	115.1	120.2	125.7	130.1
PO ₄ ³⁻ (NaH ₂ PO ₄ .6H ₂ O)	99.9	101.8	103.6	108.8	114.2	117.4	123.1	125.6
Al ³⁺ (AlCl ₃ .6H ₂ O)	99.9	10.2	5.1	0.3	0	0	0	0
Fe ³⁺ (Fe(NO ₃) ₃ .9H ₂ O)	99.9	59.4	40.8	30.3	20.2	11.9	5.3	1.8
Mg ²⁺ (MgCl ₂)	99.9	100.3	102.8	104.7	107.6	109.3	111.9	113.7

Effect of the TISABs on the F⁻ determination in the presence of some interfering ions:

The effect of the various kinds of TISABs upon the fluoride ions determination was investigated with or without the interfering ions. A series of experiments were carried out using the desired concentrations range of the individual synthetic interfering ions with the 30 mL solution containing 5.0 mg/L F⁻ and addition of constant volume (10 mL) of various Kinds of TISABs. These solutions were put into a polyethylene beaker at room temperature. The contact time for masking or complexing the most interfering ions with TISABs in these solutions is 24 h prior the measurement of F⁻ using ion selective electrode^(50, 51). The readings of the electrode potential were recorded with the ion meter approximately 15 min after immersing the electrode into the continuously stirred solution at 25 °C. Note that 10 mL of TISAB was added to 30 mL of sample solution, result that another dilution factor. The calibration graph for each TISAB is constructed using a series of standard fluoride ions without interfering ions. The measurements with and without interfering ions were compared. The obtained results in table 4 reveal that the cation and anion interferences yield an insignificant error in the determination fluoride ions even after adding TISAB-1 or TISAB-2. These may be attributed that the stability constants of metal-fluoride complexes are higher than those of metal ions with TISAB-1 or TISAB-2 complexes, therefore, the complexing efficiencies of the TISAB-1 or -2 with interfering ions are relatively low and the fluoride ions are not released in the solution. In the case of TISAB-3, which had a higher citrate content, the effect of the interfering ions especially aluminum and iron was lowered to a great extent, making it possible to detect 99% of the fluoride in the determination, as well as in case of the TISAB-4, the effect of the interfering ions especially Al³⁺ and Fe³⁺ was also lowered. The previous study showed that the TISAB-4 containing CDTA was not as effective as TISAB-3 in lowering the effect of aluminum ions⁽⁴³⁾. This is investigated that, the TISAB containing CDTA was not able to de-complex most iron or aluminum fluoride complexes. Accordingly, it has been possible to mask the most interfering ions in the working solutions using TISAB-3 containing higher citrate content.

Table (4): Effect of various TISABs on the determination efficiency of F⁻ in the presence of some interfering ions.

Interfering ion	Concentration of interfering ion (mg/L)	Measured concentration and recovery percent (% R) of F ⁻ ions							
		TISAB-1		TISAB-2		TISAB-3		TISAB-4	
		[F ⁻](mg/L)	% R	[F ⁻](mg/L)	% R	[F ⁻](mg/L)	% R	[F ⁻](mg/L)	% R
Ca ²⁺ (CaCl ₂)	0	4.99	99.9	4.99	99.9	4.99	99.9	4.99	99.9
	10	5.01	100.	5.01	100.2	4.99	99.9	4.98	99.7
	50	5.18	103.	5.06	101.2	4.98	99.7	4.96	99.2
	100	5.42	108.	5.22	104.4	4.97	99.5	4.93	98.5
	200	5.61	112.	5.39	107.8	4.96	99.2	4.91	98.2
	300	5.82	116.	5.49	109.8	4.93	98.5	4.89	97.7
	400	6.05	120.	5.58	111.6	4.92	98.3	4.85	97.1
SO ₄ ²⁻ (Na ₂ SO ₄)	0	4.99	99.9	4.99	99.9	4.99	99.9	4.99	99.9
	1	4.98	99.5	4.98	99.5	4.99	99.9	4.98	99.6
	50	4.93	98.5	4.87	97.3	4.99	99.9	4.97	99.4
	250	4.84	96.8	4.78	95.5	4.99	99.9	4.95	98.9
	500	4.65	92.9	4.56	91.2	4.98	99.6	4.94	98.7
	750	4.54	90.7	4.43	88.5	4.94	98.7	4.86	97.2
	1000	4.32	86.3	4.24	84.8	4.93	98.5	4.82	96.3
PO ₄ ³⁻ (NaH ₂ PO ₄ ·6H ₂ O)	0	4.99	99.9	4.99	99.9	4.99	99.9	4.99	99.9
	1	4.98	99.5	4.98	99.5	4.99	99.9	4.96	99.1
	10	4.96	99.1	4.95	98.9	4.99	99.9	4.95	98.9
	50	4.92	98.4	4.89	97.8	4.97	99.5	4.91	98.1
	100	4.90	97.9	4.88	97.5	4.99	99.8	4.90	97.9
	150	4.84	96.8	4.85	96.9	4.98	99.7	4.88	97.6
	200	4.79	95.7	4.76	95.2	4.95	98.9	4.86	97.2
Al ³⁺ (AlCl ₃ ·6H ₂ O)	0	4.99	99.9	4.99	99.9	4.99	99.9	4.99	99.9
	1	4.01	80.2	3.81	76.2	4.99	99.9	4.99	98.9
	10	2.43	48.6	1.99	39.8	4.99	99.9	4.88	97.6
	50	1.71	34.2	1.15	23.0	4.98	99.6	4.85	96.9
	75	1.25	25.0	0.98	19.6	4.97	99.4	4.83	96.6
	100	0.86	17.2	0.73	14.6	4.95	98.9	4.71	94.1
	Fe ³⁺ (Fe(NO ₃) ₃ ·9H ₂ O)	0	4.99	99.9	4.99	99.9	4.99	99.9	4.99
1		4.00	80.0	4.19	83.8	4.99	99.9	4.98	99.7
10		2.77	55.4	2.44	48.8	4.99	99.9	4.92	98.3
50		2.65	53.0	2.18	43.6	4.99	99.9	4.88	97.7
100		2.26	45.2	1.92	38.4	4.98	99.7	4.76	95.1
Mg ²⁺ (MgCl ₂)	0	4.99	99.9	4.99	99.9	4.99	99.9	4.99	99.9
	1	5.01	100.	5.01	100.2	4.99	99.9	4.98	99.7
	10	5.07	101.	5.08	101.6	4.99	99.9	4.96	99.2
	50	5.11	102.	5.14	102.8	4.99	99.9	4.94	98.8
	100	5.19	103.	5.17	103.3	4.98	99.6	4.92	98.4

Effect of TISAB-3 dose onto the F⁻ determination in the presence of multi-components ions:

The influence of the TISAB-3 volume on the fluoride ions determination using ion selective electrode with the multi-components ions mixtures was studied. The constituents of the multi-components ions mixtures may be simulated to the composition of phosphogypsum sample solution. To study the TISAB-3 amount effect on the fluoride ions determination, a series of experiments were carried out in which the TISAB-3 amount added was varying from 2.5 to 20 ml and mixed well with 30 ml of 5 mg/L fluoride ions concentration synthetic solution that also contained a synthetic mixtures of Ca²⁺, SO₄²⁻, Si⁴⁺, Al³⁺, Fe³⁺, Mg²⁺, PO₄³⁻ and Na⁺ ions from their salts assaying 400, 950, 75, 5, 4, 5, 25 and 25000 mg/L respectively and all solutions put into a polyethylene beaker for 24 h contact time at 25 °C. The readings of electrode potential were recorded after 15 min immersing the electrode into the solution with continuous stirring at room temperature. From the obtained results (Fig. 1) reveal that the experimental recovery rate of F⁻ ions is increased with increasing the TISAB dose, where at a higher dose of the TISAB-3, the most of the multi-components ions are masked or formed complexes with the citrate ions. Accordingly, the recovery rate of fluoride determination was increased from 81.5 to 99.2% with increasing the TISAB dose from 2.5 to 10 mL and has remained constant thereafter till 20 mL added.

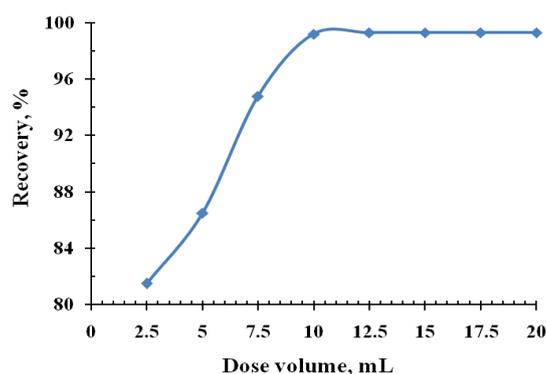


Fig. (1): Effect of TISAB-3 dose volume on the efficiency (%) of F⁻ determination in the presence of multi-components interfering ions.

Effect of the equilibration time:

To studying the effect of the contact time required for sensing the membrane on the fluoride ion selective electrode with the fluoride ions in the studied solution, several experiments were performed to determine the equilibrium time. In these experiments, 10 ml of the TISAB-3 amount added to 30 mL solution containing 5 mg/L synthetic fluoride ions concentration and a synthetic mixtures of Ca²⁺, SO₄²⁻, Si⁴⁺, Al³⁺, Fe³⁺, Mg²⁺, PO₄³⁻ and Na⁺ ions assaying 400, 950, 75, 5, 4, 5, 25 and 25000 mg/L respectively and all solutions put into the polyethylene beakers for 24 h contact time at 25 °C. The readings of electrode potential were recorded after immersing the electrode into the solution with continuous stirring for a time period ranging from 1 to 30 min at room temperature. From the obtained results (Fig. 2), it is clearly evident that beside of increasing the contact time of immersing the ion selective electrode until 15 min, the recovery rate of fluoride ions is increased to 99.2% which still constant with increasing the contact time. It is interesting in this regard to indicating that the error in the readings of electrode potential is highest at the pre-equilibrium phase that is in the first moments of the electrode/solution contact. Over time, the error diminishes and reaches a constant value. At the equilibrium system, the equilibrium between the particular ion and a membrane potential is reached, the error is minimal. Finally, the equilibration time is 15 minutes because it provided a relatively accurate determination over a wide concentration range.

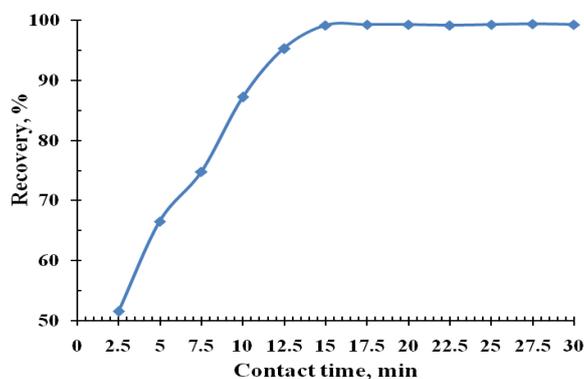


Fig. (2): Effect of the equilibration time on the efficiency (%) of F⁻ determination in the presence of multi-components interfering ions.

Fluoride ions determination in the Egyptian phosphogypsum:

From the above-mentioned results, it has been shown that the optimization conditions for the determination of fluoride ions in the presence of multi-components interfering ions using ion selective electrode are obtained. Prior to applying these conditions upon the El Nasr phosphogypsum sample, it was digested to dissolve the fused product by alkali fusion. This sample solution contains calcium, sulfate, silicon, aluminum, iron, magnesium, phosphate and sodium ions are assaying 400.1, 950.2, 72.4, 2.3, 4.1, 2.5, 25.8 and 25000.8 mg/L respectively. The interference effects of these ions on the ISE determination of fluoride can be eliminated by steam distillation or TISAB-3 addition.

The recovery rate of fluoride ions has then been determined using the optimum conditions which are 30 mL sample solution containing F⁻ mixed well with 10 mL of citrate buffer (TISAB-3) and put into a polyethylene beaker at room temperature. The contact time for masking the most interfering ions with citrate

ions in this solution is 24 h prior the measurement of F^- ions. The readings of electrode potential were recorded with the ion meter at 15 min contact time after immersing the electrode into the continuously stirred solution at 25 °C. The calibration curve was generated from the standard fluoride solutions ranging from 1 to 10 mg/L fluoride ions from its stock solution by plotting the observed electrode potential (mV) vs logarithm of F^- concentration (mg/L) to obtain a straight line (Fig. 3). Accordingly, the linear correlation coefficient (R^2) is almost 0.999 and the slope has a practical value of -56.83 mV which was nearest the ideal range. However, the negative slope (2.303 RT/F) of the normal Nernst equation has a theoretical value of -59.16 mV that indicates the ideal range at 25 °C for determination of fluoride ions. According to the calibration curve, the fluoride ion content in phosphogypsum sample solution was determined and compared with the result obtained from the steam distillation prior the spectrophotometric determination with the alizarin fluoro-complexonate method. Finally, the concentration of fluoride ions in the sample solution reached 5.19 mg/L which is relatively equal to the spectrophotometric method after distillation.

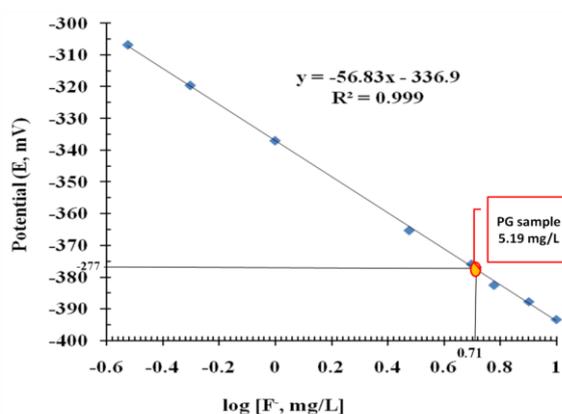


Fig. (3): Calibration curve of fluoride ions determination

IV. Conclusion

The potentiality of fluoride ion selective electrode for fluoride determination from its synthetic solutions has actually been fulfilled and the studied relevant factors have actually been optimized. It was carried out using 30 mL solution containing a synthetic F^- assaying 5 mg/L and 10 mL of citrate buffer (TISAB-3) into a polyethylene beaker at room temperature. The contact time for masking the most interfering ions with citrate ions in this solution is 24 h prior the measurement of F^- ions. The readings of electrode potential were recorded with the ion meter at 15 min contact time after immersing the electrode into the continuously stirred solution at 25 °C. The TISAB-3 has a higher citrate content that affects the interfering ions especially aluminum and iron which are lowered to a great extent because of the formation of a stable complex with citrate ions. The TISAB-3 is almost made the maximum recovery (99.2%) of the fluoride determination. Accordingly, it has been possible to generate the best calibration curve from standard fluoride solutions ranging from 1 to 10 mg/L fluoride ions from its stock solution. Accordingly, the slope has a practical value of -56.83 mV which was nearest the ideal value of the normal Nernst equation which has a theoretical value of -59.16 mV that indicates the ideal range at 25 °C for fluoride ions determination. Finally, the working phosphogypsum sample solution was successfully applied for fluoride determination that is assaying 5.19 mg/L using ion selective electrode and comparing this result with the fluoride determination by spectrophotometric technique after distillation to obtain accuracy and precision.

References

- [1]. P. Patnaik, Handbook of Inorganic Chemicals, McGraw-Hill, New York, 2003, p. 297.
- [2]. P.C. Pandey, P. Kumar, M. Rani, S. Katiyar, V. Tomar, Fluoride-induced impact of aluminium industrial power plant on plants and human inhabiting areas, *Geofizika*, 31(2), 2014, 151–168.
- [3]. S. Klaus, G. Hurth, A. Hoechst, Ullmann's Encyclopedia of Industrial Chemistry, Germany, Wiley-VCH Verlag, 2002.
- [4]. S.I. Abu-Eishah, N.M. Abu-Jabal, Parametric study on the production of phosphoric acid by the dihydrate process, *Chemical Engineering Journal*, 81(1-3), 2001, 231-250.
- [5]. L. Monser, M. Ben Amor, M. Ksibi, Purification of wet phosphoric acid using modified activated carbon, *Chemical Engineering and Processing*, 38(3), 1999, 267-271.
- [6]. M.P. Gonzalez, R. Navarro, I. Saucedo, M. Avila, J. Revilla, C. Bouchard, Purification of phosphoric acid solutions by reverse osmosis and nanofiltration, *Desalination*, 147(1-3), 2002, 315-320.
- [7]. F.N. Hattab, Analytical methods for the determination of various forms of fluoride in toothpastes, *Journal of Dentistry*, 17(2), 1989, 77-83.
- [8]. H.C.A. Filho, A.I. Júnior, M.B. Cruz, M.D. Campos, Determination of total fluoride in oral products by using of potentiometry with ion selective electrode: a critical study, *Analytical Letters*, 33(5), 2000, 819-829.

- [9]. T. Iota, T.E. Carrick, S. Rusby, O.T. Al-Naimi, M. Yoshiyama, J. F. McCabe, Determination of fluoride ions released from resin-based dental materials using ion-selective electrode and ion chromatograph, *Journal of Dentistry*, 32(2), 2004, 117-122.
- [10]. Ş. Tokaloğlu, S. Kartal, U. Şahin, Determination of fluoride in various samples and some infusions using a fluoride selective electrode, *Turkish Journal of Chemistry*, 28(2), 2004, 203-211.
- [11]. P.D. Tzanavaras, D.G.Themelis, Simultaneous flow-injection determination of fluoride, monofluorophosphate and orthophosphate ions using alkaline phosphatase immobilized on a cellulose nitrate membrane and an open-circulation approach, *Anal Chim Acta* 467(1-2), 2002,83-89.
- [12]. R.C. Stefan, J.F. van Staden, H.Y. Aboul-Enein, Determination of fluoride in toothpaste, effluent streams and natural and borehole water using a flow injection system with a fluoride-selective membrane electrode, *Pharm Acta Helv*, 73, 1999, 307-310.
- [13]. G. Wejnerowska, A. Karczmarek, J. Gaca, Determination of fluoride in toothpaste using headspace solid-phase microextraction and gas chromatography-flame ionization detection, *Journal of Chromatography A*, 1150(1-2), 2007, 173-7.
- [14]. J.E. Lefler, M.M. Ivey, Ion chromatography detection of fluoride in calcium carbonate, *Journal of Chromatographic Science*, 49, 2011, 582-588.
- [15]. I.C. Guimarães, C.C. Rezende, J.A.F. da Silva, D.P. de Jesus, Simultaneous determination of free fluoride and monofluorophosphate in toothpaste by capillary electrophoresis with capacitively coupled contactless conductivity detection, *Talanta*, 78(4-5), 2009, 1436-1439.
- [16]. N. Ozbek, S. Akman, Method development for the determination of fluorine in toothpaste via molecular absorption of aluminum mono fluoride using a high-resolution continuum source nitrous oxide/acetylene flame atomic absorption, *Talanta*, 94, 2012, 246-250.
- [17]. M.E. Khalifa, M.A.H. Hafez, Spectrophotometric and complexometric methods for the determination of thorium and fluoride using bromocresol orange reagent, *Talanta*, 47(3), 1998, 547-559.
- [18]. S. Oszwaldowski, R. Lipka, M. Jarosz, T. Majewski, Sensitive reversed-phase liquid chromatographic determination of fluoride based on its ternary systems with zirconium (W) or hafnium (W) and 2-(5-bromo-2-pyridylazo)-5-diethylaminophenol *Analyst* 123, 1998, 1529-1533.
- [19]. M.A. Faraj-Zadeh, E.G. Kalhor, Extraction-spectrophotometric method for determination of fluoride in the range of microgram per liter in natural waters, *Mikrochimica Acta*, 137(3-4), 2001, 169-171.
- [20]. J. Nishimoto, T. Yamada, M. Tabata, Solvent extraction and fluorometric determination of fluoride ion at ppb level in the presence of large excess of aluminum (III) and iron (III) by using an expanded porphyrin, saphyrin, *Analytica Chimica Acta* 428(1), 2001, 201-208.
- [21]. M. Garrido, A.G. Lista, M. Palomeque, B.S.F. Band, Fluorimetric determination of fluoride in a flow assembly integrated on-line to an open/closed FIA system to remove interference by solid phase extraction, *Talanta* 58(5), 2002, 849-853.
- [22]. M.M. Bayón, A.R. García, J.I.G. Alonso, A. Sanz-Medel, Indirect determination of trace amounts of fluoride in natural waters by ion chromatography: a comparison of on-line post-column fluorimetry and ICP-MS detectors, *Analyst*, 124(1), 1999, 27-31.
- [23]. Y. Okamoto, Determination of fluorine in aqueous samples by electrothermal vaporization inductively coupled plasma mass spectrometry (ETV-ICP-MS), *J. Anal. At. Spectrom.*, 16,2001, 539-541.
- [24]. H. Ackermann, Fluorine determinations in minerals, rocks and raw materials, *Interceram*, 4, 1978, 404-405.
- [25]. A.C.D. Newman, A simple apparatus for separating fluorine from aluminosilicates by pyrohydrolysis, *Analyst*, 93, 1968, 827-831.
- [26]. E.G. Berns, P.W. van Der Zwaan, The pyrohydrolytic determination of fluoride, *Analytica Chimica Acta*, 59, 1972, 293-297.
- [27]. R.L.Clements, G.A. Sergeant, P.J. Welb, The determination of fluorine in rocks and minerals by a pyrohydrolytic method, *Analyst*, 1971, 96, 51-54.
- [28]. A. Hall, J.N. Walsh, A rapid method for the determination of fluorine in silicate rocks and minerals, *Analytica Chimica Acta*, 45, 1969, 341-342.
- [29]. B.L. Ingram, Determination of fluoride in silicate rocks without separation of aluminum using a specific ion electrode, *Analytical Chemistry*, 42, 1970, 1825-1827.
- [30]. R.A. Nadkarni, Multitechnique multielemental analysis of coal and fly ash, *Analytical Chemistry*, 52, 1980, 929-935.
- [31]. B. Fabbri, F. Donati, Sample fusion at low temperature for the potentiometric determination of fluorine in silicate materials, *Analyst*, 106, 1981, 1338-1341.
- [32]. J. Thomas Jr., H.J. Gluskoter, Determination of fluoride in coal with the fluoride ion-selective electrode, *Analytical Chemistry*, 46(9), 1974, 1321-1323.
- [33]. M.S. Frant, J.W. Ross, Use of a total ionic strength adjustment buffer for electrode determination of fluoride in water supplies, *Analytical Chemistry*, 40(7), 1968, 1169-1171.
- [34]. A.D. Campbell, Determination of fluoride in various matrices, *Pure and Applied Chemistry*, 59(5), 1987, 695-702.
- [35]. ASTM D1179-04, "Standard Test Methods for Fluoride Ion in Water", American Society for Testing and Materials, 2004.
- [36]. S. Borjgivi, Y. Ashimura, T. Yoshioka, T. Mizoguchi, Determination of fluoride using ion-selective electrodes in the presence of aluminum, *Analytical Sciences*, 25, 2009, 1437-1443.
- [37]. T. Okutani, C. Tanaka, Y. Yamaguchi, Determination of fluoride in natural waters by ion-selective electrode potentiometry after coprecipitation with aluminium phosphate, *Talanta*, 36(10), 1989, 973-976.
- [38]. V. L. Dressler, D. Pozebon, E. L. M. Flores, J. N. G. Paniz, E M. M. Flores, Potentiometric determination of fluoride in geological and biological samples following pyrohydrolytic decomposition, *Analytica Chimica Acta*, 466(1), 2002, 117-123.
- [39]. H. Hara, C.C. Huang, Buffer composition suitable for determining very low fluoride concentrations using a fluoride ion-selective electrode and its application to the continuous analysis of rain water, *Analytica Chimica Acta*, 338(1-2), 1997, 141-147.
- [40]. M.L. Wen, N.H. Shi, Y. Qin, C.Y. Wang, Developments in the analysis of fluorides 1995-1997, *Fluoride*, 21(2), 1998, 74-80.
- [41]. F. Yin, Y. Yao, C.C. Liu, M.L. Wen, Developments in the analysis of fluoride 1997-1999, *Fluoride*, 2001, 34, 114-125.
- [42]. M. Rietjens, Decomplexation of aluminium-fluoride complexes by citrate-based buffers as a function of pH, aluminium and fluoride concentrations, *Analytica Chimica Acta*, 368,1998, 265-273.
- [43]. H. Nakajima, H. Komatsu, T. Okabe, J. Dent, Aluminum ions in analysis of released fluoride from glass ionomers, *Journal of Dentistry*, 25, 1997, 137-144.
- [44]. M.S. Corbillon, M.P. Carril, J.M. Madariaga, I. Uriarte, Fast determination of total fluoride by direct potentiometry in samples of aluminium fluoride and cryolite, *Analyst*, 120, 1995, 2227-2231.
- [45]. S. Borjgivi, T. Yoshioka, and T. Mizoguchi, Determination of total fluoride in boron-containing solutions, *Analytical Sciences*, 26, 2010, 603-606.
- [46]. M.A. Peters, D.M. Ladd, Determination of fluoride in oxides with fluoride-ion activity electrode, *Talanta* 18, 1971, 655-664.
- [47]. D.C. Harris, Quantitative Chemical Analysis, eight edition, Freeman & Co., NY, Chapter 14-17, 2008, p308-393.

- [48]. Z, Marzenko, M. Balcerzak, Separation, preconcentration and spectrophotometry in inorganic analysis, Elsevier Science B.V., Amsterdam, Netherland, 2000, 446-455.
- [49]. J.N. Dissertation, Evaluation of analytical methodologies for fluoride determination and speciation of fluoro complexes of aluminium, MS Thesis, Faculty of Science, University of Johannesburg, 2005, 199p.
- [50]. K. Nicholson, E.J. Duff, Fluoride determination in water: An optimum buffer system for use with the fluoride-selective electrode, Analytical Letters, 14(7), 2007, 493-517.
- [51]. J.H. Noh, P. Coetzee, Evaluation of the potentiometric determination of trace fluoride in natural and drinking water with a fluoride ISE, Water SA, 33(4), 2007, 519-529.