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Determination of Fluoride Concentration in Ground Water by Ion Selective Electrode

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A B S T R A C T

Potentiometric analysis of fluoride content (as F⁻ ion) in solutions by using fluoride ion-selective electrode is simple, reliable and cheap. Very small concentrations of fluoride-ions (to 10⁻⁶ mol/dm³) can be determined by fluoride selective electrode, with regulation of ion strength of a solution and control of concentration of hydroxide ions and interfering ions of metals. The content of fluorides in the samples can be determined by the method of direct potentiometer, and in the case of very low concentration by standard addition method. Electro analytical methods based on potentiometry with ion-selective electrodes seem to be the most popular and convenient methods of fluoride and chloride ion determination. Fluoride ion selective electrodes can be used to determine fluoride concentrations in drinking water due to its high selectivity, specificity and low detection limits. The advantages of this study include a short analysis time, elimination of sample pretreatment, simplicity of the measuring system and relatively low instrument cost.

Introduction

Flour belongs to a group of halogen elements and it is the most reactive non-metal. Flour is the lightest member of the group of halogen elements, and its chemical behaviour mainly differs from other halogen elements, and some of these differences are evident in its reaction in natural water. The fluoride element is found in the environment and constitutes 0.06 - 0.09 % of the earth's crust. Fluoride is not found naturally in the air in large quantities. Average concentration of fluoride in air is in the magnitude of 0.5 ng/m³ (WHO, 2004).

Fluoride is found more frequently in different sources of water but with higher concentrations in groundwater due to the presence of fluoride-bearing minerals. Average fluoride concentrations in sea water are approximately 1.3 mg L⁻¹. Water is vitally important to every aspect of our lives. Water is a risk because of the possible input and transmission of infectious pathogens and parasitic diseases. We use clean water to drink, grow crops for food and operate factories. The most common pollutants in water are chemicals (pesticides, phenols,

heavy metals and bacteria (Rowell, 2006). According to the US Environmental Protection Agency, there are 6 groups which cause contamination of drinking water: microorganisms, disinfectants, disinfection byproducts, inorganic chemicals, organic chemicals, radioactive substances. Fluorides come naturally into water by dissolving minerals that contain fluor, such as *fluorite* (CaF_2), the most common fluor mineral, apatite ($\text{Ca}_5(\text{Cl},\text{F},\text{OH})(\text{PO}_4)_3$), cryolite (Na_3AlF_6).

Amphibole minerals, such as hornblende and some sorts of mica, can contain fluor that partially replaces hydroxide ion. Rocks rich in alkali metals have a larger content of fluoride than other volcanic rocks. Fresh volcanic ash, as well as the ash of the other sediments can contribute to fluor content increasing in surface waters. Mixed minerals $\text{NaMgAl}(\text{F},\text{OH})_6 \cdot \text{H}_2\text{O}$ and $\text{Al}_2(\text{F},\text{OH})_6 \cdot \text{H}_2\text{O}$ and are rare, but can contribute to the fluoride content increasing while rinsing with water. In water that contains significant amounts of Ca^{2+} ion, it is possible to make balance and create hardly dissolving calcium fluoride. According to values for the dissolving result of calcium fluoride in water, where activity of calcium ion is 0.001 mol/dm^3 , concentration of fluoride ions is 3.1 mg/dm^3 . Total concentration of fluoride ions will be somewhat higher, which depends on ion strength and complexing effects, and it will be higher in waters where the concentration of Ca^{2+} ion is smaller (that is, in waters with low hardness) (Hem, 1985). Natural water contains less than 0.1 ppm fluoride ions, and in our waters it moves from 0.05 to more than 0.6 ppm. Mineral waters consist, on average, 0.16 to 6.45 ppm. Recommended limited value for fluoride in drinking water by World Health Organisation (WHO) and European Union (EU) is 1.5 ppm (WHO, 1984). Fluor content in water is expressed through the

free fluoride-ion concentration, whose concentration depends on origin and nature of water. This form is dominant in many water samples, although other forms of dissolved fluor can be present. Fluoride ion has small ion radius, so it shows great tendency to behave as ligand. Fluoride ion, because of that, forms a great number of different complex ions, where central ion has a large coordination number (mostly 6). Fluor forms stable complexes in water with Al^{3+} , Be^{2+} and Fe^{3+} ions, and with boron it forms mixed fluoride-hydroxy complexes. As fluoride ion has the same electricity and almost the same radius as hydroxide ion, these ions can mutually change in mineral structures.

Table.1 International and national drinking water standards of fluoride contents

Fluoride guideline value drinking water standards	Recommended minimum value (mgL^{-1})	Maximum Value (mgL^{-1})	Reference
WHO	0.5	1.5	WHO, 1993
USA			
Primary	0.5	4.0	US EPA, 1985
Secondary	0.5	2.0	
ADA	0.7	1.2	
Agency for Safety Food, B&H	-	1.5	Statute, 2007

The main source of fluor intake is drinking water and food, and secondary are stomatology prophylactic preparations. To date there are not reliable data about minimal daily nutritive requirements for fluor. Fluoride ion in traces in drinking water helps in growth and development of healthy, resistant teeth and bones. In many researches it was determined that fluorides are efficient in prevention of dental caries. Teeth enamel is mostly made of mineral hydroxyapatite. Hydroxyapatite contains hydroxide ion, which fiercely attacks acids (results of bacteria in mouth where they are

feeding with sugar), as a difference from much weaker basis, fluoride-ion in fluoroapatite (Dalmacija, 2000). Surplus of fluorides in organism can provoke teeth and skeleton fluorose. Fluorides inhibit many enzymes. Affected enzyme contains metal ion which unites with fluoride and creates metal-fluoride complex. Fluor in organism has its optimal, security-tolerant and toxic dose, which depends of person's age, weight and health. In the first year of life the optimal content of fluor is 0.045 mg/kg of body mass, tolerant 0.073 mg/kg, chronically toxic 0.150 mg/kg. Optimal dosage of fluor for adults is 0.020-0.025 mg/kg of body mass (www.mineralwaters.org). The sources of water pollution with fluorides are above all industrial waste waters from the production of aluminium, copper and nickel, steam generating stations, then phosphate minerals treatment, production and usage of phosphorus fertilizers, usage of fluor - based pesticides, production of glass, cement, glues and adhesive means. Transport and form of fluorides in water depends on environment pH value, water hardness and the presence of ion changeable substances, such as alumina. In waste waters fluorides can be present in the form of weak and highly toxic hydrofluoric acid (HF) whose toxicity can be seen in its characteristic to penetrate into tissue, because small molecules of HF quickly move through skin to tissue and damage it permanently.

Primary drinking water standards are those that must be enforced. Secondary drinking water standards are non-enforceable guidelines regulating contaminants that may cause cosmetic effects (such as skin or tooth discoloration) or aesthetic effects (such as taste, odour or colour) in drinking water (USEPA, 1985). The WHO maximum guideline value of 1.5 is higher than the recommended value for artificial

fluoridation of water supplies, which is usually 0.5 - 1.0 mgL⁻¹ (WHO, 2004).

Fluoride selective electrode

The most important electro analytic method for determination of fluoride ion in water solution is usage of ion selective electrode for fluorides. Fluoride selective electrode is very sensitive, and temperature range of electrode goes from 0 to 50°C. For potentiometric analysis of fluoride ion, in commercial usage, there are mostly used electrodes with homogenic membrane made from fluoride lanthana (LaF₃), which was first suggested by Frant and Ross (Frant and Ross, 1966; Frant, 1994). Active phase of fluoride selective electrode makes monocrystal LaF₃ which is doping by Eu²⁺ ions, in order to decrease membrane ohm resistance. The great selectivity of electrode is in the fact that only fluoride ions are included in the process of diffusion (Cammann, 1979). Commercially available electrodes are made by putting the electro-active material into the electrode carrier. The electrode carrier is the most common organic polymer substance (PVC, epoxy resin, polypropylene, Teflon etc.). The interior of the electrode carrier is filled with sodium chloride solution of 1 mol/dm³ concentration and sodium fluoride solution of 0.01 mol/dm³ concentration, inner referent electrode is Ag/AgCl electrode. The detection limit of monocrystal ion selective electrodes depends on the product of solubility of hardly dissolved compound in test solution. Even if the test solution doesn't contain fluoride ions, when the fluoride selective electrode plunge into the solution it will come to LaF₃ dissolving, and concentration of La³⁺ and fluoride ions will be adequate to values that are countable from the product of LaF₃ dissolving (Bralić et al., 2001). This means that in the solution there will always be present low, constant,

concentration of fluoride ions, so the applicability of ionometry for fluoride ion is from $5 \cdot 10^{-7}$ mol/dm³ to 1 mol/dm³ of fluoride.

Basic theory

The potentiometric method is based upon measurements of the potential that measures electromotive force of a galvanic element. Direct potentiometric determinations are almost always performed using ion selective electrodes (ISEs), which are capable of rapid and selective measurements of analyte concentration.

Ion-selective potentiometry (ISP) is a nondestructive method, which means that the sample can be used for further analysis. Ion selective electrode (ISE) such as chloride or fluoride, which is used in our investigation, as detector provides a range of possibilities in the analysis of samples of biological material. An ion selective electrode generates a difference in electrical potential between itself and a reference electrode.

The output potential is proportional to the amount or concentration of the selected ion in solution. The concentration is a measure of the number of ions in a specific volume. The definition assumes that all of those ions behave in the same manner. However, ions do not always behave similar to one another: some are effective i.e. exhibit properties associated with that ion, and some are not effective. The number of effective ions is called the activity of the solution. It is therefore reasonable to assume that the electrode will measure the activity rather than the finite concentration of the ions. In dilute solutions though, the ionic activity and concentration are practically identical but in solutions containing many ions, activity and concentration may differ.

This is why dilute samples are preferred for measurement with ISE's.

It is possible to 'fix' the solution so that activity and concentration are equal. This can be done by adding a constant concentration of an inert electrolyte to the solutions under test. This is called an Ionic Strength Adjustment Buffer (I.S.A.B.). Thus the ion selective electrode will measure concentration directly. Activity can also be an important quantity to measure; for instance, it is the activity of calcium in blood that is physiologically important, and not the concentration. The measured electrode potential, E, is related to the activity of an ionic species by the Nernst Equation.

$$E = E^{\circ} + 2.3 RT/nF \log \text{ACTIVITY}$$

Where E° = a constant for a given cell

R = the gas constant

T = the Temperature in Kelvin

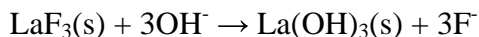
n = the ionic charge

F = the Faraday constant and the expression RT/nF is termed the Slope Factor

For example, when measuring Potassium ions, (i.e. $n = +1$), the slope factor at 298K (25°C) has a value of 59.16 mV. This is termed the Ideal Slope Factor, and means that for each tenfold change in Potassium concentration, an ideal measuring system will sense a mV change of 59.16. The measurement of slope factor gives an indication of the performance of the electrode system.

Fluoride selective electrode is very selective to fluoride ions, but at the same time, in a certain amount, it is selective to hydroxide ion. Adjustment of pH value with buffer is necessary because fluoride and hydroxide ions have the same electricity and similar ion radius, so hydroxide ions can interfere in the measurement of the fluoride selective

electrode. In acid solutions hydrofluoric acid is formed, to which the fluoride selective electrode is not sensitive. In that way, with solution pH values decreasing, the activity of fluoride ion in solution also decreases, so the measurement will not be reliable. On the other hand, in highly basic solutions a thin layer of $\text{La}(\text{OH})_3$ is formed on the surface of the sensor part:

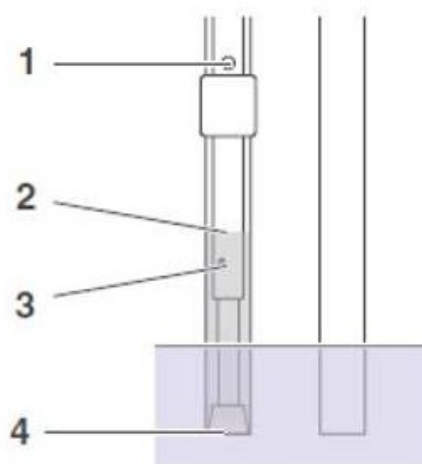


In this way, the concentration of fluoride ions in solution increases, that is, with the increasing of solution pH values, electrode potential of the ion selective electrode becomes more negative. Accordingly, it can be concluded that pH value of the solution during the measurement by the fluoride selective electrode must be in the range 5.00-7.00. Before the measurement with the fluoride selective electrode, all precautions must be taken to remove all organic uncleanliness from the solution, above all chloroform (CHCl_3).

Determination by the fluoride selective electrode means previous calibration with the solution with known concentration. During the measurement of concentration by the fluoride selective electrode, it is advisable, instead of calibration with two points, to construct calibration diagram, by EMS measurement in 5-6 standard solutions of different concentrations. This calibration diagram is then used to determine of fluoride ions concentration in the sample by EMS measurement and reading from calibration curve. If the fluoride solutions are highly dilute, concentration of fluoride ions is determined by standard addition method.

Figure.1 Schematic representation of reference and an ion-selective electrode

In this figure 1-indicate the filling opening for the bridge electrolyte, 2- fluid level of the bridge electrolyte, 3- the inner junction which must be covered with bridge electrolyte and 4- the ground junction.



Materials and Methods

- NaF, dried at 100°C for 1 hour.
- Liquid NaF unknown.
- KCl (7.55 g)
- Fluoride ISE and Ag/AgCl or SCE reference electrode.
- Multimeter or pH meter capable of displaying mV potentials



Figure.2 Ion selective electrode (Orion 4 star ion meter, Model: pH/ISE).

Preparation of Standards

Dry the NaF solid for 1 hour at 100 °C. Accurately weigh out about 0.42 g of NaF, dissolve in deionized water, dilute to 100 ml in a volumetric flask and mix well. This solution is about 10⁻¹ F in NaF. Transfer 10.00 ml of the solution prepared in (2) to a 100 ml volumetric flask using a pipet, dilute to volume with deionized water and mix well. This solution is about 10⁻² F in NaF. Weigh out 7.55 g of KCl on a top-loading balance and dissolve in 100 ml of deionized water. This solution is 1 F in KCl. Prepare standard solutions in four 100 ml volumetric flasks as follows:

	ml 10 ⁻² F NaF (from 3)	ml 1F KCl
(I)	1.00	10.00
(II)	2.00	10.00
(III)	5.00	10.00
(IV)	10.00	10.00

Dilute each flask to volume with deionized water and mix well.

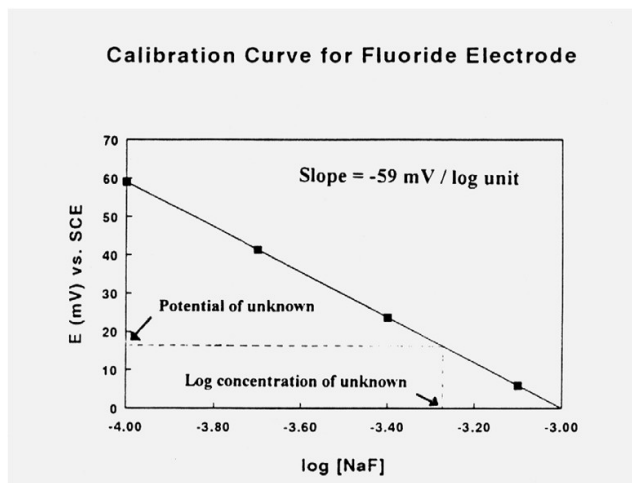


Figure: 3 Calibration curve for Fluoride Electrode

Results and Discussion

Accurately calculating the molarity of NaF for each of the standard solutions. Plotting a

graph of the logarithm of [NaF] in the standard solutions vs E. The best line is determined through the four standard solution experimental points. Slope of the calibration is determined. (Slope = dE/dlog[NaF]). Utilizing the calibration curve, the concentration of NaF in “prepared” unknown solution is determined. This is reported as percent fluoride (% w/v) in the “prepared” unknown.

Fluoride-selective electrode today has primary role for determination of fluorides in drinking water, and it is used for determination of fluorides in: drinking water (Li and Liu, 1995; Li and Ge, 1991; Ji, 1982; Wang, 2003), mineral water (Dimitrijević et al., 1990; Gigos et al., 1984), waste waters (Yamada et al., 1988; Lai and Tang, 2003; Golovanova and Sivokonev, 1986), ground waters (Ion et al., 2005; Kaniewski et al., 1985) and sea water (Sun, 2002). The advantage of ion selective electrode usage for determination of fluoride ion is in a wider range of linearity, short time of response, non-destructivity of samples and there is no contamination of samples.

Conclusion

Potentiometric determination of fluoride content in solutions by usage of the fluoride electrode is simple, cheap and reliable. All negative interfering effects that can influence the method of determination are eliminated by the usage of TISAB buffer. The content of fluorides in samples is determined by the method of direct potentiometry and, in the case of very low values, by standard addition method. Method ISP when it proved more effective, fast and reliable enough to determine fluoride ions in the water. Additionally, it has an advantage over any other analytical method because it is non-destructive and allows the use of samples for other types of

analysis. Based on the results obtained it can be concluded that there are many advantages of using ion-selective potentiometry (ISP) in reference to standard spectrophotometric and Mohr's methods, because measurements with the ISP are faster, efficient and reliable. It does not require the use of many different chemicals, and does not require any preparation of samples before analysis, which directly affects the economic availability. Electro analytical methods based on potentiometry with ion-selective electrodes seem to be the most popular and convenient methods of fluoride and chloride ion determination. Fluoride selective electrodes can be used to determine fluoride concentrations in drinking water due to its high selectivity, specificity and low detection limits. The advantages of this study include a short analysis time, elimination of sample pretreatment, simplicity of the measuring system and relatively low instrument cost.

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