

The Advantages of the Use of Ion-Selective Potentiometry in Relation to UV/VIS Spectroscopy

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Summary

Electro analytical methods have a long history of development. Ion-selective potentiometry is one of the electro analytical methods. There are some advantages of the use of Ion selective potentiometry (ISP) which is accurate, fast, economic and sensitive in relation to the standard method, UV/VIS spectroscopy. The development of potentiometric ion-selective electrodes is a very interesting field because it has a wide range of applications in determining ions in water and other mediums. The use of ion-selective electrodes enables the determination of ion species in a trace. Ion-selective electrodes are suitable for analysis in industry, for control processes, for physiological measurements and environmental monitoring. In recent years it was used for the determination of many ions in the food industry such as determination of calcium in milk products, fruit juice and different kinds of vegetables. In our experiment measurement of bottled water using ISP showed lower level of fluoride compared to measurement by UV/VIS spectroscopy. This results confirmed higher sensitivity of ISE in reference to UV/VIS spectroscopy. By our experimental data we can conclude that the concentration in examined sample was within the allowed concentration according to World Health Organisation.

Key words

ion-selective potentiometry, ion- selective electrode, advantages

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Introduction

The essential difference between spectrophotometric and potentiometric measuring is that spectrophotometric measure is based upon application of electromagnetic radiation while potentiometric measure is based upon measurements of the potential that measures electromotive force of a galvanic element. The potentiometric method is non-destructive and it means that tasted samples can be used in the future (Mentus, 1999). The basic idea of ion selective electrodes is the measuring of electrode potentials (voltages) and from that determining the concentration of analyte in the solution. Measuring voltages requires two electrical contact points. One is a reference electrode whose potential is constant. The other is a sensing electrode, whose potential varies with concentration of analyte.

$$E_{\text{sensing}} - E_{\text{reference}} = E_{\text{measured}}$$

An ion-selective electrode is a sensor for potentiometric determination of ion species (Campbell, 1997). Ion-selective membrane is a key component of all potentiometric ion sensors (Durst, 1969). The function of an ion-selective electrode is based upon selective diffusion of charged species from one phase to other making a difference in potential. When an electrode is put in the tested solution then at the moment it establishes flux of ions across the membrane in direction of solution which consist lower activity of mobility of ions. As ions carry charge, establishes the electric potential which opposes further movement of ions, and a condition of equilibrium is attained in which potential across the membrane preventing further movement of ions.

The ions that can be measured in this way are: anions, cations and gases in solution. In this work will be presented some advantages of using ion-selective potentiometry as one of the methods for determining of fluoride in the sample of bottled drinking water.

Electrochemical sensors are very attractive for on-site monitoring of pollutants (APHA, 1976; Wang, 1995). Ion selective electrodes offer direct and selective detection of ionic activities in water samples. Such potentiometric devices are simple, rapid, inexpensive and compatible with on-line analysis. Many ion selective electrodes are commercially available and routinely used in various fields (Harynuk, 2009). Monitoring of water sources and drinking water for different trace elements has become very important (Campbell, 1997).

Fluorine (F) is an important essential element. Fluoride is present in various environmental, clinical and food samples. Small amounts of fluoride are vital for the human organism, but it's toxic in larger amounts. Fluoride is known as a constituent of bones, teeth, soft tissues and body fluids. Excessive intake of fluoride results in fluorosis. According to the World Health Organisation (WHO) the maximal allowed concentration of fluoride in drinking water is from 0.5 to 1.0 mg/L.

Ion Selective Electrodes are membrane electrodes that respond selectively to ions in the presence of other ions.

The use of Ion Selective Electrodes in environmental analysis offer several advantages over other methods of analysis.

The expense is considerably lower than of the other methods, such as Atomic Absorption Spectrophotometry or Ion Chromatography. ISE determinations are not subject to interferences such as colour in the sample.

A large number of indicator electrodes with good selectivity for specific ions are based on the measurement of the potential generated across a membrane (Skoog et al., 1998).

For fluoride the sensing electrode surface is a crystal of LaF_3 doped with a little europium fluoride, EuF_2 . The crystal has some fluoride vacancy sites (due to the EuF_2) allowing a response to external fluoride. Determining the concentration of an unknown sample requires calibration of ion-meter.

Previously the determining of fluoride in drinking water, fruit juice, bottled water, toothpaste and so on was thoroughly investigated.

Material and methods

In this work were used classic and instrumental methods for chemical analysis. The classic method means the use of gravimetry for determining sulphate and volumetry for determining chloride. The instrumental methods of analysis are UV/VIS spectrophotometry and electroanalytical method such as ion-selective potentiometry.

In this experimental work were used classic methods of chemical analysis and instrumental methods of analysis optic methods such as UV/VIS spectrophotometric method and electro analytic method it means ion-selective potentiometry. Determining of fluoride ions in drinking water is possible by potentiometric method and spectrophotometric method. In this work the analysis of contents of fluoride in drinking water by potentiometric method, The name of the ion-meter which was used is MICROPROCESSOR pH/ION Meter pMX 3000 WTW (Harynuk, 2009). As a reference electrode was used the electrode type WTW R 500, as an ion-selective electrode was used WTW fluoride ion-selective electrode F 500. WTW pH - electrode was used for determining of pH. The spectrophotometer type UV/VIS CECIL 2021 was used for analysis of fluoride by spectrophotometric method with zirconium (IV) ion oxychloride and alizarin S (Bratovic, 2008).

For preparing and analysis of sample supra pure chemicals (Merck) were used: sodium fluoride (NaF), potassium nitrate (KNO_3) – as an external solution for a reference electrode; CH_3OH (methanol) – for cleaning of membrane, sodium salt of an alizarin-sulfone acid (alizarin S), zirconium-chloride ($\text{ZrOCl}_2 \cdot 8 \text{H}_2\text{O}$), concentrated H_2SO_4 and concentrated HCl .

Results

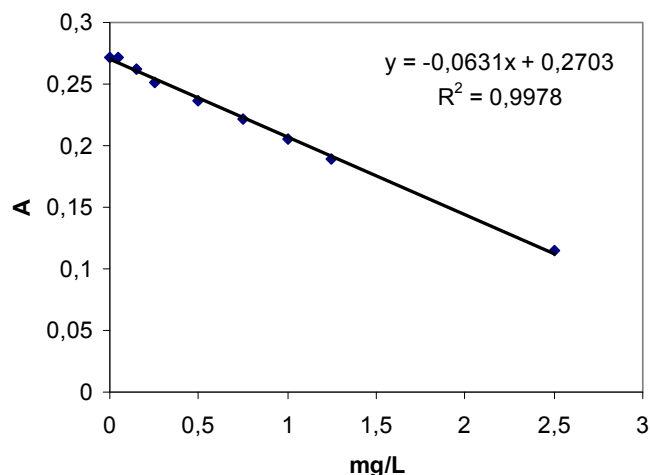
In this experimental work the sample of imported bottled water on the market in Bosnia and Herzegovina was analysed. In this sample first of all was determined pH value and it was 7.16. The measured potentials by fluoride ion-selective electrode for our sample are given in Table 1. The measured absorption of the wave length was 0.226 nm. So, the average

Table 1. The potentials measured by fluoride ion-selective electrode are given

Number of measure	Potential, E (mV)	Concentration, C (mg/L)
1	-18.55	0.660
2	-17.50	0.632
3	-17.70	0.637
4	-18.70	0.664

Table 2. Data for construction of the calibration curve for spectrophotometric determining of fluoride

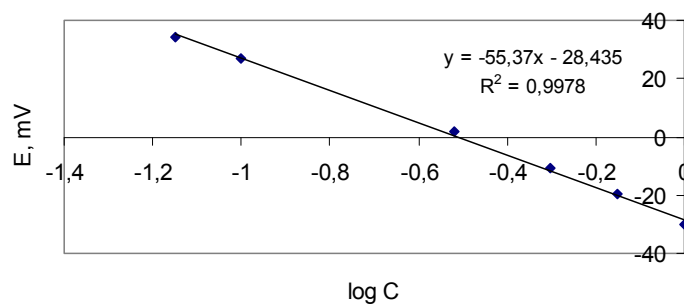
Order number	C _F , (mg/L)	Absorption
1	0.00	0.272
2	0.05	0.271
3	0.15	0.262
4	0.25	0.252
5	0.50	0.237
6	0.75	0.221
7	1.00	0.206
8	1.25	0.189
9	2.50	0.115

**Figure 1.** The calibration curve for determining of fluoride by spectrophotometric method

concentration of fluoride that we determined by potentiometric method was 0.648 mg/L, in reference to 0.7 mg/L determined by spectrophotometric method (Bratovic, 2008). Generally, in order to determine the concentration of fluoride in samples was necessary to construct a calibration curve for both of methods. For potentiometric determination of fluoride a plot of measured potential (mV) versus logarithm value of concentration was constructed, and used to determine the concentration of fluoride in an unknown sample. For ISEs, that plot would plot measured potential versus log (concentration), with a linear response expected, based on the form of the Nernst equation (Serjeant, 1984). For spectrophotometric determination of fluoride the plot measured absorption versus concentration was drawn. In Figures 1-2 are given calibration curves for spectrophotometric method and

Table 3. Data for the construction of a calibration curve for potentiometric determining of fluoride.

C (mg/L)	0.07	0.1	0.3	0.5	0.7	1.0
Log C	-1.15	-1.0	-0.52	-0.301	-0.15	0.00
Potential (mV)	34.2	27.1	1.6	-10.7	-19.7	-30.3

**Figure 2.** The calibration curve for determining of fluoride by potentiometric method

potentiometric method and in Tables 2 and 3 are given data about the construction of calibration curves (Bratovic, 2008).

Discussion

The concentration of fluoride in the bottled water on declaration from the producer was 0.69 mg/L, for which measurement we suppose the spectrophotometric method was used. According to these results it's clear that the use of an ion-selective electrode (potentiometric method) is a more sensitive method in reference to spectrophotometric method. Except, measuring by ion-selective electrode is fast, because it isn't necessary for pre-treatment of the sample, in addition the number of interfering ions is considerably less in reference to spectrophotometric determining. In this sample interfering ions weren't present in upper concentrations which are the allowed value, so that pre-treatment wasn't necessary. Also, data about pH value that was 7.16 means that the sample had an optimal pH value. Namely, the optimal pH value for WTW fluoride ion-selective electrode ranges 5-9. All pH values that are above or below this level require use of the TISAB reagent (Total Ionic Strength Adjustment Buffer).

Conclusion

In conclusion there are many advantages of using ion-selective potentiometric method in reference to spectrophotometric method. Therefore, the potentiometric method is considerably cheaper than other techniques such as atomic absorption spectrophotometry (AAS) or ion chromatography (IC), in addition it's easy to use, the measures are fast, non-destructive, and it's possible to direct measure in troubled and viscous solutions and it has a wide range of applications. Ion-selective potentiometry has some disadvantages such as: possible deviation from Nernst's equation for potential which depends on change of temperature in surroundings, shift po-

tential and ion activity. However, these disadvantages can be fast and easy to eliminate. Therefore, if shift of the potential is present it is necessary to do a re standardisation or when we need regulation of ion-activity it is necessary to use buffer to fix ion strength, such as TISAB reagent. But the presence of interfering ions in the spectrophotometric method represents a more complicated problem and it takes considerably more time in reference to application of ion-selective potentiometry. In this work water in which concentration of possibly interfering ions was analysed and wasn't over allowable limit for those methods. We obtain this data using chemical analysis. By our experimental data we can conclude that the concentration in this sample is within the allowed concentration according to World Health Organisation. Determining of trace elements in drinks and food generally, such as water and milk products is of great significance for human health because of daily consumption of certain amounts. Therefore, a continual monitoring of trace elements in food products will surely insure and promote the health of humans.

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