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Determination of Iodide and Fluoride in *Brassica Oleraceae* Var. *Acephale* with Ion Selective Electrodes

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Author's contribution

The sole author designed, analyzed and interpreted and prepared the manuscript.

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ABSTRACT

Black dandelion is widely grown in the Black Sea region, consumption as food is quite high. There are many trace elements important in terms of nutritional value. Goitre disease, which is common in this region, is caused by iodide deficiency. Fluoride is of great importance for the health of the teeth. Therefore, in our study, we wanted to measure the iodide and fluoride found in the most consumed dandelions in this region with iodide and fluoride selective electrodes.

The black cabbage samples were dried to constant weighing. It was made soluble by wet burning method. Iodide and fluoride ions were determined by dilution. Our electrode consisting of ion exchange, PVC and plasticizer has a sensitivity of 59 mV to 10^{-5} - 10^{-1} M iodide. Our electrode, which is composed of calcium fluoride and less soluble silver salts, shows a sensitivity of 28 mV to 10^{-5} - 10^{-1} M fluoride. Iodide and fluoride measurements can be made with our electrodes which are not sensitive to any other anion and cation.

Keywords: Determination; fluoride; iodide; selective electrode; Brassicia oleracase var. Acephale.

1. INTRODUCTION

In the literature, a fast and simple Differential Pulse Polarographic (DPP) method for the determination of trace elements in a certain form of cabbage is described. This vegetable is commonly used as food in Turkey, especially in the Black Sea region. Using DPP polarograms of

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wet digested cabbage samples (leaf) in pH 2 and 4 acetate buffer Mo, Cr, Se, Pb, As and Zn quantities were determined [1]. The best separation and determination condition for Cu and Fe was in EDTA at pH 6.5, and for Ni and Zn it was ammonia buffer at pH 9.8. The trace element quantities in digested leaf samples were as follows: Se(IV) about 40 *μ*g/g, As(III) 83 *μ*g/g, Cr(III) 23 *μ*g/g, Zn(II) 60 *μ*g/g, Mo(VI) 5 *μ*g/g, Pb(II) 7 *μ*g/g, Fe(III) 3 *μ*g/g and Cu(II) 95 *μ*g/g (Somer et al. 2006). Only 3 elements, Cu, Pb, Zn and Ni(II), were determined in stalk samples of the same cabbage [2].

For the determination of fluoride ions in the literature, the most widely known fluoride ion selective electrode was developed from the LaF_3 membrane [3]. The slope of this electrode against fluoride concentration is 59 mV.

In one study, the fluoride contents of tea and soil were determined from tea fields. The amount of fluoride in the tea glass during brewing was examined. Here, measurements were made with fluoride selective electrode [4].

Thorium, calcium and rare earth fluorides are also used in solid electrode construction due to their low solubility. The electrodes obtained from these salts were also found to have high sensitivity to fluoride. It has been used in many samples for fluoride analysis [5]. However, since normal precipitates of these fluorides tend to be gelatinous, a detailed investigation of the precipitation procedures was necessary. In a recent study [6], a fluid selective electrode with LaF_3 membrane and stainless steel internal contact was prepared.

In one of our studies, solid crystal electrode was made by mixing low soluble CaF_2 salt, silver sulfur and selensulphide in certain ratios. The sensitivity of this electrode to fluoride was 28 mV. Fluoride analysis was performed in black pepper with this electrode [7-8].

To determine the amount of fluoride in food, it is necessary to remove fluoride from the matrix. This study suggested the use of a microwave oven and 7 mol / L nitric acid for the simple, rapid dissolution of food for fluoride analysis. The analyte was then measured with a fluoride ion selective electrode. Various stages of the method are optimized. The limit of detection (0.130 mg / kg), accuracy (92%), recovery (84-101%) and sensitivity (1-8%) were determined. These analytical properties are satisfactory and have demonstrated the suitability of the fluoride analysis method in various types of foods [9].

The first iodide selective electrode was prepared in 1961 by Pungor and Hollos [10] using silver iodide and parafilm. This electrode was used for the determination of iodide in mineral waters in Hungary. At the same time, the determination of the sulfur dioxide, SO_2 gas iodine solution was carried out by reducing the iodide formed by reduction.

In 1971, an AgI-Ag_2S solid state electrode with a life of 35 days was prepared. This solid crystal electrode has a high sensitivity to iodide. In addition to iodide, it was found to be sensitive to silver ion and this electrode was called Ruzicka type iodide electrode [11]. This electrode was used by Budirmir and Momir [12] to determine cyanide in alcoholic beverages.

The aim of this work was to develops an electrode selective for iodide ion using ion exchanger as the active material. In the present study, solid membrane electrodes were prepared using tridodecylmethylammonium iodide (TDMAI) ion exchanger active material, PVC as inert matrix and dibutylphtalate (DBF) as plasticizer in different compositions, also was to prepare a new electrode for fluoride ion using CaF_2 as active material. This study, solid state electrodes were prepared using CaF_2, Ag_2S and Cu_2S. Their optimum working conditions were investigated and interference studies have been made. Iodide and fluoride ions in Brassica oleraceaevar. Acephale were determined by these electrodes.

2. EXPERIMENTAL

2.1 Chemical and Materials

Reagent grade chemical were used without further purification. Stock solutions were prepared with doubly distilled water and kept in dark. In order to keep the ionic strength constant, 0.1 M $NaNO_3$.

2.2 Instruments

A JENWAY 3040 Ion Analyzer has been used for potantial measurements and 924036 double junction Ag/AgCl reference electrode was used as the outer reference electrode. Chiltern H531 magnetic stirrer was used.

2.3 Preparations of Iodide Selective Electrodes

20% TDMAI (tridodecylmethylammonium iodide), 60% PVC, 20% DBF, 4.2 cm petri dish with a total membrane mass of 0.3 g were dissolved in 5 mL THF. The solvent was removed for 1 day. The resulting membrane was adhered to the PVC hose with a PVC cap using a PVC solution. The solvent was allowed to stand again for 1 day. The electrode was charged with 2 mL of a solution containing Ag / AgCl electrode as the internal reference electrode and 0, 1 M I^- and 0.1 M Cl^- as the reference solution. After the electrode was conditioned in $1.0x10^{-4}$ M iodide solution, the measurements were started [13].

2.4 Preparations of Fluoride Selective Electrodes

Total mass of 0.1 g 70% Ag_2S, 10% Cu_2S and 20% CaF_2 was crushed in mortar and then pelleted by hydraulic press. 7 mm diameter 0.1-0.3 mm thick pellets were adhered to the glass tube with epoxy resin in contact with the silver wire pellets. The resin was allowed to dry for one day [7].

2.5 Preparations of Brassica oleraceaevar Acephale

The Brassica type cole, which is commonly used in the Black Sea region as the main food, was collected in samples from the city of Giresun, located on the Black Sea coast. It has long and separate green-blue leaves. They were first separated as leaves and stalks, cut into small pieces after washing and then dried in an oven at about 105°C until constant weight. About 10 g of it was wet digested in a long-necked 100 mL flask with an acid mixture HNO_3:$HClO_4$ (7:1). First 10 mL of this acid mixture was added and it was left overnight with a glass funnel covering the mouth of the flask. The next day the flask was heated over a flame by turning the flask until all nitrogen oxide fumes were given off. When the digestive sample turned. The digested sample was cooled to room temperature, the funnel was rinsed into the flask with water and the contents were transferred into a 10 mL calibrated Teflon flask, making up to the mark with distilled water [14].

3. RESULT AND DISCUSSION

3.1 Characteristics of Iodide Selective Electrode

Many factors have been studied to increase the sensitivity of the iodide-selective membrane electrode and the properties of the electrode are listed below [13]: 20% TDMAI (tridodecylmethylammonium iodide), 60% PVC, 20% DBF electrode inclination is $1.0x10^{-5}$ - $1.0x10^{-1}$ M I^- against 59 mV (Fig. 1). Total membrane mass is 0.3 g and does not show sensitivity to pH. Iodide ion selective electrode displayed very good selectivity for fluoride ion with respect to sodium, potassium, calcium and magnesium cations and to chloride, nitrate, sulfate and phosphate anions (Table 1) [15].

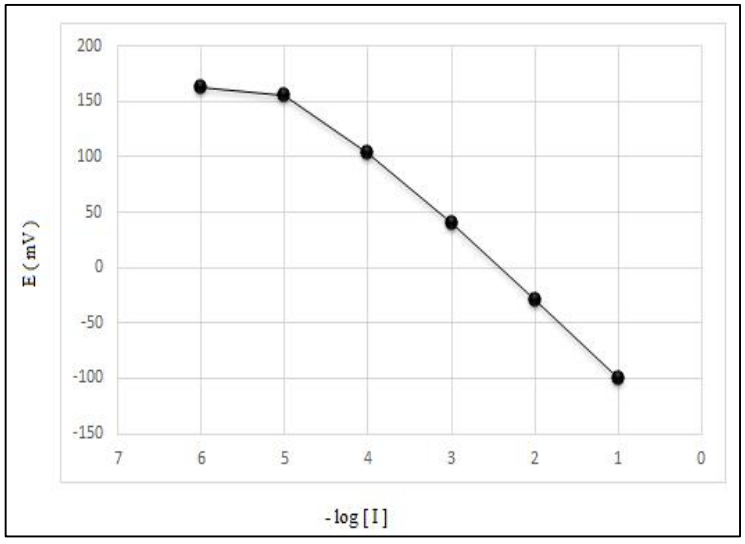

Fig. 1. Calibration curve of iodide-selective membrane electrode due to iodide concentration

Table 1. Selectivity coefficients of iodide selective electrode against some anions and cations

Ions	$K_{A,B}^{pot}$
Cl^-	$3x10^{-3}$
NO_3^-	$8x10^{-3}$
SO_4^{-2}	$6x10^{-4}$
PO_4^{-3}	$3x10^{-4}$
K^+	$3x10^{-3}$
Na^+	$8x10^{-3}$
Ca^{+2}	$1x10^{-4}$
Mg^{+2}	$5x10^{-3}$

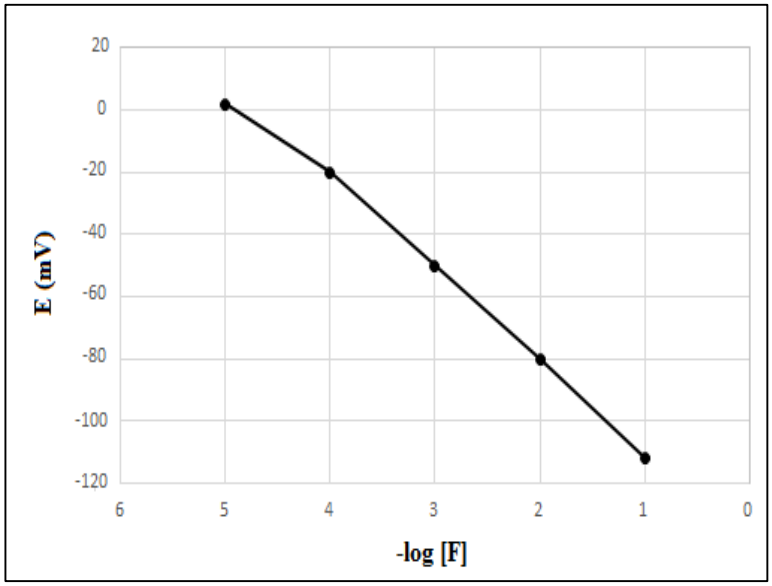

Fig. 2. Calibrationgraph of fluoride- selective electrode based on fluoride concentration

Table 2. Selectivity coefficients of fluoride selective electrode against some anions and cations

Ions	$K_{A,B}^{pot}$
Cl^-	$3x10^{-3}$
NO_3^-	$8x10^{-3}$
SO_4^{-2}	$6x10^{-4}$
PO_4^{-3}	$3x10^{-4}$
K^+	$3x10^{-3}$
Na^+	$8x10^{-3}$
Ag^+	$1x10^{-2}$
Ca^{+2}	$1x10^{-4}$
Cu^{+2}	$2x10^{-4}$
Mg^{+2}	$5x10^{-3}$

Table 3. Determination and comparison of iodide and fluoride in *Brassica oleraceaevar. Acephale*

Ions	Concentrationdeterminedby ISEprepared (ppm)	Concentrationdeterminedby Orion Brand ISE (ppm)	% 90 Güven seviyesi ve N=4 ölçüm için	
			$F_{Experimental}$ ($F_{Critical}$=9,28)	$t_{experimental}$ $t_{critical}$=2,53
I^-	24 ± 1,1	25 ± 1,4	1,36	0,58
F^-	3,8 ± 0,3	3,8 ± 0,5	1,96	0,76

3.2 Characteristics of Fluoride Selective Electrode

Many factors have been studied to increase the sensitivity of the fluoride-selective electrode and the properties of the electrode are listed below [7]: 70% Ag_2S, 10% Cu_2S, 20% CaF_2 electrode inclination is $1.0x10^{-5}$ -$1.0x10^{-1}$ M F^- against 28 mV (Fig. 2). Total mass is 0.1g and does show sensitivity to pH at 1-8. Fluoride ion selective electrode displayed very good selectivity for fluoride ion with respect to sodium, potassium, silver, copper, calcium and magnesium cations and to chloride, nitrate, sulfate and phosphate anions (Table 2).

3.3 Determination of Iodide and Fluoride in *Brassica oleraceaevar. Acephale*

After increasing the sensitivity of our prepared fluoride and iodide-selective electrodes, the amount of fluoride and iodide in the *Brassica oleraceaevar. Acephale* samples we dissolved were calculated. Fluoride and iodide in black tea were also calculated with commercial electrodes, with the results given at the 95% confidence level and in the table below for five measurements. The t-test was performed to compare the mean values of the results obtained from both electrodes. It was found that the average values of the analysis results obtained from both commercial and developed electrodes were close to each other (Table 3).

4. CONLUSION

These electrodes are used for the determination of iodide and fluoride. The iodide selective electrode we prepared is 59 mV sensitivity to iodide between 10^{-5}-10^{-1} M, and the fluoride-selective solid crystal electrode based on calcium fluoride (CaF_2) we developed is 28 mV sensitivity between 10^{-5}-10^{-1} M. As a result of the analysis using these electrodes, 1 g *Brassica oleraceaevar. Acephale* was found to be in the range of 95% confidence level and 24 ± 1.2 µg iodide and 3.8 ± 0.3 µg fluoride in four measurements (Table 3).

COMPETING INTERESTS

Author has declared that no competing interests exist.

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