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All-Solid-State Iodide Selective Electrode for Iodimetry of Iodized Salts and Vitamin C

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ABSTRACT

A laboratory-made all-solid state iodide selective electrode, with Ag_2S-AgI coated on a graphite rod recovered from dry cell battery, was prepared according to previous procedures. The electrode's linear response to iodide was in the concentration range of 10^{-6} M to 10^{-1} M with a slope of 56.85 mV/decade and a detection limit of 6×10^{-7} M. Iodate recovery test for laboratory formulated iodate-iodized salt was found to be 98.6 % with a standard deviation of 1.14%. The titratability of the iodized salt solution was at least 10-200 ppm potassium iodate (6-120 ppm iodine), exhibiting distinct endpoints in the range wider than the ones set in regulatory standards and reflecting that QC monitoring in production and stability decline of iodine content upon storage can be performed with the electrode method. On the basis this potentiometric titration, the application of the laboratory-made iodide electrode (vs. a saturated calomel reference electrode) was extended to the determination of iodine in commercial iodized salts. In all the iodine assays, the iodate-iodized salt was initially treated with acid and an excess of iodide before titration against $Na_2S_2O_3$ solution. The iodine content in table salts iodized with iodide was determined by direct potentiometry. The electrode was further used for vitamin C (ascorbic acid) determinations in pharmaceutical tablets and orange juice by back titrating excess I_3^- against standard $Na_2S_2O_3$ in acidic media. The overall outcome is that the iodide ISE can be used as sharp endpoint indicator for these titrimetric reactions in place of the well known official, but visually monitored, starch- triodide end-point reaction detection.

Key words: Solid state iodide selective, Electrode, Graphite, Vitamin C.

INTRODUCTION

Biomedical importance of iodine and supplementation in table salt

Iodine is an essential nutritional factor with important biochemical functions such as mental development, and basic metabolisms[1]. In areas where water and soil and foods are deficient in the amount of iodine required by normal diet, iodine supplements in table salts are administered, using iodate or iodide for iodization. The established requirement of thyroxin in the thyroid gland is

ascribed to the chief action of iodine in the human body which plays an important role in the efficient conversion of beta-carotene to vitamin A. The most familiar iodine deficiency disorder (IDD) arising from low iodine diets is goiter. The other consequences of IDD are elaborated in other reports[2].

Goiter is one of the nutritional problems with public health significance in Ethiopia. One out of every 1,000 people is a cretin, and about 50,000 prenatal deaths are occurring annually due to iodine deficiency disorders. A baseline survey of goiter prevalence conducted among five endemic regions and four non-endemic regions from 1988 to 1991 revealed that both the endemic and non-endemic regions were found to have a higher goiter prevalence rate than previously reported[3,4]. As per WHO recommendation, the safe and adequate dietary intake of iodine for infants to adults ranges from 50 to 200 microgram per day the intake requirements increasing from infants/children to pregnant/lactating women[5].

Salt iodization

This is known to be the most effective long-term public health intervention for achieving optimal iodine nutrition. Effective salt iodization is vital for the sustainable elimination of IDD. Many countries have adopted mandatory iodization programmes for table salt, signifying the importance of this element to public health.

Stability iodide and iodate in iodized salts

Most countries including Ethiopia used potassium iodate to iodize table salts. Potassium iodide is less stable than potassium iodate, as it can be oxidized to elemental iodine by oxygen or other oxidizing agents, especially in the presence of impurities, such as metal ions and moisture, which catalyze the reaction. To avoid this problem, 3 a reducing agent, typically dextrose ($C_6H_{12}O_6$) is added to reduce back any iodine formed to the colorless iodide ion. Even so, the actual availability of iodine from iodized salt at the consumer level can vary over a wide range as a result of variability in the amount of iodine in the iodization process as well as the uneven distribution of iodine in the iodized salt within batches, stability loss due to salt impurities, environmental, storage, packaging distribution conditions, as well as due to food processing, and cooking[6]. According to the WHO/ UNICEF/ICCIDD, the loss of iodine from production to household has been estimated to be upto 20% [7].

Monitoring iodine levels in table salt

The AOAC iodometric titration procedure [8] is used to monitor the amount of iodine, be it in the form iodide or iodate added table to salt. The method involves the well known starch indication of end point (Eq. 3)

$$I^- + 3Br_2 + 3\,H_2O \rightarrow IO_3^- + 6Br^- + 6H^+ \quad ...(1)$$

$$IO_3^- + 6H^+ + 8I^- \rightarrow 3I_2 + 3H_2O \quad ...(2)$$

$$I_2 + 2S_2O_3^{2-} \rightarrow 3\,I^- + S_4O_6^{2-} \quad ...(3)$$

In the AOAC official method, a sample of iodide-iodized salt using all the steps in equations 1-3. Evidently, iodine in salts iodized with iodate is determined only using the last 2 steps, (Eqn. 2 and 3).

Monitoring iodine levels is therefore important for stability reasons and for quality control during the production of iodized salts. The determination of iodine and its related compounds is also important for monitoring its levels in a variety of matrices pharmaceuticals foods, fodder, water, clinical and biological materials, pharmaceutical preparations and environmental samples[3].

L-Ascorbic acid

L-Ascorbic acid (vitamin C) is widely distributed in plant and animal tissues and is involved in the metabolism of various substances in vivo. The reversible oxidation of L-ascorbic acid to dehydro-L ascorbic acid is the basis for its physiological activities, stabilities, and technical applications[9]. It is found in citrus fruits, green peppers, red peppers, strawberries, tomatoes, broccoli, brussels sprouts, turnip and other leafy vegetables. The beneficial effects of vitamin C 4 against the common cold may be caused by its antioxidant properties[10]. The deficiency of vitamin C leads to many diseases, the best known of which is scurvy. The recommended dietary allowance for Vitamin C in ranges from 40 mg/day for infants to 120 mg/day for breastfeeding mothers[11].

Vitamin C assay methods

A large number of methods have been reported for the determination of acid ascorbic: titrimetry, voltammetry, potentiometry, spectrophotometry, flow injection analysis and chromatography[12].

A titrimetric method with 2, 6-Dichlorophenolindophenol (DCIP) has been used as the titrant for the determination of ascorbic acid. The method is based on the reduction of DCIP with ascorbic acid in acidic solution. It is an official method, for many pharmaceutical preparations, which do not contain Fe (II), Sn(II), Cu(I), SO_2, SO_3^{2-} and $S_2O_3^{2-}$ ions. Moreover, DCIP has been found to oxidize thiols[13]. Iodide Ion Selective Electrodes Halide (X-) ion- selective electrodes are generally prepared by co-precipitation of a silver halide and Ag_2S. To an equal molar solution of potassium halide and sodium sulfide excess silver nitrate solution is added till complete precipitation to be used as a halide ion selective electrode is [14].

$$KX\ (aq) + Na_2S\ (aq) + 3AgNO_3(aq) \rightarrow AgX(s) + Ag_2S(s) + KNO_{3(aq)} + NaNO_{3(aq)} \quad ...(7)$$

Commercial iodide ion-selective electrode consists of a compressed pellet of silver sulfide and silver iodide.

The main objective of this work was to construct and assess the analytical application of laboratory constructed solid state iodide ion selective electrode coated on graphite rod recovered from a dry cell battery to determine iodine in iodide salts and the amount of ascorbic acid pharmaceutical products and in raw orange juices by a back titration iodometry[5].

EXPERIMENTAL

Reagents and Samples

Reagents

Potassium iodate 99.5 % (BDH, England), Potassium chloride (Riedel-de Haen, AG), Potassium nitrate (Research Chemicals Ltd), Potassium iodide (BDH, England), Sodium thiosulfate (Riedel-de Haen, AG), Sodium Chloride (Oxford Laboratory Reagent, Extra pure (99.5%) India, Sodium carbonate (BA, A.A.U), Sodium sulfide (BDH, England), Silver nitrate (Scharlau Chemie S.A, EU), Paraformaldehyde film (American can company, America), and distilled water were used throughout the experiments.

Samples

Iodized salts purchased from supermarkets were manufactured by (a) Saudi Salt Refinery, Saudi Arabia (label claim 70-100 mg/Kg as iodine), (b) Klinge Foods Ltd, Scotland, 47.5 mg/Kg as iodine) (C) American Garden product, USA (0.006% as potassium iodide). The Vitamin C tablets purchased from local pharmacies were produced from the Ethiopian Pharmaceuticals Manufacturing Industry S.C. and Chemical Industrial Development (Egypt). The latter is sold as Effervesce Vitamin C tablet. Egyptian Orange fruit juice, and whole Ethiopian orange (yellow and Green orange) were also randomly purchased from supermarkets.

Apparatus and Instruments

Potentiometric measurements were made at room temperature using Jenway Model 3345 Ion Meter with the graphite coated electrode recovered from a dry cell, against Ag/AgCl external reference electrode (Hanna Model HI5412). Stable potentials were recorded within 1-5 minutes of stirring using a teflon- coated magnetic stirring bar.

Electrode preparation

A 2-cm long graphite rod taken from used dry cell was cleaned and inserted into a ball point pen holder so that 1.5 cm length of the rod was protruding out from the pen. The electrode was dip-coated by keeping it into freshly prepared saturated solution of sodium sulfide, and silver nitrate respectively for 30 minutes in each solution. The surface was washed several times with water. The same procedure was repeated using saturated solution of potassium iodide and silver nitrate 6 to precipitate the electro-active species Ag_2S and AgI onto the graphite rod. Part of the coated rod (0.5 cm) was covered by para-formaldehyde film to avoid the passage of test solution into the bare part of the copper cable which was used to connect the electrode with the ion meter. The electrode was rinsed with small drops of distilled water. If necessary, 2-3 drops of mercury metal was added into the pen holder from the top position to insure easy electrical contact between the graphite

electrode and the copper wire. The electrode was allowed to dry current air in a hood for 2 hours and finally conditioned for at least an hour before use[15-16].

Solution preparations

Preparation of calibration standards. 0.1 M stock solution of iodide was prepared by dissolving 4.15 g of KI in 250 ml volumetric flask. Serial tenfold dilutions of the stock solution were used to prepare solutions down to $1x10^{-8}$ M iodide. The diluent was 0.1 M KNO_3 to keep the ionic strength of all the solutions constant at 0.1.

Standardization of sodium thiosulfate

8.7 g of $Na_2S_2O_3$ was prepared by dissolving in 500 ml (about 0.07 M) freshly boiled distilled water containing 0.05 g of Na_2CO_3. This solution was kept in a tightly capped amber bottle. 0.01 M KIO_3 was prepared by weighing 1.07 g of the salt and dissolving in a 500 ml volumetric flask. 50.00 ml of 0.01 M KIO_3 solution was transferred into titration flask and 2 g of solid KI and 10 ml of 0.5 M H_2SO_4 was added to it.

Preparation of Iodized salt solution for recovery study

25 gram of 99.5% NaCl was dissolved in 100 ml of 7.5x10-6 M KIO3 to make the content of latter about 47.5 ppm, the middle value for iodine content according to the Ethiopian standard. This solution was acidified with 1.0 ml of about 0.3 M H_2SO_4 and 2 gram of KI was added in excess to solubilize the iodine generated as triiodide. Titratability study of iodate-iodized salt. 1000 ppm of stock KIO_3 was prepared in 250 ml volumetric flask. From this, solutions of KIO_3 10 ppm, 50 ppm, 100 ppm, 150 ppm, and 200 ppm were prepared in 200 ml flasks by serial dilutions of the stock solution. Excess KI (190 mg/l final) and 0.3 ml of 0.3 M H_2SO_4 were added to each before the titration of each serially diluted KIO3 solution. 7

Vitamin C and iodine level determinations in Samples

Determinations of vitamin C

Ten tablets of vitamin C, or the vitamin emptied from 10 capsules, were weighed and crushed to powder for homogenization. 200 mg of this powder was dissolved in 60 ml of 0.3 M H_2SO_4. 2 g of KI and 50 ml of 0.01 M KIO_3 was added to produce triiodide ion. A known volume of orange juice was similarly treated with excess of the triiodide-generating solution. The reactions were allowed to proceed for 2 minutes each and the excess I^-_3 back titrated potentiometrically with standard thiosulfate solution.

Determination of iodine in iodized salts

Analysis of iodine contents in iodate-iodized commercial salts and known mixtures were made by dissolving 25 g of the sample with 100 ml distilled water and acidifying the solution with H_2SO_4 to generate free iodine from the iodate in the salt sample. Excess KI was added to solubilize the free iodine as I_3^- The solubilized iodine so formed was potentiometrically titrated with standard thiosulfate solution with iodide electrode as end point indicator.

For samples iodized with iodide salts, the iodine contents were directly found from the calibration curve.

RESULTS AND DISCUSSION

Calibration of the electrode

The potential response of the cell in mV for the Ag_2S-AgI membrane electrode, coupled with the saturated calomel reference electrode, plotted against - log [I^-] behaved according to E = -85.97 + 56.85log [I^-] (R = 0.99984). The electrode showed linearity over the concentration range of 10^{-6} - 10^{-1} M with a slope of 56.85 mV per decade change in concentration of iodide ion at 25°C. The slope reflects a Nernstian relationship and is a well-behaved solid state membrane electrode. The detection limit of the electrode was found to be $6,0\times10^{-7}$ M with standard deviation of 1.35 (n=10) at 5×10^{-4} M iodide. Four sensors had shown response times within 1-5 minutes and could be used for at least 4 months without any considerable divergence in potential responses[8].

Standardization of sodium thiosulfate

Standardization of sodium thiosulfate, for use as titrant, was made by using iodide electrode. The KIO_3 in acidic solution and treated with excess of iodide was titrated against a fresh solution of thiosulphate. The concentration of the thiosulphate from the potentiometric titration curve was found to be 0.071 M.

Recovery Study for laboratory prepared iodized salts. The fitness for purpose in the use of the iodide electrode for the determination of iodine content in iodate-iodized salts was made by recovery studies by measuring iodine content through titration of laboratory-formulated iodate iodized salt solution with $3x10^{-3}$ M $Na_2S_2O_3$ using iodide selective electrode vs SCE. Triplicate measurements were made to observe the repeatability of the experiment. The end point volumes recorded were 15.1 ml , 15.3 ml and 15 ml (15…+- sd) under repeatability conditions. The iodate recovery was found to be 98.6 % (64.6 mg of iodine out of 65.5 mg iodine per Kg NaCl) with a standard deviation of 1.14%. The results prove that this method can easily be used for quantification of iodate in commercial iodized salts.

Table 1: Iodine and iodate contents of commercial iodized salts produced in different countries and formulated iodized salt.

Product	Added or Label value (mg/Kg)			Found (mg KIO3/Kg) ±SD, n=3		
(Production date)	I_2	KIO_3	KI	I_2	KIO_3	KI
Lab-formulated 05/2009	47.5	65.45	- 46.90	64.63±0.739	-	
Saudi Arabia 9/2008	70-100	96.46	-137.80	- 78.44	108.08±0.815	-
Saudi Arabia 2/2007	70-100	96.46	-137.80	- 72.72	100.20±0.914	-
Scotland, 11/2007	47.5	65.45	- 42.45	58.5±1.20	-	
America, 09/2008	43.5	-	60	34.8	-	48.0±0.99

Table 2: Vitamin C content of commercial orange juices

Orange sample	mg of vitamin C per 100 ml* of
orange juice Orange (Egyptian, yellow)	51.92 ± 1.10
Orange (Ethiopian, partially yellow)	41.4 ± 1.50
Orange (Ethiopian, green)	32.4 ± 1.30 *

Mean ± SD, n = 3 for each sample

Table 3: Comparison of performances and the cost of the coated graphite electrode with commercial electrodes

Parameters	ELIT Solid-state Crystal membrane* [19]	Jenway Iodide Selective Electrode** [20]	This work –Coated graphite electrode
Electrode slope at 25°C	54±5 mV/decade	-59.16mV/decade ±3mV	56.85 mV/decade ±0.5mv
Linear range	$5x10^{-7}$ to 1 M	$5x10^{-7}$ to 1 M	$5x10^{-7}$ to 1 M
Time for stable reading	< 1 to > 5 min	1-5 min	
Detection Limit	0.06 ppm	0.06 ppm	
Recalibration	Once per day	Once per day	Once per day
Interferences	Ag+, CN- and S^{2-}	Ag+, CN- and S^{2-}	Ag+, CN- and S^{2-}
Potential Drift	2mV per day	2mV per day	3 mV per day
Price of ISE	250 USD	Incomparably cheap	

Titratabilty Study of potassium iodate with $Na_2S_2O_3$

Titratability of different concentration of KIO3 (in presence of the same excess of iodide and the acidity) with $Na_2S_2O_3$ was studied. Fig.3 shows the titration curves with inflection points to locate the potentiometric end points for solutions ranging from 10 ppm to 200 ppm KIO_3 (6-120 ppm iodine)[9].

Analysis of Laboratory-formulated and commercial iodized salts

In this work, the iodine contents of different commercial iodized salts were estimated. The results of replicate analyses (n = 3) showed that determined values for samples 2 and 3 were within the range of the label claims by the manufacturers. However, the iodine contents of all other iodized salt samples were found lower than the label value.

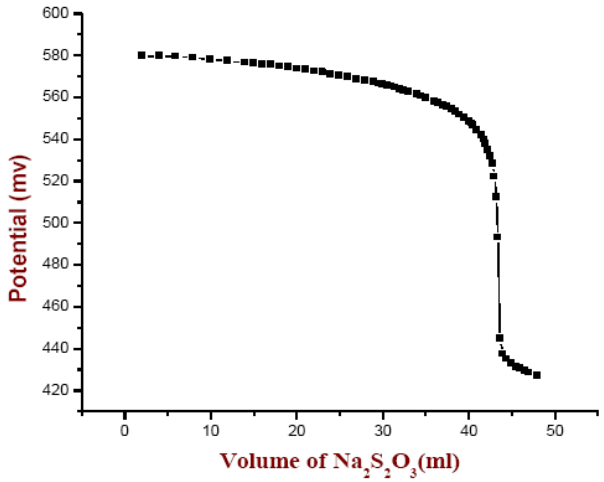

Fig. 1: Titration of $Na_2S_2O_3$ (about 0.07 M) by potentiometric titration of 50 ml of 0.01 M with KIO_3

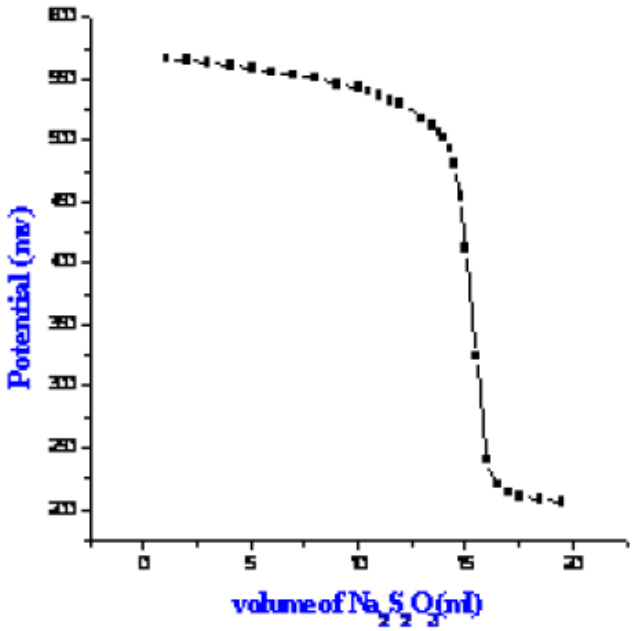

Fig. 2: A typical potentiometric titration of laboratory-formulated iodized salt (47.5 mg iodine /Kg NaCl, or 65.4 mg iodate/kg NaCl) with 3×10^{-3} M $Na_2S_2O_3$; End point volume 15 ml

This can be attributed to stability factors and in-homogeneity of the products. It is established that the actual availability of iodine from iodized salts at the consumer level can vary over a wide range because of uneven distribution of iodine in the product[17] loss of iodine due to salt impurities, packing and environmental conditions during storage and distribution. Moreover, even though sample 2 & 3 were purchased from the same manufacturer the amount of iodine calculated in these samples is different this may be to varied due to their production dates. Sample three, which had been produced earlier than sample 2 has lost more iodine relative to sample 2. Iodine losses from point of production to consumption can even be well below 50% [17].

The tests with formulated iodized salts solutions cover iodine contents not only in the standard range (40-60 ppm iodine for the Ethiopian Standard) but also iodine contents well below the unstable storage conditions. The result also shows that under-dose and overdose quantities of iodine in salts can be monitored in the quality control of iodization programmes.

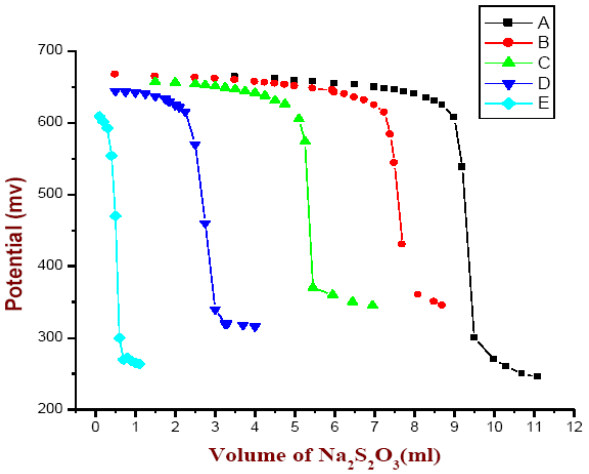

Fig. 3 Titration of 25 ml of A) 200 ppm, B) 150 ppm, C) 100 ppm, D) 50 ppm, E) 10 ppm KIO3 each in the presence of 190 mg/l potassium iodide with $2x10^{-4}$ M $Na_2S_2O_3$

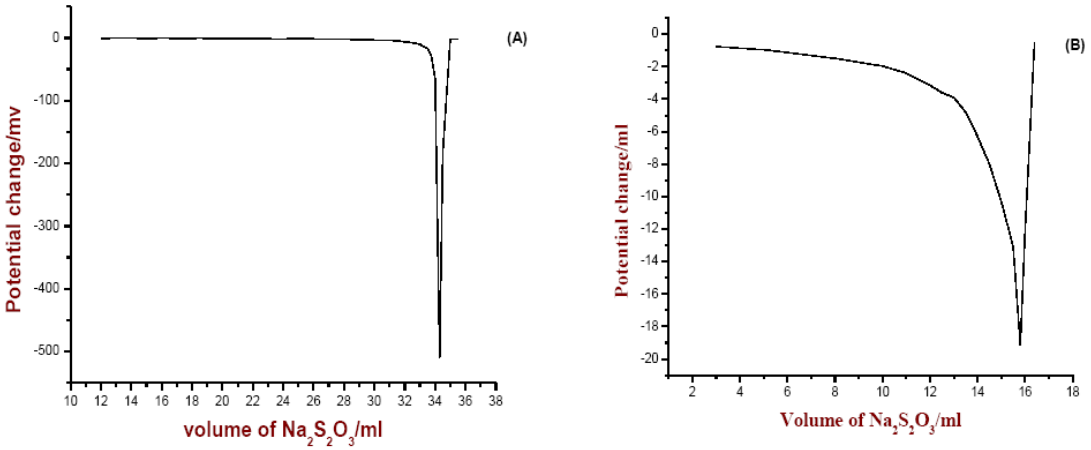

Fig. 4: First derivative titration curves for the titration of vitamin C in pharmaceutical products (A) Effervescent tablets (Chemical Industry Development, Egypt; (B) Vitamin C tablets from the Ethiopian Pharmaceutical Manufacturing Industry

Analysis of pharmaceutical products

Differential potentiometric titration curves which are sharp, smooth, and symmetric; hence, one can more easily used to locate end-points, indicating the normal behavior of solid-state iodide selective electrodes. These electrodes were found to be suitable for this type of oxidation reduction titration and they were employed in this work.

For tablet B the amount of vitamin C from the local manufacturer (Ethiopian Pharmaceutical Manufacturing Industry) was found to be 431.5 ± 1.05 mg (labeled value 500 mg, production year 2008). In the case of tablet A (Effervescent tablets, Egypt; expiry date 15/07/2009) the measured vitamin content was 451.66 ± 0.89 mg against the label value of 1000 mg. When the experiment was conducted, it was just two months away from the expiry date of the Egyptian product (July 2009). It is evident that both tablets had measured vitamin C lower than the labeled quantities The vitamin C contents recorded in the triplicate measurements of both pharmaceutical products were evidently less than the label values. Ascorbic acid is a well known reducing agent and storage over a long time could be a cause for the reduced amounts in the products kept for long periods. Although a systematic study is required, this experiment clearly shows that the quality control of such pharmaceutical products containing ascorbic acid can be monitored with such analytical systems.

Analysis of vitamin C in commercial and in the fruit of locally grown orange

The amounts of vitamin C determined in orange juice from packed commercial products and from randomly selected orange fruit grown in Ethiopia are shown in Table 5. In this method a sample of 2.5 ml clear Orange juice (Greece) obtained by fruit pressing was diluted with distilled water to a final volume of 10 ml. The USDA food composition database shows that the total ascorbic acid in raw orange juice is 50 mg per 100 g juice[18]. One report shows that the concentration level of vitamin C in orange juice is 30.48 mg/100 ml. Other results indicate a vitamin C content of 33 –50 mg/ 100 ml for orange juice (Valencia) obtained by squeezing the fruits[19]. The results from our work vary within about 32 mg/ml and 41 g/100 ml for the green orange and for the nearly yellow orange, respectively. These experiments were done without systematic sampling and did not even identify the type of the oranges, but still in good agreement with data from the cited international reports. Still, validation of our potentiometric titration method for the content of ascorbic acid in oranges cultivated in Ethiopia is proposed from further work through comparison with an official method.

Comparison with other Iodide Electrodes

Table 3 also shows that most of the performances of these electrodes are comparably useful as the commercial ones[20-21]. The simplicity of preparation invites laboratories to design and apply to real sample analysis. Like the commercial electrodes, the inferences from the reported electrode Ag+, CN- and S^{2-} is expected since the sensor material is Ag_2S-AgI coating on the conducting graphite electrode. Table 3 here

CONCLUSION

The application of laboratory-made very low cost all-solid-state coated graphite iodide ion selective electrodes provide a rapid and inexpensive method for the determination of iodide in the range of 10-6- 1.0×10^{-1} M iodide. The performance of these electrodes is comparable with the expensive commercial electrodes with respect to the linear range, and response time. The steps in these potentiometric methods are comparably short; e.g. the rapid determination of ascorbic acid in the simply filtered orange juice. The electrode is applicable to direct potentiometric titration of iodized salts and back titration of vitamin C. Recovery tests with laboratory formulated iodate-iodized salts show that locating end points using the fabricated iodide ISE can be used to determine iodate from 10 ppm to 200 ppm KIO_3 (range 6-120 ppm iodine). This covers iodine contents in such products not only in the standard range (40-60 iodine) but also iodine contents needed to be monitored when well below unstable storage conditions. The result also shows that underdose and overdose quantities of iodine in salts can be monitored in the quality control of iodization programmes. Additionally, the set-up can applied to design experiments both direct potentiometry and titration methods, in undergraduate and graduate curricula for measuring L-ascorbic acid in tablets and orange juice as well as iodine levels in iodide- and iodate-iodized salts[12].

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