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Potentiometric Determination of Iodide in Magnesium Fluoride by Iodide Electrode

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Abstract

Iodide in samples containing magnesium fluoride was determined by using iodide selective electrode. Detecting the limit for iodide determination was around $5x10^{-5}$ M with a standard deviation ranged from ± 0.3 to ± 0.6. Quantitative methods including; standard addition method, Potentiometric titration by using a Gran plot paper for an equivalent point determination and a direct method were used for the analysis. Dissolution of magnesium fluoride samples was investigated in various acids (HCl, HNO_3, HClO4, and H3PO4). Good recovery of iodide was obtained by using hydrochloric and phosphoric acids for dissolution. Interference of uranyl ion and halide ions, F^-, Cl^-, and Br^- on iodide response was also studied. This method can be used for the determination of iodide in magnesium fluoride obtained from uranium metal production.

Introduction

Various applications of iodide electrodes were given in the literatures. A coated tabular solid-state electrode was incorporated into a flow injection system (1). Davey et al., (2) used an iodide electrode for the potentiometric flow-injection system and also used it for the pharmaceutical preparation. A PVC membrane electrode based on a nickel (II) tetraazaannulene macrocyclic complex as the carrier is described by Ying et al., (3). The electrode was used for the iodide determination. Linear responses to iodide from 8.0×10^{-6} to 1.0×10^{-1} M with slope -57.7 ± 0.2 mV/decade. The electrode can be used for the determination of iodide in drug preparations. Two methods for the determination of I^- in raw and processed milk were examined by Melichercik et al.(4) . A simple ion-specific electrode method was compared against HPLC reference technique. The ISE method had a significant positive bias relation to the HPLC. Both methods yielded good recoveries for I^- on spike samples, ranging from 87 to 114% for ISE and 91 to 100% for HPLC. A novel iodide-selective electrode was prepared by Jalali et al.(5) based on an iodide-miconazol ion-paired complex which was used as an ion-exchanger of a plasticized-PVC membrane. The electrode exhibits a Nernstain slope of -59.8 ± 0.5 mV / decade for I^- ion over concentration range of $1.0 \times 10^{-5} - 1.0 \times 10^{-2}$ M with the detection limit of 7.0×10^{-6} M. The electrode was applied to the determination of iodide in water samples and blood serum. Martinovic and Radic(6) describe a kinetic potentiometric method for the determination of thiols by using an electrochemical cell with a commercial iodide selective electrode. The calibration graphs are obtained in the RSH concentration which ranges from 1.0×10^{-5} to 1.0×10^{-3} M. The applicability of the proposed method was demonstrated by the determination of chosen compounds in pharmaceutical dosage forms.

In the event of a nuclear reactor accident, the major public health risk would likely result from the release and dispersion of a volatile radio-iodine. These radio-iodine are concentrated in the thyroid. Dayem et al.(7) studied the physiological inhibition of the thyroid function and determination of the iodide concentration in plasma.

In this work iodide was determined in samples of magnesium fluoride by using iodide selective electrode. Electrode parameters were investigated and quantitative methods were used for the determination of iodide recovery. Different acids were used for dissolution of the samples. Also interference was studied.

Experimental Part

Apparatus

1. Electrode potentials were recorded on microprocessor Orion model 901 ionalyzer (potentiometer). Iodide electrode used was Orion model 94-53A connected with model 90-02 double junction reference electrode.
2. pH meter type Orion EA940 with combined glass electrode type 91-02 was used for pH adjusting of the solution.
3. Gran's plot paper 10% volume correction, Orion 90-00-90

Reagents

1. Stock solution (0.1M I^-): dissolve 1.656 gm of KI in 100 ml de-ionized water. The standard solutions were prepared from serial dilutions of the stock solution (reference 8).
2. Uranyl ion solution (10 mg / ml): dissolve 2.130 gm of uranyl nitrate in 100ml of de-ionized water.
3. Silver solution (0.1 M): dissolve 1.7 gm of $AgNO_3$ in 100 ml of 70% ethanol (reference 8).
4. Fluoride, chloride, and bromide ions standards (100 µg/ ml) were obtained from Orion Company.
5. All solutions were prepared from analytical grade chemicals dissolved in de-ionized water.

Procedure

1. Sample preparation: two methods were used for sample preparation: extraction of 0.5 gm magnesium fluoride sample containing iodide with 100 ml water and the second was dissolving of the sample. Dissolution was achieved by dissolving of 0.5 gm of MgF_2 in 3 ml of concentrated phosphoric acid and complete the volume to 100 ml. 10 ml of the sample was neutralized by NaOH or NH4OH in order to determine the iodide by the electrode. The best results were obtained by using 0.1 M NH4OH.
2. Standard addition method: the following equation was used for measuring the total iodide ion as given by Moody et al. (9).

$$Co = C\Delta \, [1 / (\text{antilog} \, \Delta E / S) - 1]$$

Co = concentration of unknown solution

Δ E = potential difference before and after the addition of the standard to the unknown solution
S = slope of the electrode

$C\Delta = (Vs\ Cs) / VO$

Cs = concentration of the standard added
Vs = small volume of the standard added
VO = volume of the unknown solution

Results and Discussion

The properties of ion-selective electrode were evaluated which were mainly the slope and the linear range of the calibration plots. Iodide electrode was calibrated several times in standard solutions ranged from 10^{-1} M to 10^{-6} M I^-. The slopes obtained from the calibration curves were ranged from 58 to 60 mv / decade and the linearity ranged from 10^{-1} M to 2×10^{-4} M. Detection limit for the iodide electrode estimated from the calibration curve was around 5×10^{-5} M. The precision of the analytical system varies with the concentration of the analyte, and the standard deviations for iodide were determined in standard solutions between 10^{-5} M and 10^{-3} M, iodide concentrations were varied from ±0.6 to ±0.3

Standard addition method, potentiometric titration and a direct method were applied to analyse synthetic samples containing magnesium fluoride as a matrix with various quantities of potassium iodide ranged from 0.076 % to 1.5 % iodide. The values of iodide recovery by these methods are listed in (Table 1). The results of iodide recovery by titration were obtained from the titration of the samples with silver nitrate and a Gran's plot paper that was used for an equivalent point determination.

Interference effects of uranyl ion and halide ions on iodide electrode response were also studied. Electrode potential for two samples of magnesium fluoride containing 10^{-3} M and 10^{-4} M iodide were recorded in the presence of various concentration of uranyl ion ranged from 0 to 10 mg / ml. (Fig. 1) shows the effect of uranyl ion concentration on iodide electrode potential at two different iodide concentrations (10^{-3} M and 10^{-4} M). It can be seen from the figure that the uranyl ion interferes with iodide ion when the concentration of uranyl ion exceeds 1000ppm. A sharp change in potential was noticed at 10.01 mg / ml uranyl ion. Halide ions (F^-, Cl^-, and Br^-) at a concentration ranged from 0 to 100 µg / ml in the samples of magnesium fluoride containing 10^{-4} M and 10^{-3} M iodide do not effect the electrode calibration. Variation of the electrode potentials for the iodide determination in the presence of interfering halide ions are listed in (Table 2). Constant values of electrode potential were noticed which indicate that there are no interference of halide ions on the iodide determination. Also the fluoride comes from magnesium matrix which can not effect the electrode response during the iodide determination. Dissolution of magnesium fluoride samples containing iodide was achieved in the acids (HCl, HNO3, H3PO4, and HClO4). A good result for iodide recovery was noticed when hydrochloric and phosphoric acids were used for dissolution. (Fig.2) shows the iodide recovery by a direct method and a titration by using Gran's plot paper for samples of magnesium fluoride containing 10^{-3} M and 10^{-4} M iodide. Hydrochloric and phosphoric acids are suitable acids for sample dissolution.

Conclusion

Iodide selective electrode can be used for the iodide determination in magnesium fluoride samples containing low level of iodide concentration. A suitable procedure for sample preparation by the dissolution of magnesium fluoride containing iodide in hydrochloric acid or phosphoric acid and adjust the solution to pH 6 in order to determine the iodide ion by the electrode. This method can be used for the determination of an iodide in magnesium fluoride obtained from uranium metal production.

References

1. Vanstaden, J.F. and Freseniu's, Z. (1986) Anal.Chem. 325: 247-251
2. Davey, D.E.; Mulcahy, D.E. and O'connel, G. R. (1990) Talanta 37: 313-316
3. Ying, M.; Yuan, R.; Zhang, X. M.; Sung, Y. Q.; Li, Z. Q.; Shen, G. L. and Yu, R. Q. (1997)Analyst 222 : 1143 – 1146.
4. Melichercik, J.; Szijarto, L. and Hill, A. R. (2006) J. Dairy Sci., 89: 934 – 937.
5. Jalali, F.; Rajabi, M. J.; Bahrami, G. and Shamsipur, M. (2005) Analytical Sciences 21 (12): 1533-1535
6. Martinovic, A. and Radic, N. (2007) Analytical Letter 40 (15): 2851 – 2859.
7. Dayem, M.; Navarro, V.; Marsault, R.; Darcourt, J.; Lindenthal, S. and Pourcher, T. (2006) Biochimie 88 (11): 49 – 55.
8. Marczenko, Z (ed) (1976)"Spectrophotometer Determination of Elements" Joun Wiely & Sons INC. New York .
9. Moody,G.J. and Thomas,J.D.R.(eds) (1971) "Selective Ion-Sensitive Electrodes" Merrow,Watford .

Table (1) Iodide determination for synthetic samples containing magnesium fluoride as a matrix by iodide selective electrode

I^- % Calculated	I^- % Found		
	Direct method	Standard method	Titration method
0.076	0.081 σ =0.0048 error%=+6.58%	0.081 0.012 +6.58%	0.074 0.0029 -2.63%
0.153	0.155 σ =0.0042 error%=+1.31%	0.153 0.0054 0.0%	0.158 0.006 +3.27%
0.305	0.302 σ =0.012 error%=-0.98%	0.316 0.029 +3.61%	0.302 0.018 -0.98%
0.532	0.528 σ =0.018 error%=-0.75%	0.578 0.13 +8.6%	0.521 0.035 -2.07%
0.757	0.746 σ =0.064 error%=-1.45%	0.83 0.060 +9.64%	0.689 0.051 8.98%
1.50	1.508 σ =0.034 error%=+0.53%	1.595 0.105 +6.33%	1.503 0.035 +2.00%

Table (2) Effect of halide ions on electrode potentials for iodide determination in magnesium fluoride samples

Concentration of halide interfering(µg/ml)	Electrode potential (mV)					
	Fluoride		Chloride		Bromide	
	10^{-3} M I^-	10^{-4} M I^-	10^{-3} M I^-	10^{-4} M I^-	10^{-3} M I^-	10^{-4} M I^-
0	-181.8	-129.4	-186.4	-87.5	-170.8	-122.1
10	-183.6	-128.7	-189.8	-83.9	-171.7	-118,9
20	-181.5	-129.5	-188.2	-85.0	-171.0	-120.2
30	-182.1	-127.9	-187.5	-88.7	-170.3	-120.6
40	-183.1	-129.8	-187.1	-87.9	-172.1	-118.6
50	-183.1	-130.1	-185.3	-85.9	-171.0	-117.7
60	-182.6	-132.7	-186.1	-86.8	-170.8	-114.9
70	-182.8	-127.9	-184.7	-86.1	-168.5	-119.4
80	-183.7	-124.3	-187.0	-85.5	-171.4	-115.3
90	-183.2	-126.5	-185.3	-88.5	-169.9	-113.8
100	-182.8	-129.3	-182.1	-85.5	-169.0	-114.2

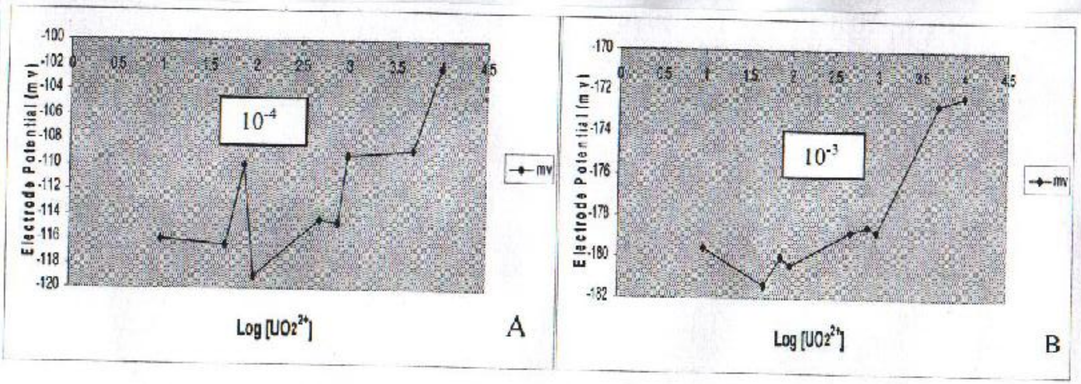

Fig. (1) Effect of Uranyl ion concentration on electrode potential of two MgF2 samples containing 10^{-4} M I^- (A) and 10^{-3} M I^- (B)

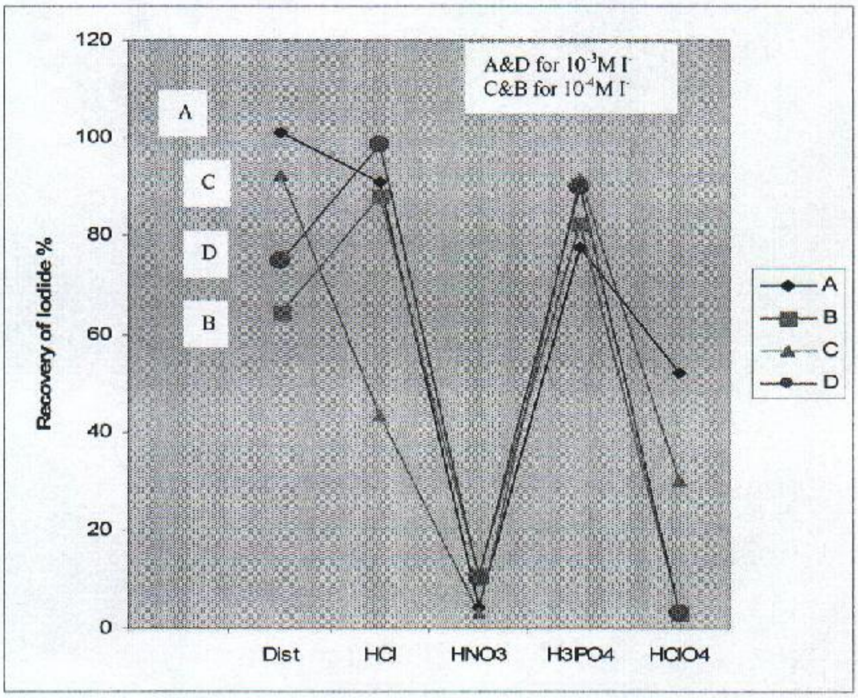

Fig. (2) Effect of dissolution of MgF2 in various acids on iodide recovery (iodide determined by direct method curve A and B, titration method curve C and D)

مجلة ابن الهيثم للعلوم الصرفة والتطبيقية المجلد 21 (4) 2008

تعيين اليود جهديا في فلوريد المغنيسيوم بواسطة قطب اليود الأنتقائي

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الخلاصة

عينت النسبة المئوية لليود في نماذج من فلوريد النغنيسيوم بواسطة قطب اليود الأنتقائي.حد التحسس لتعيين اليود بواسطة القطب كان بحدود $5x10^{-5}$ M والأنحراف القياسي يتراوح من 0.3 ± الى 0.6 ± .

استخدمت طريقة الأضافات القياسية، الطريقة المباشرة و التسحيح الجهدي باستخدام طريقة كران لتعيين اليود. تمت اذابة نماذج فلوريد المغنيسيوم بحوامض مختلفة ومركزة وهي ($HClO4$, $H3PO4$, HNO_3, HCl) وكانت اعلى نسبة لليود تم ايجادها عندما استخدم حامض الهيدروكلوريك وحامض الفسفوريك للأذابة. كما ودرست التداخلات الحاصلة على استجابة قطب اليود عند التعيين من قبل ايونات اليورانيل وايونات الهاليدات (Br^-, Cl^- , F^-). يمكن استخدام الطريقة في تعيين اليود في فلوريد المغنسيوم الناتج من انتاج معدن اليورانيوم .