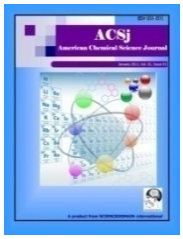

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Extraction, Preconcentration and Spectrophotometric Determination of Ethylene Glycol in Antifreeze Samples

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Authors' contributions

This work was carried out in collaboration between all authors. Author HSJ designed the study, performed the statistical analysis, wrote the protocol, and wrote the first draft of the manuscript. Author ATF Supervise and managed the analyses of the study and the literature searches. All authors read and approved the final manuscript.

Research Article

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ABSTRACT

Aims: Using a simple and sensitive spectrophotometric method for the indirect determination of ethylene glycol by Malaprade reaction. The method was based on the extraction and preconcentration of iodine.
Place and Duration of Study: Samples: Antifreeze samples were purchased from markets (Erbil, Kurdistan region, Iraq), between April 2011 and August 2011.
Methodology: A method was developed for the determination of ethylene glycol (EG) in antifreeze samples. The method was based on the oxidation of EG with excess potassium periodate in slightly acidic medium; then, extraction and preconcentration of iodine was formed from the reaction of remained periodate with iodide. The decrease in the absorbance of extracted iodine is used to monitor the reaction spectrophotometrically at 515 nm.
Results: The optimum reaction conditions and other analytical parameters were evaluated. Beer's law is obeyed in the concentration range of 0.2–10 µg/ml (R= 0.9963) and 7.0–36 µg/ml (R= 0.9964) with detection limits of 0.08 µg/ml. The effect of interfering species on the determination is described.
Conclusion: Through the proposed method, a sensitive, low cost, selective, accurate and precise method has been described for the determination of ethylene glycol in antifreeze

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samples with no interferences from antifreeze additives.

Keywords: Ethylene glycol; extraction; preconcentration; spectrophotometry; antifreeze.

1. INTRODUCTION

The amount of some species in various real samples is lower than the quantification limits of the instrumental techniques. Therefore, the assessment and evaluation of trace amount of such species at trace levels require an efficient preconcentration and/or separation step prior to their analysis. For these reason, various separation and/or preconcentration techniques based on the nature of the samples and the concentration level have been used to overcome these limitations [1].

Periodate has been extensively used as an ingredient for the indicators used in catalytic-kinetic analysis involving redox processes. It is of importance for oxidizing many organic and inorganic compounds [2,3]. Periodic acid and its salts were proposed for cleavage of α–glycol groups (vicinal diols) by Malaprade in 1928 [4–7]. Later it was shown that compounds of other types, in particular, α–hydroxyaldehydes, α–hydroxyketones, and α–aminoalcohols, are also oxidized [4].

The periodate oxidation is used for the determination of the number of adjacent hydroxyl groups, elucidation of the polysaccharide structure [8], and corroboration of the glycoside structure [9]. The α–glycol group is cleaved at the C–C bond with an equimolar amount of periodate; the reaction is applicable for cis- and trans diols and α–aminoalcohols [10].

The mechanism of the periodic acid-induced oxidation of glycols is given in Fig. 1 [10–15]. Depending on the reaction conditions and the structure of the compound oxidized, the limiting stage of the process can be either formation of the cyclic intermediate or its destruction. The overall reaction rate depends on the ratio of three constants: Ko, the rate of the formation of the intermediate; Kd, its dissociation rate; and Kr the rate of its conversion into reaction products.

As mentioned above, periodate oxidation is used for the quantitation of α–glycol groups, which can be easily done on the basis of periodate consumption or iodate formation [16,17]. Because of the specificity of the reaction, many materials may be determined in the presence of others by investigating the products of the oxidation [18]. There are several quantitative methods of periodate determination in the presence of iodate, most of which are based on the titration of the periodate excess [4].

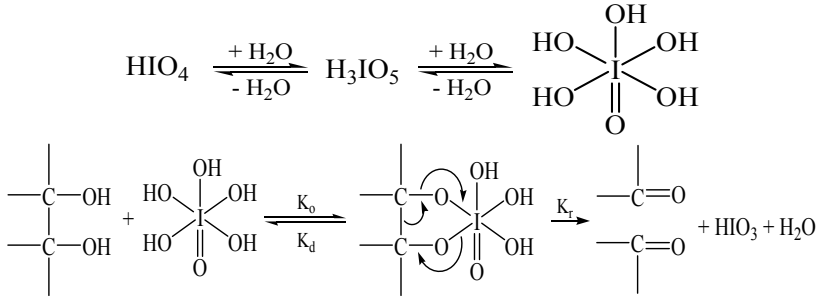

Fig. 1. The mechanism of the periodic acid-induced oxidation of 1,2-glycols

The wide applications of EG in both industrial and engine coolants have prompted extensive literature on its determination. Most of the analytical methods employed for the determination of EG are chromatographic methods including gas chromatography (GC) [19,20], GC-MS [21,22], high-performance liquid chromatography (HPLC) [23,24], LC [25], TLC [26]. Also, spectrophotometric methods are among the most analytical methods used for EG determination in antifreeze [2,27–34]. Other reported methods include amperometry [35], fluorimetry [36,37] and chemiluminescence [38].

In this work, a simple, sensitive, fast and low-cost spectrophotometric method for the indirect determination of ethylene glycol in antifreeze samples using Malaprade reaction is proposed. The method based on the liquid-liquid extraction and preconcentration of iodine formed from the reaction of excess periodate with iodide. Many methods have been reported for determination of periodate. However, most of them are either not sensitive enough or lengthy operations and/or are subject to interferences from ions such as iodate and bromate. In addition, some of them higher cost from the proposed method (e.g. GC-MS) as an additional disadvantage.

2. EXPERIMENTAL

2.1 Apparatus

Absorption spectra were measured using UV-Vis spectrophotometer (CECIL CE 3021, 3000 Series) in a 1.0 cm quartz cell. A JENWAY 6405 UV-Vis. spectrophotometer was used for the absorbance measurements and a digital pH meter (WTW, inolab 740 Germany) equipped with a combined glass-calomel electrode was used for pH measurements. The temperature was controlled by using of a Lab. Companion-BS-11 (Korea) model water bath.

2.2 Reagents and Samples

All chemical solutions were prepared with analytical grade reagents and the solutions were prepared with distilled water (DW).

Ethylene glycol (EG): A stock standard solution of ethylene glycol (1.0 mol/L) was prepared by diluting 56.3 ml of EG (99 %, BDH) to 1.0 L with distilled water. It was stored in a dark bottle, and protected from daylight. The working standard solutions were prepared by suitable dilution.

Potassium periodate (KIO_4) solution: A 0.01 mol/L solution was prepared by dissolving 2.3 g of analytical-reagent grade potassium periodate (solubility 4.20 g/L 20 °C) (RIEDEL-DE HAEN AG SEELZE-Hannover) in distilled water and standardising the solution iodimetrically [18]. The solution was diluted as required, just before use.

Buffer solution: A 35.59 g of disodium hydrogen phosphate dehydrate ($Na_2HPO_4.2H_2O$) (RIEDEL-DE HAEN AG SEELZE-Hannover) was dissolved in distilled water, the pH is adjusted with 0.10 mol/L citric acid (21.01 g in 1.0 L, C6H8O7.H2O) (HM – G.P.R.) and dilute to 1.0 litre [39].

Potassium iodide (KI): Iodide solution (0.10 mol/L) was prepared by dissolving 1.66 g potassium iodide (solubility 140 g/100 ml 20 ºC) (BDH) in D.W. and diluting to the mark with

D.W. in a 100 ml volumetric flask. Working solutions were prepared by serial dilution of the stock solution as required.

Sample preparation: 1.0 g of antifreeze was dissolved in water, and the resulting solution was diluted to the mark with water in a 100 ml volumetric flask. Then 10 ml of this solution was diluted 1000 fold [2]. 5.0 ml of this solution was analyzed for ethylene glycol, as described in preliminary procedure.

2.3 Preliminary Procedure

An aliquot of standard EG solution (5.0 ml, 50 µg/ml) was transferred to a 25 ml volumetric flask. Then 1.0 ml of Na_2HPO_4/citric acid buffer (pH 4.0) and 2.0 ml of 1.0×10^{-2} mol/L periodate solution was added and the flask was allowed to stand for 4 min at room temperature. The excess of periodate was determined by adding 1.0 ml of buffer solution (pH 7.0) and 1.0 ml of iodide solution (0.1 mol/L) and shaking for 1 min. The resulting solution was diluted to the mark with distilled water and transferred into a 100 ml separating funnel. It was then extracted with 5 ml of carbon tetrachloride (CCl_4) by shaking 2 min. The solution was allowed to stand for 1 min. The absorbance of the solution was measured against the blank solution at 515 nm in a 1 cm quartz cell. The difference between the absorbance of the blank and sample solutions at 515 nm was used as an analytical signal.

3. RESULTS AND DISCUSSION

A method was developed for the spectrophotometric determination of microgram amounts of ethylene glycol based on rapid oxidation of the compound with periodate, followed by spectrophotometric determination of the extracted iodine after reaction of excess periodate with iodide at pH 7. Decrease in absorbance is directly proportional to EG concentration. Reagent blank showed maximum absorbance at 515 nm.

Different organic solvents have been tested as components of systems for extraction and preconcentration of the iodine formed from aqueous layer.

3.1 Absorption Spectra

Under the conditions of the preliminary procedure, the purple color product showed a maximum absorbance at 515 nm (λmax). The absorption spectrum of the product is shown in Fig. 2. The decrease in absorbance corresponding to consumed periodate and in turn EG concentration was obtained by subtracting the decrease in absorbance of the test solution (EG–test) from that of the blank solution (periodate–blank).

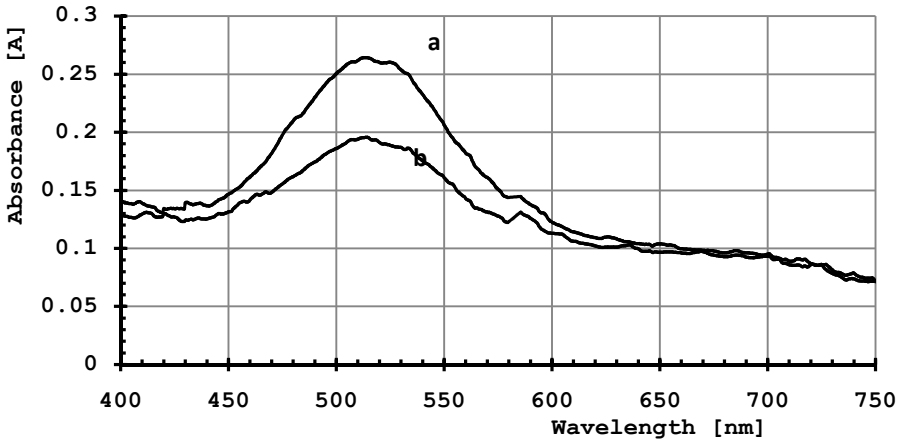

Fig. 2. Absorption spectra of (a) reaction mixture without EG (b) using 10µg/ml EG

3.2 Optimization of Experimental Conditions

In order to take full advantage of the procedure, the reagent concentrations and reaction conditions were optimized. Various parameters were tested.

To obtain the most suitable data from the presented pre-concentration system, the effect of different parameters such as type and pH of buffer, volume of buffer solution, amount of periodate, iodide concentration, different solvents, temperature and mixing time were studied and optimized. The optimization procedure is carried out by varying a parameter while the others were kept constant. A 10 µg/ml EG solution was used for all the measurements and three independent experiments were carried out for each optimized variable.

3.2.1 Effect of buffer

Of all of the variable conditions of the chemical reactions, effect of pH of the reaction medium upon the rate of reaction is mostly significant [40-43]. In general, α–glycols, hydroxyaldehydes, hydroxyketones, and diketones are oxidized fastest in a slightly acidic medium (pH 3.0–5.0), whereas α–amino alcohols, amino aldehydes, aminoketones, and diamines require a neutral or slightly alkaline medium (pH 7.0–8.0) for optimum rate of oxidation. When the oxidation proceeds in a stepwise manner, an inverse relationship is usually observed, but conversely, the oxidation of simple glycols proceeds faster at pH 3.0–5.0 [18].

Accordingly effects of acids on the EG–periodate reaction were investigated. It was found that using of acid decreases the absorbance, because the rate of oxidation is retarded somewhat in solutions of high ionic strength [12]. This effect is controlled by the use of buffers. Generally the buffer used does not cause anomalous results when the oxidation is compared with one in an unbuffered medium at the same pH [18].

Different buffers were tested. Best results obtained with Na_2HPO_4/citric acid; therefore, it was selected as a buffer agent. The effect of pH was studied for the pH range of 3.0–5.5 with 10 µg/ml EG (Fig. 3). The results show that by increasing pH values up to 4.8, the absorbance increased, whereas at higher pH values, the sensitivity decreased, because at

higher pH, overoxidation occurs readily. The small fragments produced by the primary oxidation, for example, formaldehyde, formic acid, and glyoxylic acid, are oxidized at a rate dependent upon the pH of the medium, the concentration, and the molar excess of periodate. In addition, the aldehydic products of glycol-cleavage are very sensitive to alkali. These materials reduce several times as much periodate in an alkaline medium as in a slightly acid medium [18]. Thus a pH of 4.8 was selected.

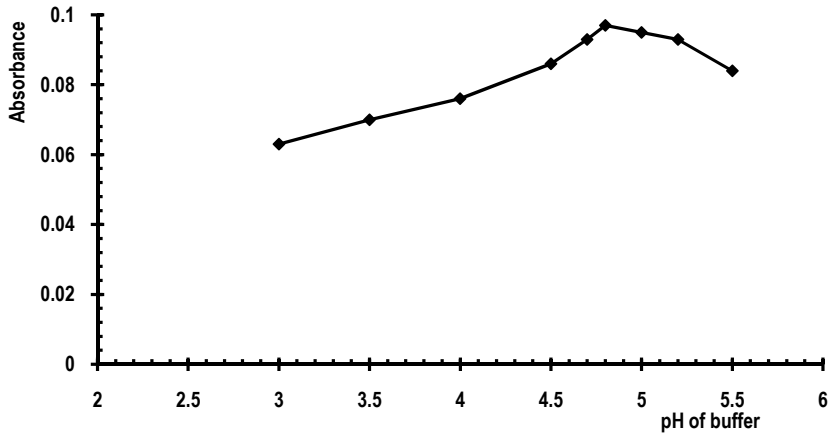

Fig. 3. Effect of buffer pH on the determination of EG

The influence of buffer volume on the peak heights was also studied over the range 0.2–4.0 ml. The results showed that it has no effect on the peak height. Therefore, 1.0 ml citric acid/sodium citrate buffer was selected for further study.

3.2.2 Effect of potassium periodate

Periodate is always used in excess of that required for primary oxidation. Several hours or even a day may be required for completion of the reaction when only the calculated amount of periodate is used. Liberation of iodine during the course of periodate oxidation has frequently been reported in the literature. This phenomenon can generally be attributed to the absence of sufficient periodate. When insufficient oxidant is used, complete reduction of periodate to iodate occurs, followed by reduction of iodate and the liberation of iodine [18].

Therefore, the effect of potassium periodate concentration on sensitivity was studied as shown in Fig. 4. Increase in periodate concentration caused an increase in the absorption signals up to 1.6×10^{-3} mol/L, which is measured as a difference between blank and EG signal and then decreases significantly. At periodate concentrations higher than 1.6×10^{-3} mol/L, the increase in blank and EG absorbance with increasing periodate concentration is not linear. Thus the analytical signal obtained from the difference between blank and EG decreases at periodate concentrations higher than 1.6×10^{-3} mol/L. At very low periodate concentrations the rate of primary oxidation is apt to be so slow that the data obtained are difficult to interpret, while at high concentrations nonspecific oxidations may occur [18].
Therefore, the periodate concentration of 1.6×10^{-3} mol/L was chosen as the best concentration for further studies.

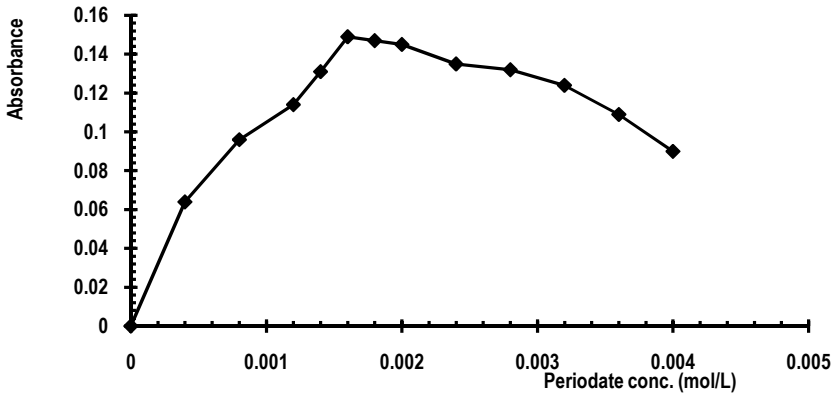

Fig. 4. Effect of potassium periodate concentration

3.2.3 Effect of buffer solution

In the presence of 10 µg/ml EG effects of some buffer solutions were examined namely: Na_2HPO_4/citric acid (3.0–8.0), K_2HPO_4/KH_2PO_4 (5.8–8.0), Na_2HPO_4/NaH_2PO_4 (6.0–7.5), disodium hydrogen phthalate/sodium dihydrogen orthophosphate (5.8–8.0), dipotassium hydrogen phthalate/potassium dihydrogen orthophosphate (5.8–8.0) and potassium dihydrogen orthophosphate/sodium hydroxide (5.8–8.0). Among them, Na_2HPO_4/citric acid was selected as a buffer agent because the difference in absorbance of analyte and blank gave highest value.

The effect of pH using Na_2HPO_4/citric acid as a buffer agent on the reaction was studied in order to obtain maximum selectivity and to find the most suitable sensitivity. The results in Fig. 5 shows that at pH values higher than 7.2 only periodate reacts with iodide (iodate did not react). However iodate reacted at pH values lower than 5.5 [44]. Therefore, a pH of 7.2 was selected as the optimum pH in order to increase the selectivity of the proposed method.

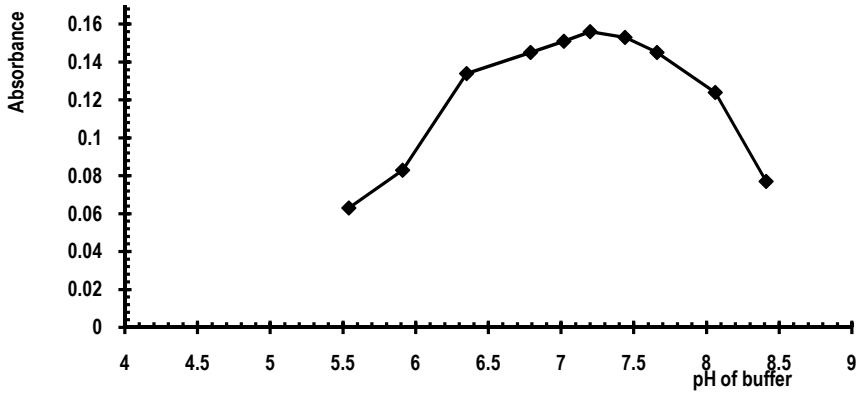

Fig. 5. Effect of pH on the determination of EG

The effect of buffer volume was also studied in the range of 0.1 – 4.0 ml, and it was found that it had no effect on the sensitivity of the method. Thus the buffer volume of 1.0 ml was selected for further work.

3.2.4 Effect of potassium iodide

The effect of iodide concentration was investigated in the range of 4.0×10^{-4} to 1.4×10^{-2} mol/L. The results are shown in Fig. 6, with an increase in the iodide concentration up to 6.8×10^{-3} mol/L, the analytical signal increases beyond which no significant changes are indicated. Therefore, the iodide concentration of 6.8×10^{-3} mol/L was selected for further studies.

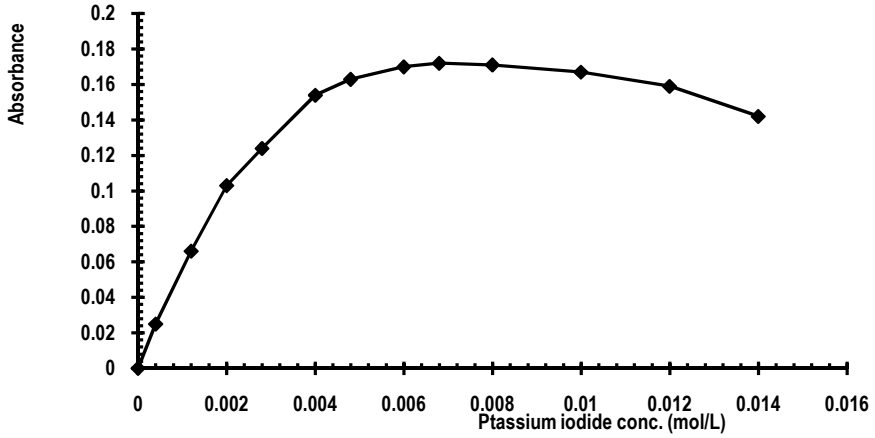

Fig. 6. Effect of potassium iodide concentration

3.2.5 Selection of organic phase

Under the optimized conditions effects of different solvents were studied for the aim of extraction and preconcentration. Amyl alcohol, benzene, carbon tetrachloride, chloroform, cyclohexane, hexane, petroleum ether and toluene were tested as extracting solvents. Best result was obtained with carbon tetrachloride.

Iodine (I_2) is nonpolar. As a molecule composed of large iodine atoms, it has an extensive electron cloud. Thus, the molecule is easily polarized, and iodine could interact with water (a polar molecule) by dipole/induced dipole forces. Carbon tetrachloride, a tetrahedral molecule, is not polar. As a consequence, it can interact with iodine only by dispersion forces. Water and CCl_4, could interact by dipole/induced dipole forces, but the interaction is expected to be weak.

As a result of mixing of these three compounds, iodine dissolves to a small extent in water to give a brown solution. When this brown solution is added to a separating funnel containing CCl_4, the liquid layers do not mix, the more dense CCl_4 layer (d=1.58 g/ml) is underneath the less dense water layer. When the separating funnel is shaken, however, nonpolar I_2 dissolves preferentially in nonpolar CCl_4, as evidenced by the disappearance of the color of I_2 in the water layer (top) and the appearance of the purple I_2 color in the CCl_4 layer (bottom) [45]. Carbon tetrachloride (CCl_4) was the best (Table 1) and thus this solvent was employed in all our investigations of the extraction of the iodine.

Table 1. Effect of different solvents on the extraction of formed iodine

Solvent	Absorbance
Amyl alcohol	0.000
Benzene	0.158
Carbon tetrachloride	0.170
Chloroform	0.165
Cyclohexane	0.143
Hexane	0.133
Petroleum ether	0.140
Toluene	0.166

The effect of CCl_4 volume in the range 3.0–5.0 ml for the iodine extraction was investigated. Decreasing of the solvent volume increases the sensitivity of the method due to preconcentration of the iodine formed. Solvent volumes less than 3.0 ml cannot be used due to volume of the cuvette. Therefore, a CCl_4 volume of 3.0 ml was selected for the further work.

3.2.6 Effect of temperature

In most cases, the cleavage of α-glycols and certain related substances by periodate occurs readily at room temperature and is stoichiometrically complete in a relatively short period of time [18].

To study the effect of temperature on the EG determination, the solution containing 10 µg/ml EG and periodate and that containing the KI were either heated or cooled to the required temperature. Then 3.0 ml of CCl_4 was poured into this solution after 1 min, then after 2 min shaking and 1 min standing the mixture was introduced into the quartz cell with 1 cm thick. The determination procedure was then followed. Since the absorbance reading, the formed color was not affected by raising the temperature, measurements were carried out at room temperature, ~25ºC.

The effect of temperature was studied in the range of 15–60ºC. The results in Fig. 7 show that the analytical signal increased by increasing of temperature from 15 to 30ºC. After 30ºC, the difference between the absorbance's of the blank and sample solutions decreases, because the rate of cleavage of glycols is greater at higher temperatures than at room temperature; however, a variety of side reactions occur to a much more marked extent [18]. Therefore, a 30ºC was used throughout the study.

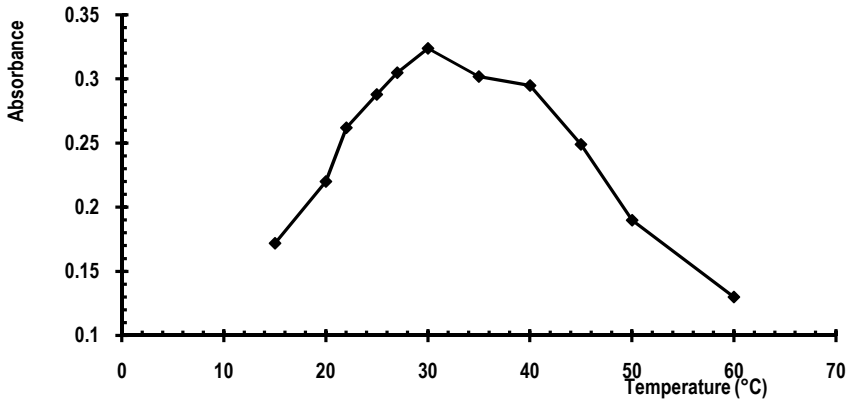

Fig. 7. Effect of temperature

3.2.7 Effect of time

Simple and unhindered α–glycol and α–amino alcohol groupings will be nearly completely oxidized in 5–10 minutes at their pH of optimum reaction if a moderate excess of periodate is present. Usually somewhat longer periods of time are required for the oxidation of α–hydroxyaldehydes, α–hydroxyketones, α–ketoaldehydes, α–diketones, and the corresponding amino derivatives. When periodate oxidations are continued for a period of time longer than several hours, the oxidant will be reduced to some extent by the oxidation of small fragments liberated in the course of the primary oxidation [18].

Thus, the effect of time on the absorbance under optimized experimental conditions was examined by changing the mixing time. As indicated in the literatures the reaction of EG and periodate depends on time [2, 18, 31]. Effect of mixing time of them on the sensitivity of the method was studied in the range of 0.3–30 min. The results obtained (Fig. 8) showed that the absorbance increased continuously. A mixing time of 5 min was chosen for further use because at 5 min the absorbance duplicated and after that the increase in absorbance is low.

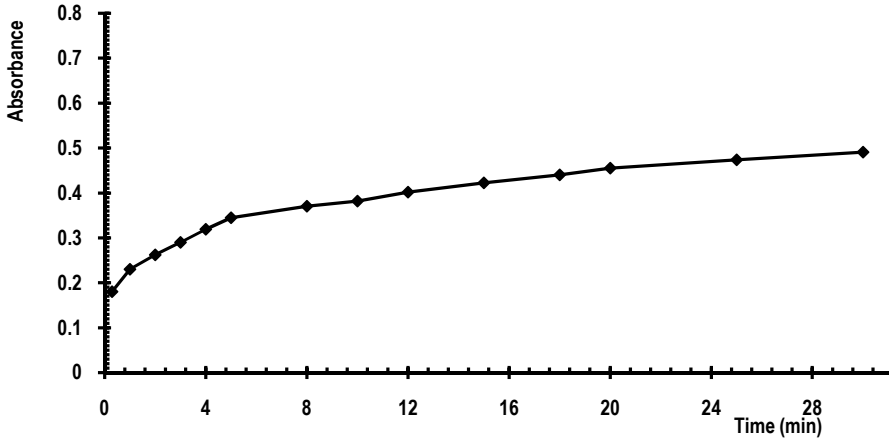

Fig. 8. Effect of time on the reaction of EG and periodate

The mixing time of the excess of periodate with buffer and iodide solution (time 2) was varied from 0.3 to 10 min. the mixing time of 1 min was selected for the subsequent investigations. The time required for extraction (shaking time – time 3) was another item considered in the optimization of this system. This item was of concern because enough time had to be allowed for the extraction of produced color from liquid phase. Maximum absorbance intensity was observed after 1.0 min shaking of separating funnel. The absorbance of final product (time 4) was measured continuously at room temperature for 10 min and it was a constant value after 1 min as shown in Fig. 9. Therefore, maximum absorbance intensity was observed after 5.0 min for EG + periodate, 1.0 min for KI, 1.0 min shaking and 1.0 min. The total time required for one determination was about 9–11 min. Therefore, the use of this simple procedure for analysis of EG may be considered as time saving compared to some another techniques.

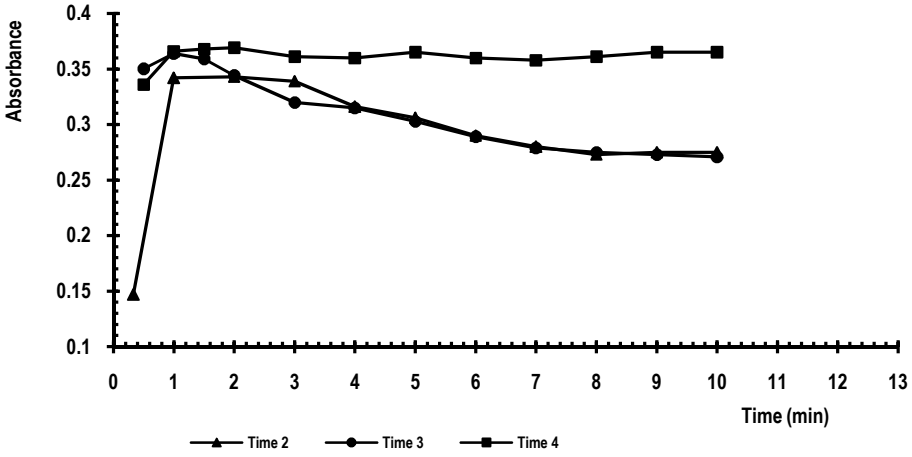

Fig. 9. Effect of reaction time

3.2.8 Stability of developed color

The stability of the reaction product was evaluated and constant absorbance readings were obtained after more than one month of standing at room temperature without any change in color intensity.

3.3 Recommended Procedure

A volume of 5.0 ml from various concentrations of standard EG solutions were transferred to 25 ml volumetric flasks each containing 1.0 ml Na_2HPO_4/citric acid buffer (pH 4.8) and 4.0 ml of 0.01 mol/L KIO_4, and the solution allowed to react for 5 min at 30°C water bath. Then 1.0 ml of Na_2HPO_4/citric acid buffer (pH 7.2) and 1.7 ml potassium iodide solution (0.1 mol/L) was added and mixed well for 1 min. The mixture diluted to 25 ml.

The solution of volumetric flask was transferred into a 100 ml separating funnel. It was then extracted with 3.0 ml of carbon tetrachloride (CCl_4) by shaking 1 min. The solution was allowed to stand for 1 min. The absorbance was measured at 515 nm against the blank solution in a 1 cm quartz cell.

4. CALIBRATION GRAPH

Under the optimum conditions, a standard calibration graph was constructed by plotting difference of analyte and blank absorbance's versus EG concentration (µg/ml) (Fig. 10). Two linear calibration graphs were obtained for EG from 0.2 to 10 µg/ml and from 7.0 to 36 µg/ml.

The statistical parameters were given in the regression equation calculated from the calibration graphs. The linearity of calibration graphs was proved by high values of the correlation coefficient (r) and the small values of the y-intercepts of the regression equations. Relative standard deviation of response factors for the proposed spectrophotometric method was calculated and recorded in Table 2. In accordance with the formula, the detection limit was found to be 0.08 µg/ml for EG (for S/N value of 3).

A percentage relative standard deviation (RSD%) as precision and a percentage relative error (E%) as accuracy of the suggested method were calculated. The precision was carried out by three determinations at 3 different concentrations in this spectrophotometric method. The precision and accuracy results are shown in Table 3. These results of accuracy and precision show that the proposed method has good repeatability and reproducibility.

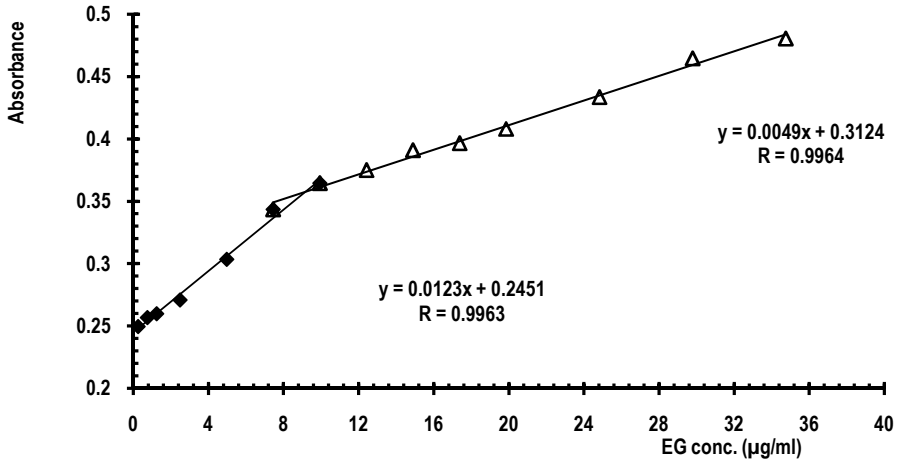

Fig. 10. Calibration graph for the determination of EG

Table 2. Illustrates the statistical and optical treatment of calibration graph of EG

Analyte	Linear range (µg/ml)	Correlation coefficient (R)
Ethylene glycol	0.2 - 10.0	0.9963
	7.0 - 36.0	0.9964

Table 3. Accuracy and precision of the proposed method.

Analyte	Analyte concentration (µg/ml)		E%	RSD %
	Standard solution	Calculation from proposed method		
EG	5.0	4.85	– 3.00	2.49
	15.0	15.08	0.53	1.76
	25.0	24.88	– 0.48	0.69

5. EFFECT OF INTERFERENCES

In order to evaluate the selectivity of the proposed method for the analysis of antifreeze samples, the effects of the presence of inhibitors and additives which can occur in real samples were tested. The tolerated limits for the interfering species are shown in Table 4 with relative errors less than 5.0%.

It was found that the presence of organic inhibitors in antifreeze samples, such as mercaptobenzothiazole compounds (e.g. mercaptobenzothiazole, alkali metal mercaptobenzothiazoles, etc.), di-isopropyl amine nitrite, mono-, di- and tri-ethanol amine and salts thereof, etc. that may be used in combination with the alkali metal meta borate inhibitor did not interfere with the determination of EG at the levels normally found in antifreeze samples (0.0001 to 0.5%) [46,47].

Sodium fluorescein do not effect on the absorbance at the levels normally found in antifreeze samples due to dilution (1.0 ml of antifreeze solution was diluted about 50,000 fold).

Table 4. Study of the effect of interferences on the proposed method

Interfering species	Maximum Allowable Concentrations (µg/ml)	Ethylene glycol (µg/ml)		Recovery %	Tolerable Concentration Ratio**
		Added	Found*		
Borate	20	10	9.96	99.6	2.0
Phosphate	20	10	10.02	100.2	2.0
Silicate	20	10	9.99	99.9	2.0
Sodium fluorescein	1	10	10.03	100.3	0.1
Benzoic acid	20	10	10.11	101.1	2.0
Iodate	20	10	9.87	98.7	2.0

** Mean of three replicate analyses*

*** Tolerable Concentration Ratio with no interference [Conc. Interferent (µg/ml) / Conc. EG (µg/ml)]*

6. APPLICATION

The proposed method was successfully applied to the determination of EG in antifreeze samples. The results are shown in Table 5 indicate that the EG content measured by the present method was in good agreement with those obtained by the iodometric standard method [2,44]. A comparison using t-test at confidence level 95% ($t_{calculated}$= 1.65 < t_{table} = 2.57) indicate that there is no significant difference among the achieved results using these two methods.

From the values of F-calculated 1.37 < F-table 5.05 [48, 49] with a confidence limit of 95% for five degrees of freedom 5, the results indicated that there is no significant difference between the precision of two methods.

Table 5. Application of the developed method in the analyses of EG in antifreeze samples

Trade name	Manufacture	Labeled amount (%)	Detectable amount (%)		E %
			Proposed method *	Standard method **	
Prista Ready Antifreeze	Turkey	42 %	41.24	42.13	– 2.10
Fuchs Antifreeze (Summer Coolant)	Germany	50 %	53.23	52.28	1.82
Deepen Cam Suyu Antifirizi	Turkey	36 %	35.55	36.25	– 1.93
Sea Horse Antifreeze	Turkey	50 %	53.84	51.63	4.28
Dynagel	Poland	50 %	49.78	49.75	0.06
Plyn Do Chlodnic 2000 National Antifreeze	U.A.E.	50 %	48.96	48.15	1.68

** Average of five replication (n=5).*
*** Standard method (Iodometric titration).*

7. CONCLUSION

The present method has the advantages of high sensitivity. On the other hand, the proposed method is low cost, selective, accurate and precise as indicated by the good results of the antifreeze samples. The results obtained by the proposed spectrophotometric method compared well with those obtained by reference method [2,44].

The sensitivity of this method is not less than that obtained for determination EG using spectrophotometric [31,50-52], GC [53] or amperometric [35] methods that gives linear ranges between 40-200, 0.6-3.0, 15-125, 27-281, 5.0-10,000 and 12.4-310.4 µg/ml respectively. The proposed method is less time consuming (about 9-11 min/sample) comparing with some other spectrophotometric methods [52,54] that need about 30 and 20 minutes respectively for total analysis. In addition, some of them like GC-MS [21,22] and HPLC [23,24] higher cost from the proposed method as an additional disadvantage of the proposed method.

The proposed method could be applied successfully for the determination of ethylene glycol in pure form, as well as antifreeze solutions, with no interferences from antifreeze additives.

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COMPETING INTERESTS

Authors have declared that no competing interests exist.

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