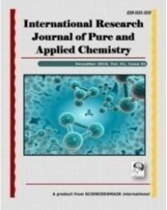

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Reverse Flow Injection–Spectrophotometric Determination of Ethylene Glycol in Antifreeze Solutions via Periodate–*o*-Tolidine Reaction

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Authors' contributions

This work was carried out in collaboration between both 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. Both authors read and approved the final manuscript.

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ABSTRACT

Aims: A reverse flow injection analysis technique was developed for the spectrophotometric determination of ethylene glycol in antifreeze solutions.

Place and Duration of Study: Antifreeze solutions were purchased from oil-changers (Erbil, Kurdistan region, Iraq), between April 2011 and August 2011.

Methodology: The method based on the inhibition effect of ethylene glycol on the reaction of periodate and *o*-tolidine in the presence of acetic acid. The decrease of blue meriquinone absorbance with ethylene glycol was used to monitor the reaction spectrophotometrically at 630 nm. Influences of chemical and physical parameters were evaluated. Selectivity of the method and the suitable conditions for sample analysis were investigated.

Results: Working on optimized conditions, the detection limit was 10 µg/ml with correlation coefficient of 0.9983. The relative standard deviations observed at 40, 100 and 160 µg/ml were 3.27, 1.81 and 0.80% respectively and the analytical throughput was 52 s/h. Possible interferences that related to the determination of ethylene glycol in antifreeze solutions were studied and the

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results showed that foreign species caused less than ±5.0% error.

Conclusion: Six samples of commercial antifreeze solutions were analyzed according to the developed procedure not presenting any statistical difference in relation to the results obtained by standard method.

Keywords: Ethylene glycol; reverse flow injection; o-tolidine; periodate spectrophotometry; antifreeze.

1. INTRODUCTION

Ethylene glycol (EG) is widely used in both industrial and engine coolants, and its applications have prompted extensive literature on its determination. Several methods have been reported for the determination of EG, these methods include chromatographic methods including gas chromatography (GC) [1,2], GC-MS [3,4], high-performance liquid chromatography (HPLC) [5,6], LC [7], TLC [8]. Also, spectrophotometric methods are among the most analytical methods used for EG determination in antifreeze [9–17]. Other methods include amperometry [18], spectrofluorimetry [19,20] and chemiluminescence [21].

Periodate is an important oxidant which can oxidize many inorganic and organic compounds. Most of the oxidizable organic compounds have groups amino, imino, carboxyl or diol on adjacent carbons. The reaction between periodate and the above mentioned groups is well known as the Malaprade reaction [22-25], and was used for the indirect determination of 1,2-diols and related compounds [2,3]. Periodate is exclusively associated with the oxidation of metal ions, polyhydroxy compounds and in catalytic applications at trace level. Determination of periodate is important in organic chemistry, biology and life sciences [22].

Trace levels of this ion have been extensively used as ingredients for indicator in catalytic-kinetic analysis involving redox processes and for the determination of the number of adjacent hydroxyl groups, elucidation of the polysaccharide structure [26], and corroboration of the glycoside structure [27]. The α–glycol group is cleaved at the C–C bond with an equimolar amount of periodate; the reaction is applicable for cis- and transdiols and α–aminoalcohols [28].

Generally, diol-periodate reaction mechanism (Malaprade reaction) include two steeps: Formation of cyclic periodate ester, and cleavage of carbon-carbon bond to two carbonyl compounds depending on the reaction conditions and the structure of the compound oxidized as shown in Fig. 1 [28–33].

As mentioned, Malaprade reaction can be used for the determination of α–glycol groups, which can be easily done on the basis of periodate consumption or iodate formation [34,35]. Many materials may be determined in the presence of others by investigating the products of the oxidation because the reaction is specific [36].

o-Tolidine (OT) [2-tolidine or 4-(4-Amino-3-methylphenyl)-2-methylaniline] widely used as a reagent or indicator in analytical, clinical and forensic chemistry, such as in the analytical determination of chlorine [37,38,39], gold [40], iodine [41], hemoglobin [42], corrogeenon ester sulfate [43], ruthenium [44], manganese [45], bismuth [46], indirect determination of cyanide and thiocyanate [47] and anionic surfactants [48].

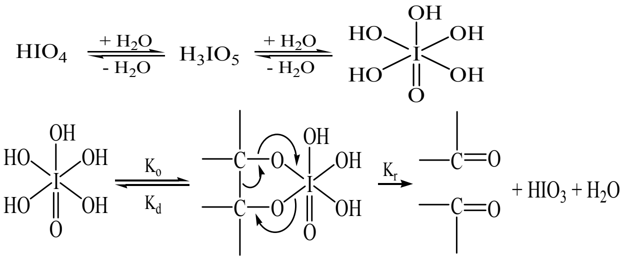

Fig. 1. The mechanism of the periodic acid-induced oxidation of 1,2-glycols

Willstatter and Kalb first showed that mild oxidation of benzidine (presence of H instead of methyl group in OT) produced a green substance and that upon oxidation with silver oxide or lead peroxide a deep yellow quinonoid substance was formed [49,50]. This compound (OT) contained two less hydrogen atoms than benzidine and was p,p'-diiminodiphenyl. Such fully oxidized products of diamines were termed holoquinones. In addition to the holoquinones, Willstatter and Piccard isolated colored, crystalline, partial oxidation products of diamines which were called meriquinones [51]. For example, Wurster's red is the meriquinone produced by partial oxidation of p-aminodimethylaniline. The structure of meriquinones was shown to be analogous to that of quinhydrone (Fig. 2), but meriquinones are not necessarily composed of equimolecular parts of oxidant and reductant [37].

Clark, Cohen, and Gibbs applied the above considerations to the OT test and by means of potentiometric and spectrophotometric studies explained the varying color reactions shown by OT. The reactions involved are shown on Fig. 2. From these reactions it became evident that the variations in color experienced in the OT test were due to the superimposing of different degrees of oxidation upon the effects of variable pH. The use of strong hydrochloric instead of acetic acid favors the development of (III) instead of (II) with resultant greater stability. Likewise, the concentration of OT present is important since low concentration favors the formation of the completely oxidized form or holoquinone [37].

The concept of flow injection analysis (FIA) was first discussed by Ruzicka and Hansen and then the Stewart group in the mid-1970s. Besides automation, FIA offers other advantages (e.g., simple configuration, high sample throughput, a great deal of flexibility, adaptability to various chemistries, and increased selectivity based on the kinetic nature of the measurement process). Flow analysis is considered as analytical technique where the analytical signal is based on introducing a sample by aspiration or injection, on-line sample processing, and detection of analyte in the flowing medium. The main attributes of flow analysis are on-line sample processing carried out to provide/enhance selectivity of detector response, and detection carried out during the flow of the analyte through the detector [52-54].

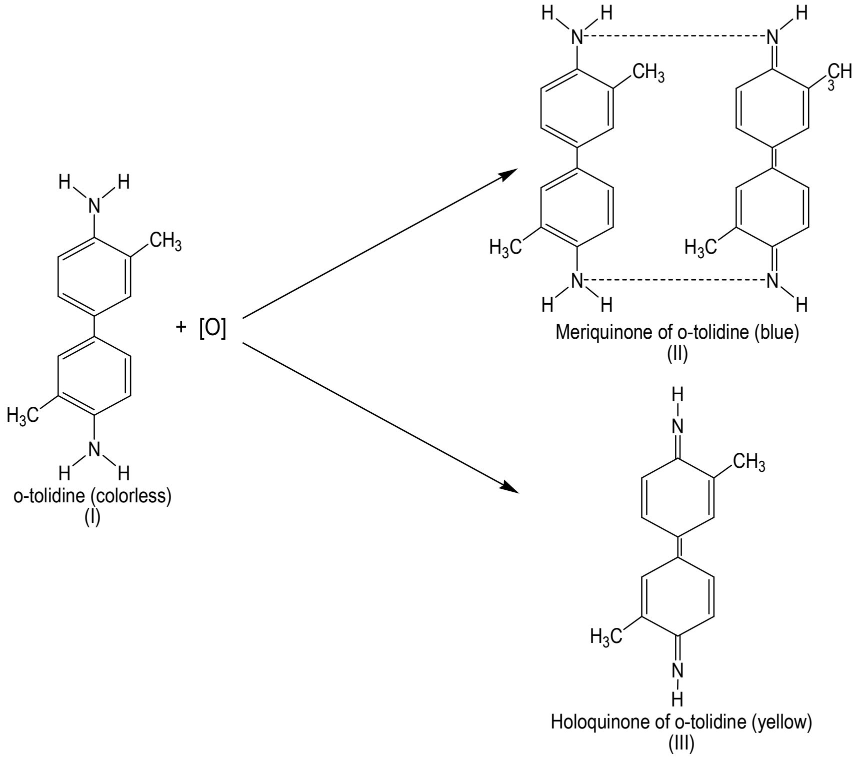

Fig. 2. Oxidation reaction of OT and formation of meriquinone and holoquinone of OT

In previous work [17] EG determined indirectly using Malaprade reaction, in which excess periodate used for oxidation of EG, then, extraction and preconcentration of iodine was formed from the reaction of remained periodate with iodide. The decrease in theabsorbance of extracted iodine is used to monitor the reaction spectrophotometrically at 515 nm. While, in this work, the excess of periodate react with OT in acetic acid medium [37,43,55-57]. The quinonediimines formed (II) have very high molar absorption coefficients (at 630 nm) and thus they can be determined even at very low concentrations using a simple, fast and low-cost reverse flow injection method, and we have studied the influence of interferences on them.

To minimize the consumption of reagent (OT) and waste production, arFIA manifold was assembled to determine EG in antifreeze solutions (Fig. 3). The reagent (OT) was injected into a sample stream, and the absorbance obtained was measured. During optimization, all samples were analyzed in triplicate, and absorbance of corresponding blank solution was subtracted.

2. EXPERIMENTAL

2.1 Apparatus

A CECIL CE 3021-3000 Series spectrophotometer was used to measure absorption spectra in a 1.0 cm quartz cell. A digital WTW-inolab 740-Germany pH meter equipped with a combined glass-calomel electrode was used for pH measurements.

The reversed flow injection system used for the determination of EG in antifreeze samples was shown in Fig. 3. It was equipped with a Desagapl - Heidelberg, England peristaltic pump (6 channels, variable speed)to drive the carrier (D.W.) or sample and the periodate streams and an actuated rotary six-port injection valve (Rheodyne-USA) supplied with variable loops.

A variable wavelength spectrophotometric (JENWAY, 6300 Spectrophotometer) with a 100 µL flow cell was used at 630 nm. PTFE (0.8-mm i.d.) tubing was used for knitted reaction coils and all flow tubing. Three mixing coils were used: coil 1: 5cm, coil 2: 120cm, and glass bead reactor (coil 3: 100 – 200 mesh, 5 cm, 2 mm i.d.). All reagents were pumped at a flow rate of 1.0 ml/min. The signal was recorded by ax-t recorder (Type PM 825A PHILIPS – one line recorder) with various amplication factors and different chart speeds. Peak height was measured for each signal. The analytical signal was calculated as blank output minus sample output (blank signal – sample signal).

2.2 Reagents and Samples

All solutions were prepared using reagent grade substances and distilled water.

Ethylene glycol: Standard ethylene glycol solution with concentration of 1.00 mol/L was prepared by diluting 56.3 ml of EG (99%, BDH) to 1.0 L with distilled water (DW). The prepared solution was stored in a dark bottle and protected from daylight. Working solutions were prepared by suitable dilution.

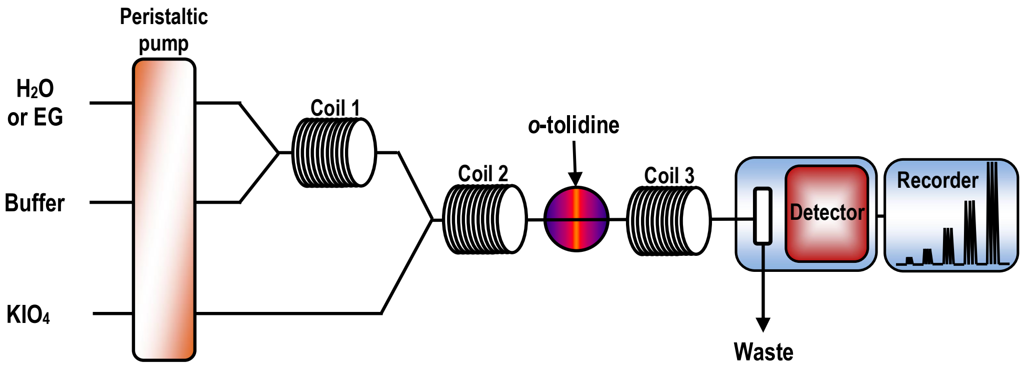

Fig. 3. Reverse flow injection manifold used for the spectrophotometric determination of EG in antifreeze solutions

Potassium periodate solution (0.01 mol/L): A 2.30 g amount of KIO_4 (RIEDEL-DE HAEN AG SEELZE-Hannover) was dissolved in 100 mLDW in a 1.00 L calibrated flask and the solution was made up to the volume with distilled water. Serial dilutions with distilled water were made to cover the working range.

Buffer solution: It was prepared by dissolving 35.59 g of disodium hydrogen phosphate dehydrate ($Na_2HPO_4.2H_2O$) (RIEDEL-DE HAEN AG SEELZE-Hannover) in distilled water, and then, the pH of this solution adjusted at 4.5 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 [58].

Sample preparation: Antifreeze sample solutions were prepared for analysis by weighting 1.0 g of antifreeze and dissolving in DW, the resulting solution was diluted to 100 ml in volumetric flask. 10 ml of this solution was diluted 1000 fold [9]. 5.0 ml of this solution was analyzed for ethylene glycol, as described in procedure (section 2.3).

Acetic acid solution (AA): 0.5 mol/L acetic acid solution was prepared by diluting 28.7 ml acetic acid (99.7%, 1.0485 g/ml – BDH) in DW and diluting to the mark with DW in a 1000 ml volumetric flask. Other solutions were prepared by serial dilution.

o-Tolidine: 0.004 mol/L OT (solubility in water 1.3 g/L was prepared by dissolving 0.114 g of the reagent (Fluka) in sufficient volume of 0.01 mol/L acetic acid solution the resulted mixture was quantitatively transferred to a 100 ml volumetric flask and diluted with the same acid solution (the pH of this solution was 3.8). It was stored in a dark bottle, and protected from daylight.

2.3 Procedure for rFIA

Conditioning of the flow injection system involved pumping 0.01 mol/L periodate through the reactor for auto zero of the detector and was followed by pumping of carrier stream solution (D.W. or EG) and waiting for baseline of detection system at 630 nm to reach a steady state. After conditioning the reagent solution (acidic OT), was injected into the EG – periodate stream. The concentration of EG is proportional to the decreasing in a peak height. When EG solution was inserted into the carrier stream, the magnitude of the signal decreased as a result of the reaction of EG with periodate.

Using the experimental setup as shown in Fig. 3, 100 µl of the 0.02 mol/L of OT reagent solution in 0.003 mol/L acetic acid was injected via injection valve into the merged streams of D.W. (or 100 µg/ml EG) with 0.01 mol/L KIO_4 solution flowing with the same flow rate of 1.0 ml/min which was then passed through a glass bead reactor where the oxidation reaction (oxidation of OT) was taken place. The resulting blue meriquinone of OT was subsequently monitored at 630 nm.

3. RESULTS AND DISCUSSION

In this work, we used periodate – OT system for the determination of EG in a reversed flow injection system. The oxidation of EG with a known excess of periodate in Na_2HPO_4/citric acid buffer (pH 4.5) is indicated by the chemical equation described in Fig. 1. Unreacted periodate react with OT and the formed meriquinone complex is detected spectrophotometrically at 630 nm as a step for the indirect determination of EG.

3.1 Absorption Spectra

The oxidative reaction between periodate and OT produces a meriquinone of OT having an absorption peak with its maximum value at 630 nm (Fig. 4). Notice that the absorption spectra of the analyte and the blank (OT blank) (curves a and b) have no absorption bands in the region that corresponds to that of the complex periodate – OT. The absorption spectra having their maximum absorbance at 630 nm. Moreover, it is interesting to note that the complex has a higher maximum absorbance value in comparison with that formed in the presence of EG. Hence, subsequent analysis of the colored complex was carried out at 630 nm.

3.2 Optimization of rFIA Method

To optimize the performance of the manifold, the absorbance of the blue meriquinone was measured as a function of buffer pH, periodate concentration, acetic acid concentration, OT concentration, reaction coil length, system flow rate and injection volume of the reagent. To reach the best operational conditions, we used a univariate method, where one variable is varied by maintaining constant the rest. In all optimization experiments, carrier solution was DW.

3.2.1 Effect of the buffer pH

EG oxidized fastest in a slightly acidic medium. Therefore, the oxidation reaction was studied at various pH values (pH 3.5–5.5). After calculation of the ΔI (blank signal – analyte signal) values which were then plotted against various pH values. Results are shown in Fig. 5. It was evident that the absorption maximum of such a meriquinone studied was increased over the pH range of 3.5–4.5. As can be seen in Fig. 5, at pH values below and above 4.5 the ΔI values decrease significantly, because at higher pH, overoxidation occurs readily and the small fragments produced by the primary oxidation are oxidized at a rate dependent upon the pH of the medium, the concentration, and the molar excess of periodate [17,59]. Hence, pH 4.5 was chosen as optimum.

3.2.2 Effect of periodate concentration

The effect of periodate concentration on the color development was examined in the range 0.003–0.032 mol/L. Both peak heights of blank and sample remarkably increased with increasing periodate concentration up to 0.015 mol/L (Fig. 6), because at low periodate concentrations the rate of primary oxidation is slow, while at high periodate concentrations nonspecific oxidations may occur [17,59]. Therefore, the concentration of 0.015 mol/L periodate was selected as optimum because it exhibited maximum ΔI value measured at 630 nm.

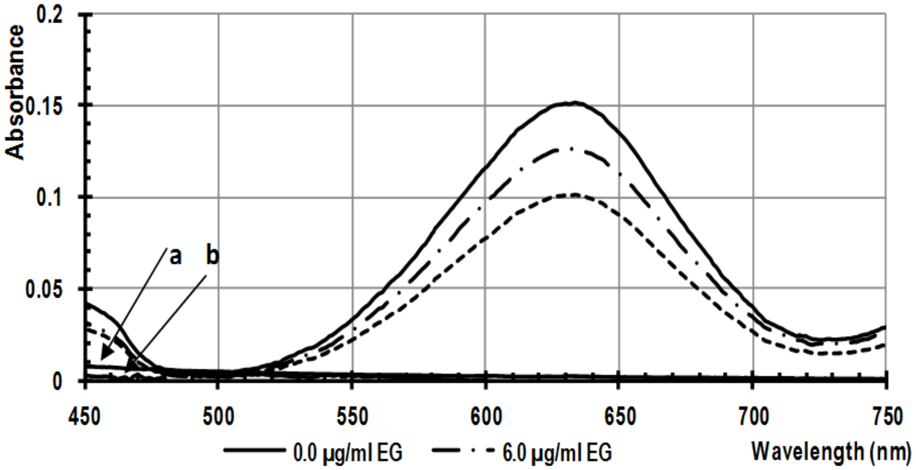

Fig. 4. Absorption spectra for the: (a) analyte, (b) blank, and formed meriquinone of OT using (0.0, 6.0 and 12.0 µg/ml) EG

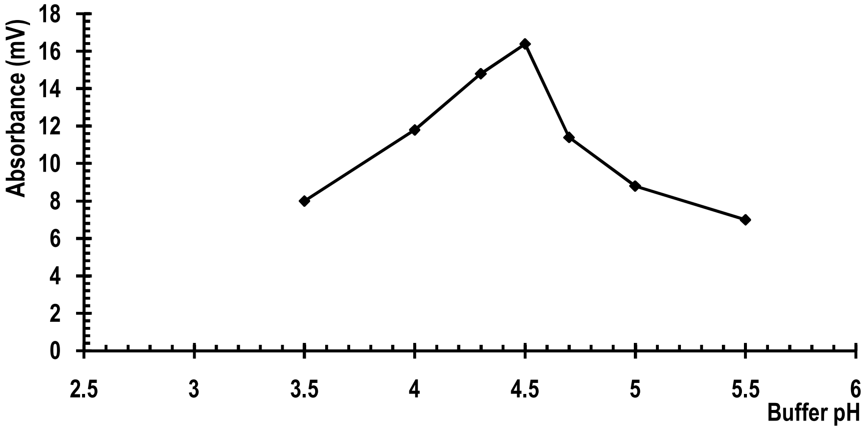

Fig. 5. Effect of buffer pH on the determination of 100 µg/ml EG

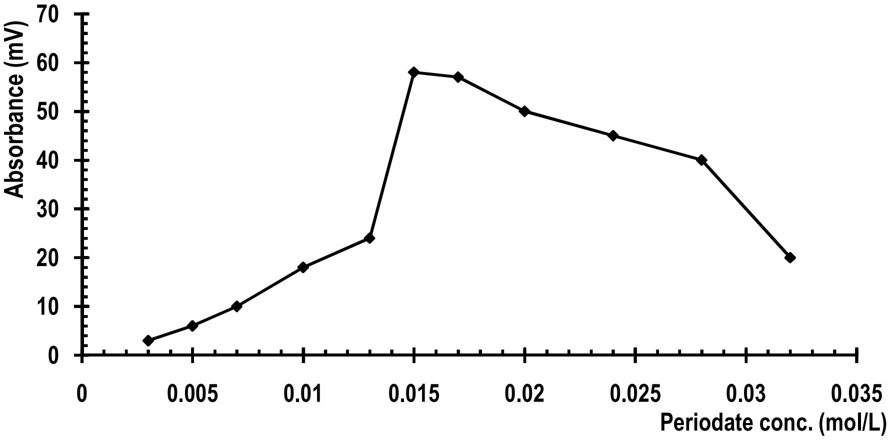

Fig. 6. Effect of periodate concentration

3.2.3 Selection of acid type and concentration

It is known that OT oxidized in acidic media [37,46]. The following media have been tried in the proposed experiments: sulfuric acid, hydrochloric acid, nitric acid and acetic acid solutions with concentration of 0.01 mol/L. It was found that the value of ΔA is very low in HCl, H_2SO_4 and HNO_3 solutions, because the use of strong acid favors the development of holoquinone instead of meriquinone [37]. Decreasing of absorbance of final product is strong in acetic acid solution and the reproducibility is better. Therefore, acetic acid was selected as the best reaction medium.

In addition to acid type, the effect of acid concentration studied. Different concentrations of acetic acid were tested. The results, graphically presented in Fig. 7, show that the maximum different in absorbance was obtained at 0.005 mol/L. At high concentration of acidthe blue compound turned yellow [46]. Accordingly, 0.005 mol/L acetic acid concentration was used throughout the measurements for EG determination.

3.2.4 Effect of OT concentration

The concentration of OT present is important since low concentration favors the formation of the completely oxidized form or holoquinone (yellow product), while high concentration of OT favors the formation of meriquinone of OT [37,46]. Therefore, it is necessary to investigate to find out the optimum OT concentration to achieve the best selectivity and sensitivity of the method. Effect of OT concentrations over the range of 0.00–0.03 mol/L were examined for determining 100 µg/ml EG in standard EG solutions.

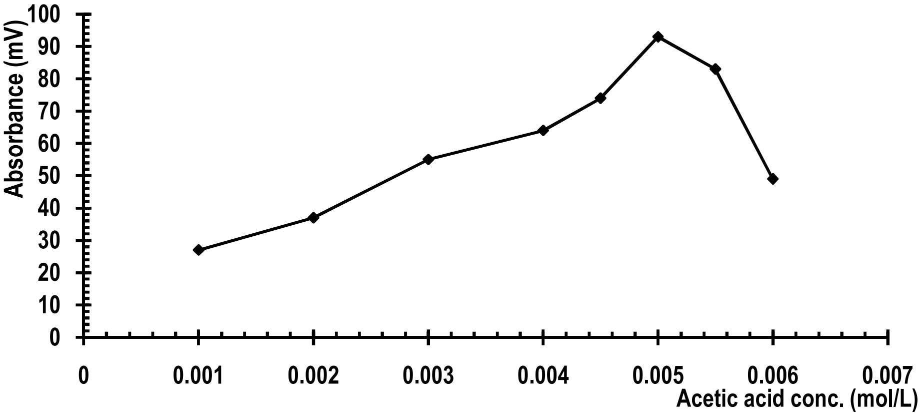

Fig. 7. Effect of acetic acid concentration

The sensitivity increased with increasing in OT concentration up to 0.02 mol/L (as shown in Fig. 8) because low concentrations of OT favors the formation of the completely oxidized form or holoquinone, while high concentration of OT favors the formation of meriquinone [37,46]. Further increase in OT concentration gave a stable signal. Therefore, the concentration of 0.02 mol/L was chosen as suitable because it provided reasonable sensitivity.

3.2.5 Effect of coil length

Using a fixed injection volume of 100 µL, the influence of independently varying the mixing coils 1, 2 and 3 (Fig. 9) on final signal response and analysis time was investigated.

Increasing the length of the mixing coil 1 that used for the mixing of buffer solution with DW or EG, from 5–50 cm, has no significant effect on the absorbance, while with longer coil the absorbance decreased. Therefore, a 5 cm length was selected as an optimum length.

Not surprisingly, increasing the length of coil 2, immediately after mixing of the periodate – EG streams results in an increased difference in a peak response because additional mixing promotes the reaction between EG and the potassium periodate. According to the results illustrated in Fig. 9, optimum coil length was found to be 180 cm that gives a maximum absorbance and higher coil lengths do not enhance the absorbance signal.

The reaction of the excess periodate with OT is rapid, and the obtained results demonstrated that using of mini–column glass bead reactor instead of coil enhanced the sensitivity of the method due to acceleration of the chromogenic reaction. The results show that an increasing the length of mini – column glass bead reactor from 0 to 10 cm increase the peak height, after that, increasing the length had no effect other than to decrease the peak response and increase the peak width. Based on these observations, a length of 5, 180 and 10 cm was chosen for coil 1, 2 and 3 respectively, and this represents a compromise between maximizing the sensitivity and maintaining an acceptable sample throughput.

3.2.6 Flow rate optimization

The contact time between EG–periodate and periodate–OT solution is very important for the reaction to proceed sufficiently close to the completeness. As this depends on the flow rate of the sample zone through the reactor, a study of the flow rate of the system was conducted. Flow rates between 0.3 and 2.2 ml/min were evaluated. This optimization is shown in Fig. 10.

A high flow rate leads to a shorter time required for each sample passing through the FI system, poor reproducibility and a high rate of sample and carrier reagent consumption. At very low flow rate (0.3 ml/min) the shapes of the obtained signals were not reproducible and the residence time was long giving rise to low sampling rate. Therefore, as a compromise the

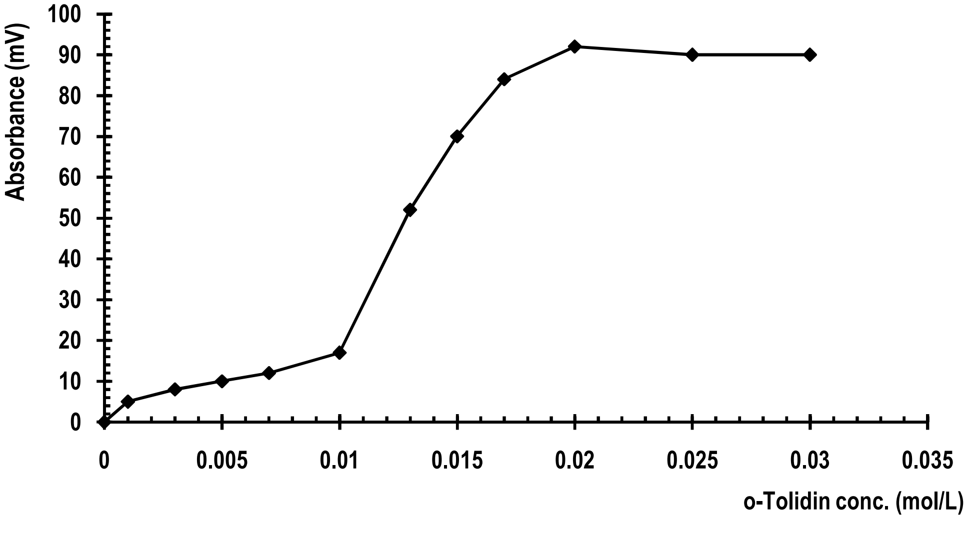

Fig. 8. Effect of OT concentration

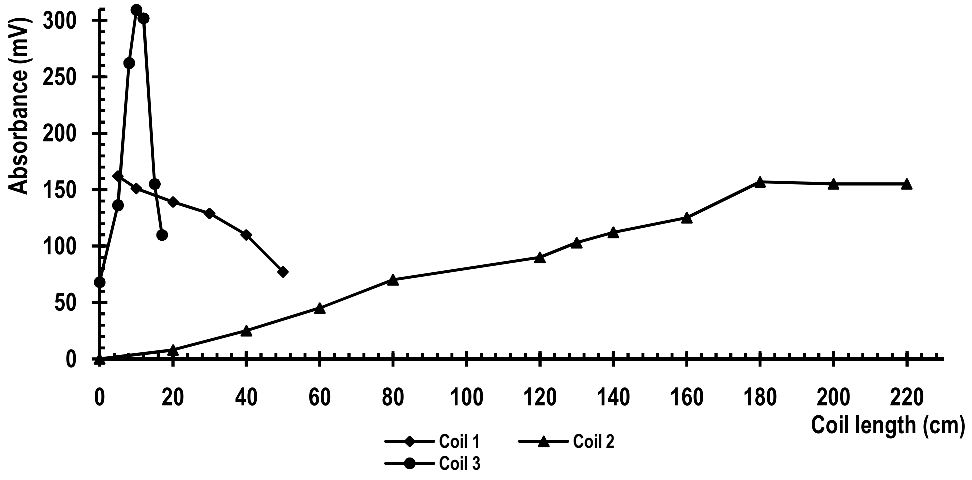

Fig. 9. Effect of reaction coil lengths

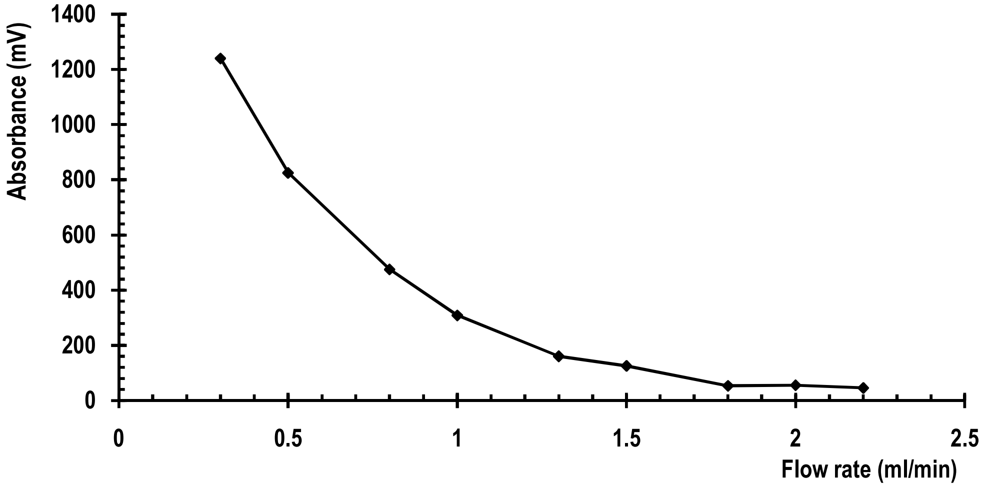

Fig. 10. Effect of system flow rate on the determination of 100 µg/ml EG

flow rate of 0.5 ml/min was selected for the subsequent investigations.

3.2.7 Effect of injection volume

The injected reagent should be sufficient for complete color development in rFIA. Therefore, it is very important to optimize the injection volume. The injected volume of the reagent was varied from 50 to 225 µL. The difference in absorbance increased with increasing reagent volume up to 100 µL, after this volume the blank signal remain constant while the analyte signal increased that's lead to decreasing of ΔI (Fig. 11). Therefore, 100 µL 0.02 mol/L OT was chosen for further work.

The best performance of the rFI spectrophotometric system used for the determination of EG was achieved in the conditions summarized in Table 1.

Table 1. Optimum conditions for the determination of EG by proposed method

Parameter	Condition
pH of buffer solution	4.5
KIO_4	0.015 mol/L
Acetic acid	0.005 mol/L
OT	0.02 mol/L
Coil 1 length	5 cm
Coil 2 length	180 cm
Coil 3 length	10 cm
System flow rate	0.5 ml/min
Injection volume	100 µL
Sample frequency	52 s/h
Wavelength	630 nm

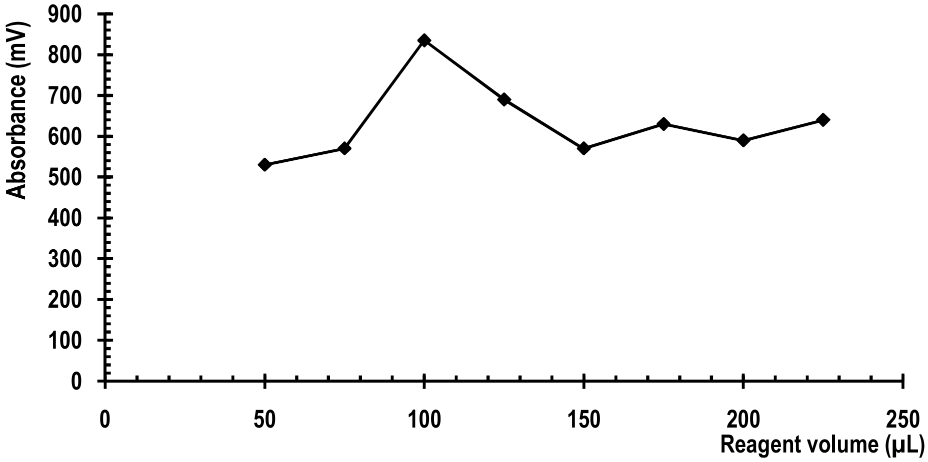

Fig. 11. Effect of reagent volume (OT volume)

4. CALIBRATION GRAPH

Using the proposed rFI spectrophotometric manifold for EG determination (Fig. 3) under the optimum conditions, the linear calibration graph over the range of 15 – 200 µg/ml EG was established (Fig. 12) which can be expressed by the regression equation y= 7.4539X + 97.87(R= 0.9983) where y represents the peak height (absorbance) in mV and x is EG concentration in µg/ml after subtraction of blank. The detection limit for EG was 10.0 µg/ml and the sampling rate was found to be 52 s/h.

The precision test was carried out by five measurements of the working standard solution with the EG concentration of 40, 100 and 160 µg/ml by calculating the relative standard deviation (RSD). The accuracy expressed in term of percentage error (E%) was studied and the results summarized in Table 2.

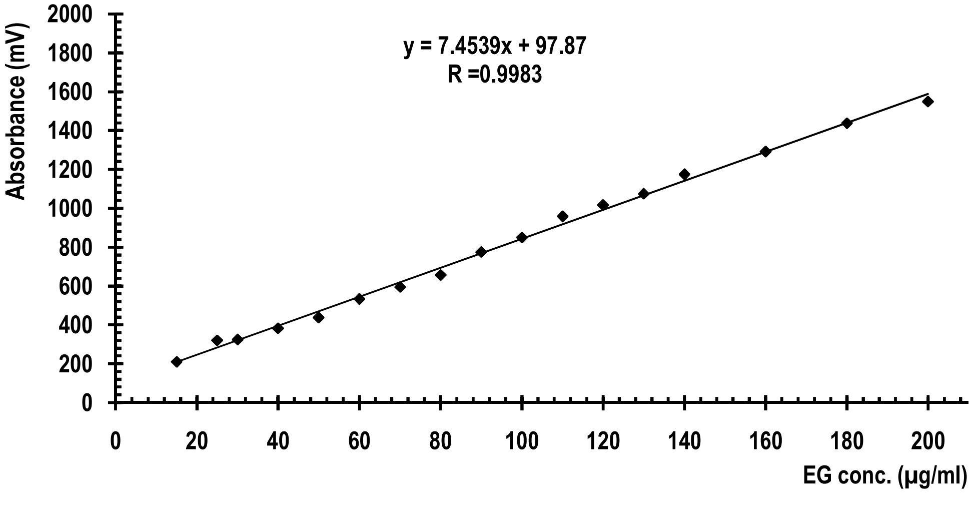

Fig. 12. Calibration graph for the determination of EG

Table 2. Accuracy and precision of the proposed method

Analyte	Analyte concentration (µg/ml)		Error %	RSD %
	Standard solution	Calculation from proposed method		
EG	40	40.24	0.6	3.27
	100	102.84	2.84	1.81
	160	162.64	1.65	0.80

5. EFFECT OF INTERFERENCES

In order to assess the possible analytical application of the proposed method to antifreeze analysis, the effect of some common chemicals used as additives was studied by adding the chemicals to solutions containing 160 µg/ml EG.

Table 3 shows maximum tolerable concentrations of the some compounds. The tolerable concentration ratios with respect to 160 µg/ml EG for interference at 5.0% level were over 12 for borate, phosphate and silicate, 20 for benzoic acid and 0.20 for sodium fluorescein. The same amount of sodium fluorescein produced positively interference because sodium fluorescein could increase the absorbance due to its color. When compared with other interferences studied, however, the concentration of sodium fluorescein in real antifreeze sample is very low (0.01–to 0.50 g/L of the antifreeze solution [17]). Therefore, the concentration of sodium fluorescein is so low in real samples that they do not interfere.

6. APPLICATIONS

The proposed method has been applied to the determination of EG in antifreeze samples collected from oil changer markets in Erbil city. Results were listed in Table 4. It was seen that results obtained by the recommended method were good agreement with those obtained by standard method (iodometric) [9,60] verified by t-test. t-Test at confidence level 95% ($t_{calculated}$= 0.73<t_{table} = 2.23) indicate that there is no significant difference among the achieved results using these two methods. The value of F-calculated that is3.27< F-table 5.05 [61,62] with a confidence limit of 95% for five degrees of freedom 5, indicate that there is no significant difference between the precision of proposed and iodometric methods.

Table 3. The effect of interferences on the proposed method

Interfering species	Maximum allowable concentrations (µg/ml)	Ethylene glycol (µg/ml)		Error %	Tolerable concentration ratio[b]
		Added	Found[a]		
Borate $(BO_3)^{3-}$	1920	160	160.60	0.38	12
Phosphate $(PO_4)^{3-}$	1920	160	157.92	– 1.30	12
Silicate $(SiO_4)^{4-}$	1920	160	155.91	– 2.56	12
Sodium fluorescein	32	160	161.95	1.22	0.20
Benzoic acid	3200	160	161.28	0.80	20
Mixture of all interfering species		160	161.55	0.97	

[a] *Mean of three replicate analyses*

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

Table 4. Application of the developed method in the analyses of EG in antifreeze solutions

Trade name	Manufacture	Labeled amount (%)	Detectable amount (%)		Error %
			Proposed method *	Standard method **	
Prista Ready Antifreeze	Turkey	42%	42.3	42.13	0.40
Fuchs Antifreeze (Summer Coolant)	Germany	50%	52.94	52.28	1.26
Deepen Cam Suyu Antifirizi	Turkey	36%	37.88	36.25	4.50
Sea Horse Antifreeze	Turkey	50%	51.71	51.63	0.15
Dynagel Plyn Do Chlodnic 2000	Poland	50%	47.32	49.75	–4.88
National Antifreeze	U.A.E.	50%	50.01	48.15	3.86

**Average of three replication (n=3).*

***Standard method (Iodometric titration).*

Table 5. Comparison of the proposed method with some other methods

Method	Linear range (µg/ml)	Analysis speed (sample/hour)	Reference
Proposed method	15-200	52	
Spectrophotometric	40-200		[14]
Spectrophotometric	15-125		[63]
Spectrophotometric	27-281	2	[64]
Gas chromatography	5-10000		[65]
Spectrophotometric	0.02-1.5	3	[66]

7. CONCLUSION

Reverse flow injection-spectrophotometric method is presented for determination of EG antifreeze samples using indirect method. The method is sensitive, simple and suitable for application to antifreeze samples. Compared with other methods, the reagents used for the assay are versatile and economical, the final products using spectrophotometric methods have maximum absorbance wavelength in the visible region and the reactions can be carried out at room temperature. The detection limit indicate that microgram quantity of EG can be accurately determined. The above Table 5 shows a comparison of the presented methods and previous reported methods in terms of detection limits, analysis speed and dynamic ranges.

The obtained results demonstrated that using of mini–column glass bead reactor instead of coil enhanced the sensitivity of the method about 20%. The proposed method could be applied successfully for the determination of EG in pure form, as well as antifreeze solutions, with no interferences from antifreeze samples.

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COMPETING INTERESTS

Authors have declared that no competing interests exist.

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