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THE DETERMINATION OF ACIDIC DEGRADATION PRODUCTS IN AQUEOUS ETHYLENE GLYCOL AND PROPYLENE GLYCOL SOLUTIONS USING ION CHROMATOGRAPHY

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Aqueous ethylene glycol and propylene glycol solutions are the principal antifreezes used as heat transfer fluids in flat-plate solar collector systems. Acidic degradation produces formed in the thermal oxidation of these solutions have been analyzed using ion chromatography (IC) and the ion-chromatography exclusion (ICE) method of analysis. The primary acidic degradation product found in the case of ethylene glycol solutions was glycolic acid. Propylene glycol solutions yielded mainly lactic acid. The presence of metallic copper significantly increased the amount of degradation products over that produced in the absence of metal. Solutions heated in the presence of metallic aluminum were only slightly more degraded than those heated without metal, but contained relatively large amounts of formic acid. Only traces of formic acid were observed when the glycol solutions were heated in the absence of metal or in the presence of metallic copper.

1. Introduction

Glycol-based aqueous antifreeze solutions have been estimated to be the most common type of heat transfer fluids for flat-plate solar collectors, accounting for approximately 36% of the fluids used [1]. Ethylene glycol accounted for slightly more than one half of this total, while propylene glycol comprised the remainder. Although the glycol-based heat transfer fluids have satisfactory physical properties, they are susceptible to thermo-oxidative degradation reactions which produce organic acids. These degradation products accelerate corrosion of metallic collector systems, particularly if the glycol solutions are not properly formulated for corrosion inhibition, or if the inhibitors are consumed before the fluid is re-inhibited or replaced. Because of the serious consequences which may result from increased collector system corrosion, the effect of the thermal oxidation of glycol-based antifreezes on the corrosion rates of metallic components in collector systems has received considerable attention [1–9]. The increase in corrosion rates has been attributed to the formation of acidic degradation products which is accompanied by a decrease in the pH of the antifreeze solution [5].

Little information has been reported on the type of the acidic degradation products in the solar fluids [10] or their rates of formation under specific operating conditions. Most of the information concerning glycol degradation comes from the automotive coolant industry. Diegle et al. [5] have indicated that the experience with

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the automotive antifreezes is probably not adequate to assess their stabilities under various collector operating conditions. Avery [4] has stated that because of the lack of information on glycol degradation, it is not possible to predict the time to fluid breakdown, or to draw definite conclusions about the lifetimes of glycolic fluids in general. In lieu of specific guidelines based on rates of degradation, recommendations have been made to monitor the fluid periodically for changes in pH and reserve alkalinity [4,7]. A significant decrease of the pH may indicate the inhibitors (buffers) have been consumed and that the fluid should be replaced. If the fluid is not monitored for changes in pH and reserve alkalinity, then it may be recommended to change the antifreeze on a periodic basis, for example, at time intervals of 1 to 2 years or less. This may not be acceptable both from the standpoint of convenience or economics, particularly if the glycol-based antifreeze has not degraded to the point where replacement is warranted.

Collins et al. [10] indicated that the primary acidic degradation products from ethylene glycol solutions may include glycolic, glyoxylic, oxalic and formic acids. However, in a study of automotive ethylene glycols solutions, they found only glycolic and formic acids, with the latter being the major constituent. This contrasts to Diegle's review in which it was reported that glycolic acid was generally accepted as the major acidic decomposition product from ethylene glycol [5]. Beavers et al. [6] found oxalic acid among the acidic degradation products of ethylene glycol. The analytical methods used in all these investigations [5,6,10] did not determine the acids directly, but made use of derivatives, or some other indirect means. Direct determination of the acidic degradation products of ethylene glycol by an instrumental method of analysis has not been described in the literature.

Even less has been reported regarding the degradation of aqueous propylene glycol. Sullivan [2] indicated that glycolic and formic acids may be formed from the thermal oxidation, although supporting experimental evidence was not presented. It may be anticipated that possible degradation products could include lactic, pyruvic, acetic and formic acids, but these possibilities have not been cited in the literature.

This paper reports an ion-chromatography (IC) procedure used to analyze aqueous ethylene glycol and propylene glycol antifreezes both before and after thermo-oxidative degradation in the presence of metallic copper or aluminum, and also in the absence of metals. In particular, the ion-chromatography exclusion (ICE) method of analysis is used to identify and quantify the major organic acid products resulting from thermo-oxidative degradation. The results of the ion chromatographic analysis are compared with pH values of the degraded solutions.

Previously ion chromatography has been used to analyze for the inorganic inhibitors and stabilizers in ethylene glycol solutions used as engine coolants but not directly for the acidic degradation products [11,12]. However, in the analysis of the inhibitors, glycolic acid has been found as a degradation product of ethylene glycol.

2. Ion chromatography

Ion chromatography is a liquid chromatographic technique for the analysis of ionic species in aqueous solution. Reviews of the technique has been given by Smith

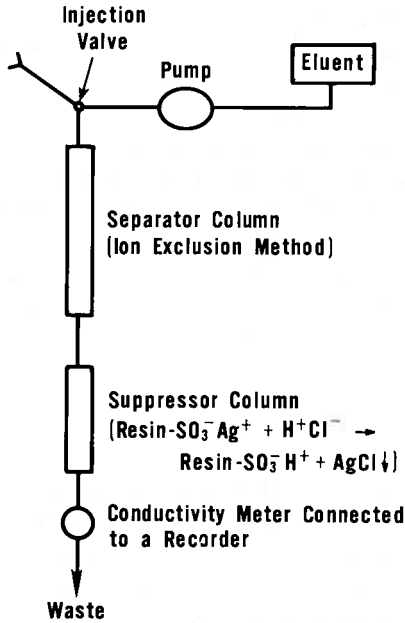

Fig. 1. Schematic of the ion chromatography analytical system.

and Chang [13] and by Mulik and Sawicki [14]. Fig. 1 shows a schematic of the system, as presented by Smith and Chang. The method used an ion exchange resin (the separator column) to separate the ions being analyzed, another ion exchange resin (the suppressor column) to reduce the conductivity of the eluent and an electrical conductance detector. The eluent is the mobile (liquid) phase used to transport (elute) the sample ions through the column system.

Ion-chromatography exclusion (ICE) is a complementary method to ion chromatography (IC). The ICE method is used for the separation of ionic and nonionic (or weakly ionic) species in aqueous solution which may not be readily separated by normal IC methods. The technique has application for the separation of strong mineral acids and their salts from weak organic acids and their salts, or weak acids from each other [15]. Simpson and Wheaton [16], and Wheaton and Bauman [17] have discussed the theory of ICE analysis.

3. Experimental

3.1. Equipment

The Dionex* ion chromatograph and ion-exchance resin columns were used for the analysis. The chromatograph was a model 12, equipped with a conductivity

* Certain trade names or company products are mentioned in the text to specify adequately the experimental procedure and equipment used. In no case does such identification imply recommendation or endorsement by the National Bureau of Standards, nor does it imply that the products are necessarily the best available for the purpose.

detector and an automatic sample injection system. The sample injection loop had a 100 μl capacity. For the ICE analysis, a high performance ICE separator column (no. 035330) and a silver-form cation exchange suppressor column (no. 030891) were used. To reduce system volume in order to improve separation efficiency, the suppressor was connected directly to the outlet of the separator column. In turn, the outlet of the suppressor was connected directly to the inlet of the conductivity cell. A cation trap column (no. 030975) was added in line before the separator column to prevent cations in solution from entering the separator. For IC anion analyses, an S2 anion separator column (no. 031019) and an ASC-1 anion suppressor column (no. 030829) were used. These two columns were connected through a valve to allow regeneration of the suppressor column.

3.2. Reagents

3.2.1. Glycols

The ethylene glycol and 1,2-propylene glycol reagents were distilled under vacuum (ethylene glycol, b.p. 93°C/13 mm; propylene glycol, b.p. 96–98°C/21 mm) before use. Only the middle distilling fractions were used in subsequent analyses.

A 9 mol/l (50 vol%) aqueous ethylene glycol solution and 9 mol/l (66 vol%) aqueous propylene glycol solution were prepared using distilled water. The solutions were maintained at 100°C in a constant temperature bath while being aerated. Aerated solutions which contained copper or aluminum coupons were also heated in the bath. Aliquots of these solutions were removed from the bath after heating for 15 days or 12 weeks for measurement of pH and analysis by ion chromatography. For the ion chromatography analysis, 1 ml of the heated solution was diluted with 3 ml of distilled water. If the initial chromatographic analysis indicated that the solution was too concentrated, the test solution was diluted as necessary and re-analyzed.

3.2.2. Acid solutions

Stock solutions (1000 ppm) of the acids listed below or their salts were prepared in distilled water and stored in a refrigerator at 5°C. Before preparation of the stock solutions, the solid reagents were dried under vacuum in a desiccator over silica gel at room temperature (about 23°C) for 24 h. The reagent grade acids or salts (which were not further purified) were used in preparation of the stock solutions: acetate (sodium salt, 99.3%); formic (aqueous reagent, 89.1% assay); glycolate (acid); lactate (calcium salt); pyruvate (sodium salt); and oxalic (acid, dihydrate). The stock solutions were used to prepare standard solutions (normally 10 ppm) for use in identifying and quantifying the acidic species observed in the ICE and IC analysis of the heated glycol solutions. The standard solutions were prepared by diluting the stock solutions with 12% aqueous ethylene glycol or 15% aqueous propylene glycol, depending on whether ethylene glycol or propylene glycol solutions were under analysis.

3.2.3. Eluents

The eluent for the ICE analysis was 1 mmol/l HCl; the IC eluent was 0.85 mmol/l $NaHCO_3$.

3.2.4. Analysis procedure

Prior to analysis, the eluent was pumped through the system for a minimum of 30 min to allow equilibration. Sample solutions were injected into the chromatograph using the automatic sampler. The sample loop was rinsed with distilled water for 2 min prior to sample loading. During ICE analysis, the eluent flow rate was 0.85 ml/min; for IC anion analysis, the eluent flow rate was 2 ml/min.

4. Results

Oxalic, glycolic and formic acids were anticipated to be the main products of the thermal oxidation of ethylene glycol (eq. (1)). A solution having a concentration of 10 ppm of each acid was subjected to ICE analysis. The acids were separated, as shown in fig. 2. Oxalic acid eluted first, followed by glycolic acid which was not completely separated from formic acid.

$$\underset{\substack{\text{ETHYLENE}\\ \text{GLYCOL}}}{HOCH_2CH_2OH} \xrightarrow[\text{HEAT}]{[O_2]} \underset{\substack{\text{OXALIC}\\ \text{ACID}}}{HOOCCOOH} + \underset{\substack{\text{GLYCOLIC}\\ \text{ACID}}}{HOCH_2COOH} + \underset{\substack{\text{FORMIC}\\ \text{ACID}}}{HCOOH} \qquad (1)$$

The primary possible degradation products from the thermal oxidation of propylene glycol solutions were anticipated to be pyruvic, lactic, formic and acetic acids (eq. (2)). A standard solution of 10 ppm of each of these acids was subjected to ICE analysis and the acids were separated as in fig. 3. In this case, lactic acid was not

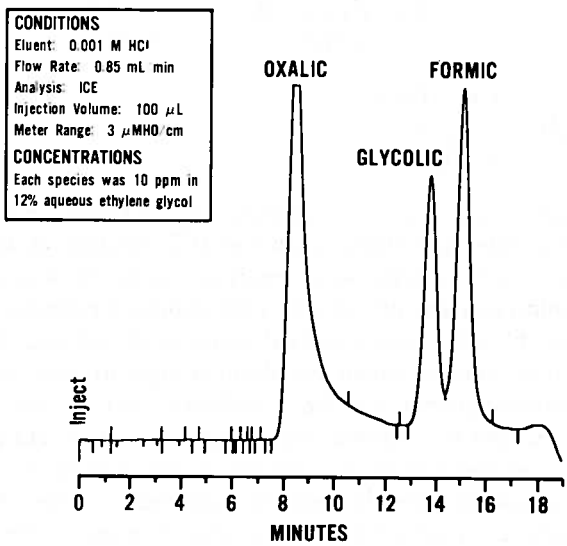

Fig. 2. Ion Chromatography Exclusion (ICE) method for separation of oxalic, glycolic, and formic acids.

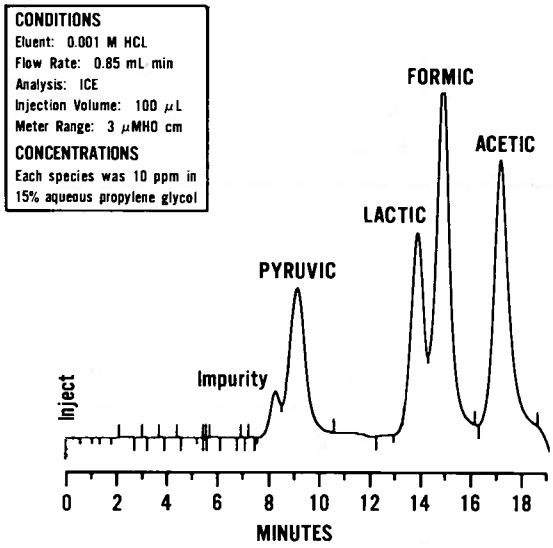

Fig. 3. Ion Chromatography Exclusion (ICE) method for separation of pyruvic, lactic, formic and acetic acids.

totally resolved from formic acid. However, pyruvic acid which eluted first and acetic acid which eluted last were totally separated from the lactic and formic acids.

$$\underset{\substack{\text{PROPYLENE}\\\text{GLYCOL}}}{CH_3CH(OH)CH_2OH} \xrightarrow[\text{HEAT}]{[O_2]} \underset{\substack{\text{PYRUVIC}\\\text{ACID}}}{CH_3COCOOH} + \underset{\substack{\text{LACTIC}\\\text{ACID}}}{CH_3CH(OH)COOH} + \underset{\substack{\text{FORMIC}\\\text{ACID}}}{HCOOH} + \underset{\substack{\text{ACETIC}\\\text{ACID}}}{CH_3COOH} \qquad (2)$$

In comparing figs. 2 and 3, it is apparent that glycolic and lactic acids had essentially identical retention times when the ICE method of analysis was used. However, these two acid anions were separated using IC anion analysis. Fig. 4 presents the IC anion analysis of: (a) a 10 ppm standard solution of oxalic, glycolic and formic acids; (b) a 10 ppm standard solution of pyruvic, lactic, formic and acetic acids; and (c) a solution which was about 40 ppm in lactic acid and 30 ppm in glycolic acid. Chromatogram (a) in fig. 4 indicates that glycolic and formic acids readily separated. Under the analysis conditions, oxalic acid had an extremely long retention time or was retained on the column. In chromatogram (b), it can be seen that lactic and acetic acids were not resolved under the IC anion analysis conditions. Formic and pyruvic acids were readily separated from each other, as well as from either lactic and acetic acids. Chromatogram (c) in fig. 4 shows the separation of lactic and glycolic acids.

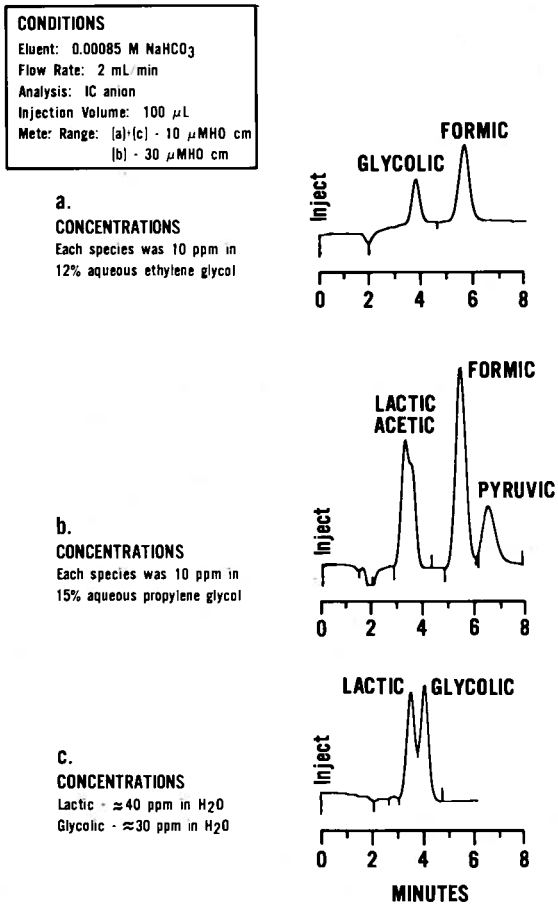

Fig. 4. Ion Chromatography (IC) anion analysis for the separation of: (a) glycolic and formic acids; (b) lactic, acetic, formic and pyruvic acids; (c) lactic and glycolic acids.

The fact that the proposed organic acid degradation products from either ethylene glycol or propylene glycol could be separated from each other indicated that the ICE method has applicability to the analysis of degraded glycol solutions. Solutions (9 mol/l) of ethylene glycol and of propylene glycol were heated in glass with aeration for 15 days or 12 weeks at 100°C. Some of these solutions contained metallic aluminum or copper; other solutions contained no metal. The pH values of the starting solutions prior to heating were 8.0 for ethylene glycol and 8.4 for propylene glycol. ICE analysis of the starting solutions showed no evidence of acid contaminants. After heating, samples of each of the solutions were subjected to ICE analysis. The qualitative results of the ethylene glycol and propylene glycol solutions heated for 12 weeks are given in figs. 5 and 6, respectively. As shown in fig. 5, the ethylene glycol solutions heated without a metal or with metallic copper present gave primarily glycolic acid as the major acidic degradation product, with minor amounts

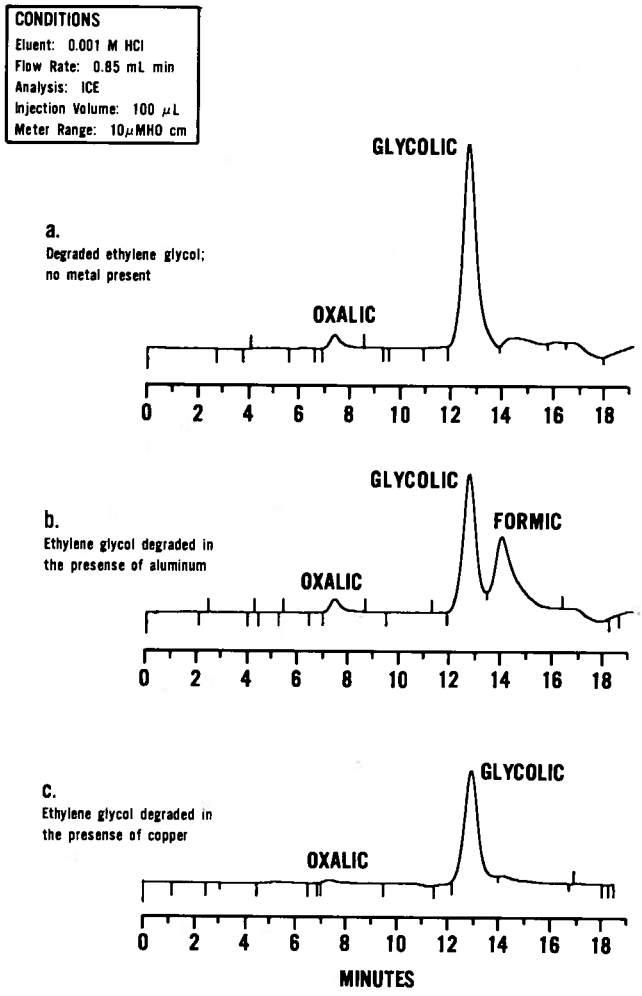

Fig. 5. ICE analysis of ethylene glycol solutions heated with aeration at 100°C for 12 weeks with or without a metal present. The concentrations were adjusted as necessary to keep the peak heights within the width of the recorder chart paper.

of oxalic acid. When heated in the presence of metallic aluminum, the ethylene glycol produced a considerable quantity of formic acid in addition to glycolic and oxalic acids. Glycolic acid remained the major acidic degradation product. In all cases, when propylene glycol solutions were thermally oxidized, the major acidic degradation product was lactic acid, with minor amounts of acetic and oxalic acids (fig. 6). In addition, when metallic aluminum was present in the propylene glycol solution, considerable quantities of formic acid were produced. Pyruvic acid was not observed in ICE analysis of the propylene glycol solutions.

The concentrations of the acidic degradation products in the ethylene glycol and propylene glycol solutions were quantified by ICE analysis using an external

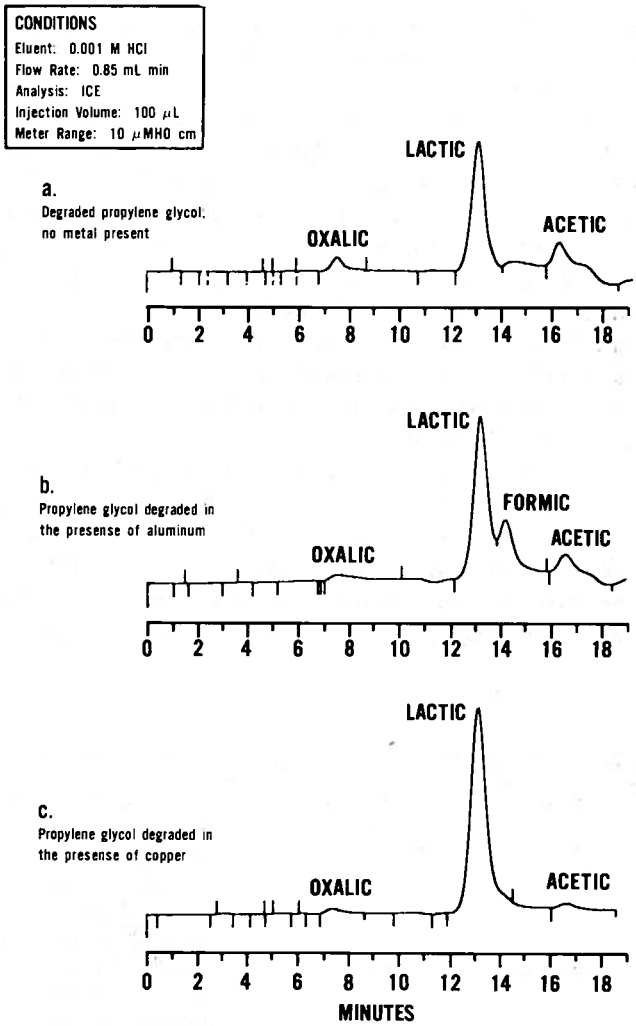

Fig. 6. ICE analysis of propylene glycol solutions heated with aeration at 100°C for 12 weeks with or without a metal present. The concentrations were adjusted as necessary to keep the peak heights within the width of the recorder chart paper.

calibration procedure with standard 10 ppm solutions of the acids in question. The results of all analyses of ethylene glycol and propylene glycol solutions are given in tables 1 and 2, respectively. These tables also give the pH values of the solutions. In the strictest sense, measured pH values may be quantitatively interpreted only in terms of hydrogen ion activity or concentration if the medium can be classified as a dilute aqueous solution of simple solutes [18]. Nevertheless, measurements of relative pH may be used to indicate a change in the acidity of the glycol-based antifreeze solutions. Bates [18] has indicated that relative hydrogen ion activity measurements

in aqueous alcohol solutions are possible, since the usual pH meters with glass electrodes display a theoretical response to hydrogen ions at alcohol concentrations up to about 90% by mass.

As indicated in tables 1 and 2, the amounts of degradation products increased with increased times of heating. The solutions heated in the presence of metallic copper underwent the greatest extent of degradation, as determined by the quantities of the degradation products present using the ICE method. The glycol solutions which did not contain a metal underwent the least extent of degradation.

The results of the pH measurements of the solutions heated for 15 days were consistent with the results of the ICE analyses. As the amount of degradation products increased, the pH values of the glycol solution were found to decrease. For example, in the case of both ethylene glycol and propylene glycol solutions heated in the presence of metallic copper, the solutions had the lowest pH values and also the greatest amount of degradation products.

The correlation between pH and amount of degradation products was not observed for the solutions analyzed after 12 weeks heating. In general, all the solutions heated for 12 weeks were found to have comparable pH values but considerably different amounts of degradation products (tables 1 and 2). This observation was attributed to the similar buffering range for these mixtures of weak organic acids and their conjugate bases formed by heating glycol solutions in the

Table 1
Comparison of pH and ICE analysis for degraded ethylene glycol solutions heated with aeration at 100°C

Heating period	Metal	Solution pH	Acidic degradation products [a]
15 days	none	6.7	oxalate – 0.6 ppm glycolate – 5 ppm formate – 4 ppm unknown substance – trace
	aluminum	6.6	oxalate – 4 ppm glycolate – 8 ppm formate – 2 ppm
	copper	4.9	oxalate – 6 ppm glycolate – 590 ppm formate – 45 ppm
12 weeks	none	3.7	oxalate – 3 ppm glycolate –110 ppm formate – 6 ppm
	aluminum	3.3	oxalate – 11 ppm glycolate – 290 ppm formate – 140 ppm
	copper	3.8	oxalate – trace [b] glycolate – 2200 ppm formate – trace

[a] As determined by ICE method of analysis using an external calibration.
[b] Estimated to be less than 0.5 ppm.

Table 2
Comparison of pH and ICE analysis for degraded propylene glycol solutions heated with aeration at 100°C

Heating period	Metal	Solution pH	Acidic degradation products [a]
15 days	none	7.0	lactate – trace [b] formate – 4 ppm acetate – 1 trace
	aluminum	6.5	lactate – 6 ppm formate – 7 ppm acetate – 9 ppm
	copper	5.0	lactate – 430 ppm formate – 25 ppm acetate – 15 ppm
12 weeks	none	4.1	oxalate – 3 ppm lactate – 84 ppm acetate – 17 ppm
	aluminum	3.9	oxalate – trace lactate – 190 ppm formate – 20 ppm acetate – 18 ppm
	copper	4.0	oxalate – trace lactate – 4680 ppm acetate – 170 ppm

[a] As determined by ICE method of anlaysis using an external calibration.
[b] Estimated to be less than 0.5 ppm.

presence of metallic copper and aluminum. In particular, as the ethylene glycol solutions were heated in the presence of copper, they gradually turned blue and greenish-blue in color, respectively. As heating continued, the colors darkened and precipitates formed. The precipitate from ethylene glycol was bright blue and that from propylene glycol was light green-blue.

The precipitates were collected, washed with water, and dried over a desiccant (silica gel). They were identified as copper (II) glycolate and copper (II) lactate, respectively, using infrared spectrophotometry. The infrared spectra were identical to those of compounds formed when glycolic and lactic acids were neutralized with copper (II) carbonate. In addition, the retention times of the precipitates, determined by ion chromatography, were identical to those of the synthesized copper (II) glycolate and copper (II) lactate, respectively.

5. Discussion

An analytical procedure using the ion-chromatography exclusion (ICE) method of analysis has been applied to the determination of acidic degradation products from aqueous glycol solutions. The ICE technique has a number of advantages for the analysis of the glycol solutions. The method detects these products at very low levels

where the response of the detector is linear with the concentrations of the compounds. This simplifies quantitation, since only a single standard solution of known concentration needs to be used. An important feature of the ICE technique is that the acidic degradation products may be readily detected in the presence of excessive quantities of ethylene glycol or propylene glycol. Since these glycols are nonionic, there is relatively little detector response as they elute through the detector. The glycols produce a baseline dip, since the glycol presence in the eluent lowers its conductivity.

The ICE method of analysis was chosen over the normal IC anion method, since the former could detect more acids. In particular, oxalic acid was not observed under the selected analysis conditions (fig. 3a), nor were lactic and acetic acids separable (fig. 4b). The IC anion method had the advantage of shorter analysis times than the ICE method for most of the acids in question. The IC anion method was useful to this study, since it was capable of resolving lactic and glycolic acids (fig. 4c).

It had been reported that glycolic acid was a degradation product from the thermal oxidation of propylene glycol [2]. When the heated propylene glycol solutions were analyzed using the IC anion method, the retention time of the major peak in the resulting chromatograms corresponded to that of lactate. Glycolate was not observed in these solutions. Addition of lactate solution to the degraded propylene glycol solution gave only one peak of increased intensity, while diluting the propylene glycol solution with a glycolate solution produced two peaks.

6. Summary and conclusions

The ion-chromatography liquid chromatographic method of analysis has been applied to the determination of acidic species in thermo-oxidatively degraded ethylene glycol and propylene glycol solutions. For either type of glycol solution, the ion-chromatography exclusion (ICE) method was suitable for separating and quantifying the degradation products. Products present in degraded ethylene glycol solutions were oxalic, glycolic and formic acids, with glycolic acid being the major constituent. Oxalic, lactic, formic and acetic acid were present in degraded propylene glycol solutions, with lactic acid being the major constituent. Heating the glycol solutions in the presence of metallic copper produced the greatest extent of degradation. Metallic aluminum increased the amount of formic acid produced in the case of both glycols. The results of the ICE analyses were compared with the pH measurements of the degraded solutions. The pH value is not a direct measure of the extent of degradation, since the degraded solutions had comparable pH values but considerably different amounts of degradation products.

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