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# Ion chromatographic identification and quantification of glycol degradation products

M. Madera<sup>a,\*</sup>, W. Höflinger<sup>a</sup>, R. Kadnar<sup>b</sup>

<sup>a</sup>*Institute for Chemical Engineering, Fuel and Environmental Technology, Vienna University of Technology, Getreidemarkt 9, A-1060 Vienna, Austria*

<sup>b</sup>*Laboratory for Exploration and Production, OMV-AG, Gerasdorferstr. 151, A-1210 Vienna, Austria*

## Abstract

In water-based heat transfer systems, frequently glycols are added to the water to obtain freeze protection. For this purpose, ethylene glycol (EG) is the most common substance used. When heated, the glycol will slowly degrade and the pH of the glycol–water mixture will decrease, leading to corrosion and foaming problems. Carboxylic acids were identified as the main degradation products. Quantification of the carboxylic acids is of importance to monitor the degradation reactions in order to identify hot spots or overheating, caused by severe heat exchanger scaling, where pH measurements will not be sufficient due to buffer substances added for corrosion protection. In this work, ion chromatographic methods have been developed to identify the main degradation products of EG in heat transfer systems and to monitor the degradation process. Possible acidic reaction products of EG are glycolic acid, glyoxylic acid, oxalic acid, acetic acid and formic acid. Separations with a Dionex AS9-HC column with Na<sub>2</sub>CO<sub>3</sub> eluents of differing concentrations showed that only trace amounts of carboxylic acids are present in aged heat transfer media. Oxalic acid can be quantified simultaneously to nitrite or molybdate which are added as corrosion inhibitors. A Dionex AS10 separation column with Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub> eluent enabled base line separation of glycolic acid, acetic acid and formic acid. Heat transfer media, which are operated in different heat transfer systems under different conditions, were analysed. A system was identified, where severe overheating due to fluid maldistribution in the heat exchanger took place.

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**Keywords:** Heat transfer; Ethylene glycol; Glycols; Carboxylic acids

## 1. Introduction

Ethylene glycol (EG) is frequently used in heat transfer systems for freeze and burst protection [1]. Due to its toxicity, some industries are replacing EG with propylene glycol.

Due to the corrosivity of glycols, corrosion in-

hibitors like molybdate or nitrite are added to protect the metals of the heat transfer system [2–4].

When heated, glycols will undergo degradation reactions. Carboxylic acids are reported in the literature as the main degradation products. Ethylene glycol is oxidized via glycol-aldehyde to glycolic acid, glyoxylic acid, oxalic acid and carbonic acid [5]. Radical reactions could result in acetic acid and formic acid in addition to polymeric products. A possible reaction pathway for the formation of acetic aldehyde which could be easily oxidized to acetic

\*Corresponding author. Fax: +43-1-40440-23323.

E-mail address: [martin.madera@omv.com](mailto:martin.madera@omv.com) (M. Madera).

acid is found in papers by Lindgren et al. [6] and Rudenko et al. [7].

The acidic degradation products were analyzed by ion-exclusion chromatography by Rossiter et al. [8,9]. In these papers, the appearance of acetic acid and glyoxalic acid in heat transfer media based on EG has not been reported.

Brown et al. report glyoxalic acid as a potential thermal degradation product [10]. Clifton et al. used pH measurements for monitoring glycol degradation [11].

In industry, mostly pH and reserve alkalinity are used as analytical techniques to control the degree of glycol degradation. Since most commercial inhibitors contain at least one substance to buffer the pH in the heat transfer system, after one or two reinhibitions, pH and reserve alkalinity will still give valuable information regarding corrosion protection. But no information can be obtained about the degree of glycol degradation.

In one heat transfer system at the OMV-AG, several problems have occurred. The most important operating parameters of the heat transfer circuit are found in Table 1. The water–EG-based heat transfer fluid turned from colorless to dark-brown. The nitrite-based inhibitor, which is added for corrosion protection, is depleted. The nitrite concentration decreased in 1 month from 300 to 10 ppm.

Since buffer substances and glycol degradation products buffer the pH in the system, pH would not provide information on the velocity of the glycol degradation. Neither would conductivity give reasonable results on the formation of acids because the inhibitors are based on sodium nitrite and caustic soda.

Table 1  
Operating parameters of the heat exchanger system

Temperature on the hot side of the heat transfer system	110 °C
Temperature on the cold side of the heat transfer system	70 °C
Volume of the heat transfer fluid	250 m <sup>3</sup>
Operating pressure	6 bar
Gas side temperature	460 °C
Flow of the heat transfer fluid	76 m <sup>3</sup> /h
Volume ratio EG/water	3:7
pH of the heat transfer fluid	8.5

In the current study, ion chromatographic methods are presented for identification and quantification of the acids present in EG-based heat transfer media. The main degradation products, which are found in the aged heat transfer fluid, were identified by combination of two methods. Acetic acid has been shown to be one of the major degradation products of EG.

## 2. Experimental

### 2.1. Instrumentation

A DX-300 gradient ion chromatographic system and a DX-120 isocratic ion chromatographic system (both Dionex, Sunnyvale, CA, USA) were used for this work. The components were detected by suppressed conductivity at 40 °C using a DS4-1 conductivity cell for the DX-120 system and a pulsed electrochemical detector in the conductivity mode for the DX-300 system.

For both systems, an ASRS-Ultra anion self-regenerating suppressor was used in the Autosuppression recycling mode with a current setting of 100 mA. Peaknet 5.1 software (Dionex) was applied for integration and calibration. An Ionpac AS9-HC was used with the DX-120 and AS10 columns (250×4 mm) were used with the DX-300 for separation. Ionpac AG9-HC and AG10 columns (50×4 mm) were used as guard columns.

### 2.2. Reagents

The chemical substances used, their providers and purities are listed in Table 2. All sample, standard and eluent dilutions were prepared using deionized water (18 M $\Omega$ ) which was obtained from a Milli-Q water purification system (Millipore).

### 2.3. Calibration standards

Stock solutions in a concentration of 1 g/l were prepared weekly by dissolving the acids in deionized water.

For calibration, working standard mixtures were

Table 2  
Substances, their purities and providers used in this work

Substance	Purity	Company
Di-sodium tetraborate decahydrate	GR	Merck, Darmstadt, Germany
Sodium carbonate	GR	Merck
Methanol	Uvasol for spectroscopy	Merck
Formic acid	98–100%, analytical reagent	Riedel-de Haen, Seelze, Germany
Acetic acid	99–100%, extra pure (glacial)	Riedel-de Haen
Glycolic acid	>99%, for synthesis	Merck–Schuchardt, Hohenbrunn, Germany
Glyoxylic acid	50% solution in water for synthesis	Merck–Schuchardt
Oxalic acid	GR	Merck, Darmstadt
Ethylene glycol	99+% (GC)	Aldrich, Steinheim, Germany

prepared daily from the stock solutions. Evaluation was carried out by calibration curves up to 25 mg/l.

#### 2.4. Ion chromatographic conditions

A volume of 25  $\mu$ l was injected and eluent flow was 1 ml/min for both chromatographic systems.

#### 2.5. Sample preparation

The samples were diluted with deionized water to the appropriate concentration and filtered through

Minisart SRP 25 0.45- $\mu$ m syringe filters which were obtained from Sartorius, Göttingen, Germany.

### 3. Results and discussion

#### 3.1. Problem detection and identification of oxalate

During the analysis of nitrite concentration in heat transfer fluids, several peaks were detected at the beginning of the chromatogram (Fig. 1). Since these peaks grew to an alarming size in one of the heating circuits, an identification of the detected substances

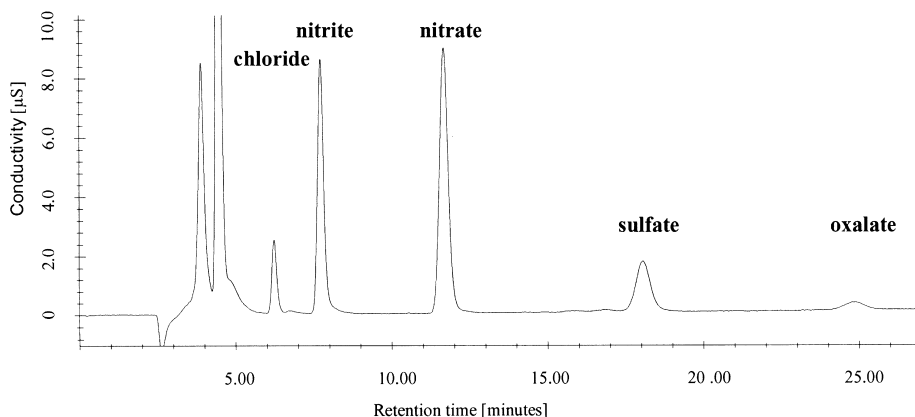


Fig. 1. Analysis of a heat transfer fluid with an AS9-HC separation column and 10 mM  $\text{Na}_2\text{CO}_3$  as eluent.

was of interest. The analytical conditions chosen for nitrite analysis (AS9-HC, isocratic  $\text{Na}_2\text{CO}_3$  eluent with a concentration of 10 mmol/l) showed two large peaks underlain with at least one smaller peak. After about 18 min, a further unidentified peak was detected.

Through injection of a standard and spiking of a sample, this peak could be identified as oxalate, one of the reported oxidation products of EG.

### 3.2. Separation with Ionpac AS10 separation column and identification of acetic acid

To separate the peaks at the beginning of the chromatogram obtained with the AS9-HC, the Ionpac AS10 column was chosen. As eluent, a 4.9 mmol  $\text{Na}_2\text{B}_4\text{O}_7$  solution was used. After 20 min, a 5-min column purge step using a 70 mmol  $\text{Na}_2\text{B}_4\text{O}_7$  solution was carried out.

Standard dilutions of formic acid, glycolic acid and glyoxylic acid showed a coelution of formate and glyoxylate with good separation of glycolate. When a sample of the aged heat transfer fluid was analyzed, instead of two peaks (one for glycolate and one for formate and glyoxylate) three major peaks were detected with several smaller peaks (Fig. 2).

Since only oxalic acid, formic acid, glycolic acid and glyoxylic acid are reported in the literature as

EG degradation products, an additional reaction product had to be assumed. A radical reaction which gives acetic aldehyde is found in literature. The aldehyde could be oxidized to acetic acid.

Consequently, standards of acetic acid were prepared. Using retention time and a spiked sample, the additional peak was identified as acetate.

### 3.3. Separation of formate and glyoxylate

Because no separation of formic acid and glyoxylic acid could be achieved with reasonable run time using the AS10 separation column, another approach had to be taken.

Since the separation mechanism differs for the AS10 and the AS9-HC, a separation of the acids with low eluent concentrations could be possible using the AS9-HC separation column. An 80% 1 mM sodium carbonate and 20% methanol solution was used as eluent. Formate and glyoxylate are separated under these conditions. Acetate and glycolate cannot be separated simultaneously but have already been identified using the AS10 column.

When a sample of the heat transfer fluid was analyzed using these conditions, only a very small peak appeared at the retention time of glyoxylate and the major peak was found for formate (Fig. 3).

From the results of both separation methods, it can

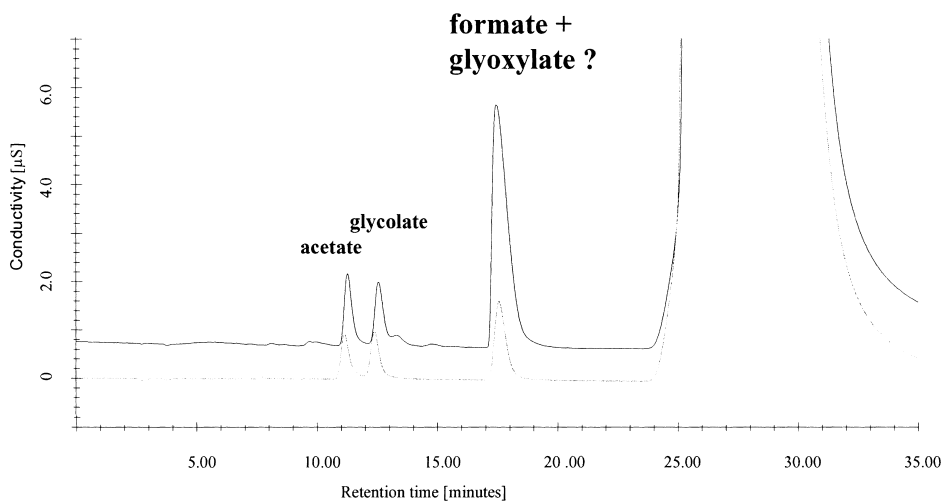


Fig. 2. Chromatogram of a 10 mg/l standard solution of acetic, glycolic and formic acids overlaid with the analysis of an aged heat transfer medium in a dilution of 1:25. An AS10 separation column with 4.9 mM  $\text{Na}_2\text{B}_4\text{O}_7$  solution was used as eluent. After 20 min, a column purge step using a 70 mM  $\text{Na}_2\text{B}_4\text{O}_7$  solution was carried out.

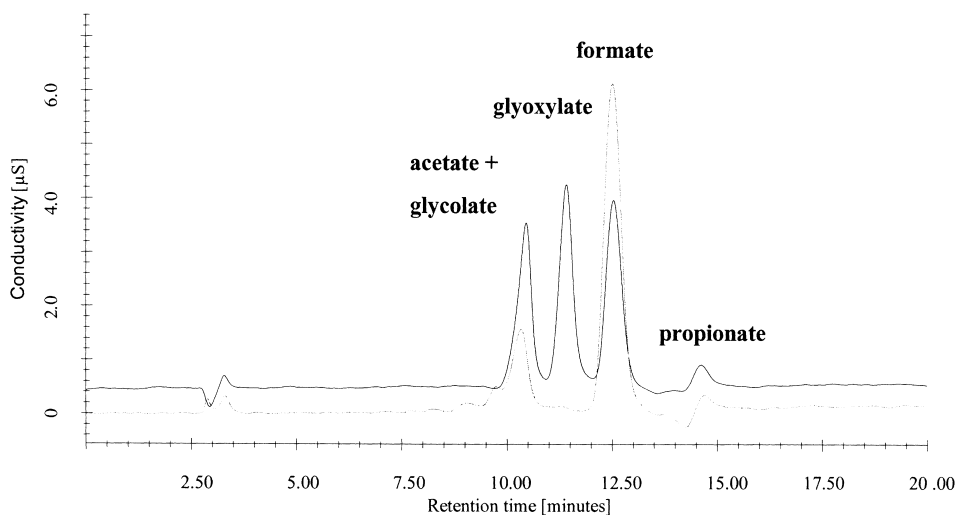


Fig. 3. A 10 mg/l standard solution of formate, glycolate, acetate, propionate and glyoxylate overlaid with an analysis of a sample of an aged heat transfer fluid, 1:25 dilution. An AS9-HC separation column was used for separation with 80% 10 mM  $\text{Na}_2\text{CO}_3$  and 20% methanol solution as eluent.

be concluded that the main degradation products of EG in this heating circuit are formic acid, acetic acid and glycolic acid. Oxalic acid is found in rather lower concentrations and only trace amounts of glyoxalic acid are present.

In Table 3, the concentrations determined for the main acidic degradation products are summarized.

#### 4. Conclusions

Formic acid, acetic acid and glycolic acid could be identified as the main degradation products of EG using the information provided by chromatograms obtained with AS10 and AS9-HC separation columns.

Oxalic acid which is also present at lower con-

centrations can be quantified simultaneously to nitrite and nitrate using an AS9-HC separation column with higher eluent concentration. Glyoxalic acid was not detected in significant amounts.

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Table 3

Maximum concentration of acidic degradation products of EG found in heat transfer fluids

Degradation product	Concentration (mg/l)
Formic acid	1920
Acetic acid	848
Glycolic acid	885
Oxalic acid	80

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