

Determination of inorganic corrosion inhibitors in heat transfer systems by ion chromatography

Rainer Kadnar^{a,*}, Martin Madera^b, Ruth Schlifke^b

^aLaboratory for Exploration and Production, OMV-AG, Gerasdorferstrasse 151, A-1210 Vienna, Austria

^bVienna University of Technology, Institute for Chemical Engineering, Fuel and Environmental Technology, Getreidemarkt 8, A-1060 Vienna, Austria

Abstract

In water-based heating and cooling circuits monoethylene glycol is frequently used as an anti-freezing agent. For corrosion protection inhibitors based on nitrite, molybdate or amines are commonly added. The determination of nitrite is usually performed by ion chromatography (IC) using an IonPac AS14 analytical column for the anion separation and a suppressed conductivity detection. Local overheating in some circuits causes degradation of ethylene glycol and leads to the formation of some organic acids. Under such chemical conditions the correct quantification of nitrite becomes a more complex analytical task due to the interference of the organic acids. This problem was solved using the IonPac AS9-HC separation column. In heat transfer systems, where nitrite is not stable, molybdate can be used as an inhibitor for corrosion protection. In these cases photometric methods are recommended for monitoring the molybdate concentration. However, due to the dark brown colour and turbidity of aged glycol solutions photometric methods were not applicable. Thus the use of IC offered a reliable alternative for the determination of molybdate, also in aged glycol solutions, using IonPac AS9-HC or AS14 columns for separation.

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1. Introduction

More than 60 heating and cooling circuits are operated by the OMV-AG. Most of them use monoethylene glycol (MEG)–water mixtures as heat transfer medium and corrosion inhibitors based on nitrite. To ensure sufficient corrosion protection, periodical monitoring routines for the nitrite concentration are performed. Most of the heat transfer

systems work without problems and normally the heat transfer fluids are clear, contain nearly no particles and are stable for many years.

However, the input of impurities and the presence of local overheating of the heat transfer fluid caused several problems in some of the heating circuits. Specifically the following problems were observed:

- (i) They became dark brown coloured and turbid, with a characteristic odour of MEG-degradation products.
- (ii) The concentration of organic acids in the solution increased dramatically.
- (iii) Nitrite was consumed rapidly, while the nitrate concentration in the systems did not change

*Corresponding author. Fax: +43-1-40440-20995.

E-mail address: rainer.kadnar@omv.com (R. Kadnar).

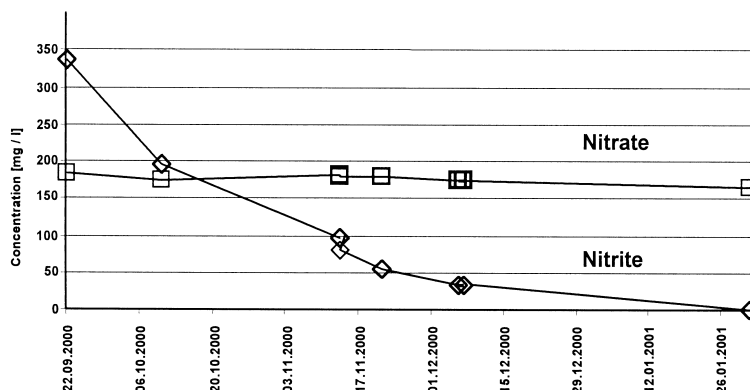


Fig. 1. Nitrite degradation in heating circuit HA. Within 4 months nitrite concentration was reduced from 340 mg/l to almost zero.

considerably (Fig. 1). Gaseous components like hydrogen or dinitrogen oxide were generated.

Ion chromatography (IC) has been used for years in corrosion science. Several publications deal with the use of IC for measuring the concentration of corrosion inhibitors in concrete [1,2]. Another interesting application of IC in corrosion science is the study of corrosion deposits, dissolved metal compounds and degradation products [3–11]. In water-based heat transfer fluids IC is normally used for the determination of the concentration of corrosive ions like chloride, sulfate or lower-molecular-mass organic acids [12–24]. In glycol-based heat transfer fluids especially Rossiter and co-workers have used IC for the determination and quantification of the thermal degradation products of ethylene and propylene glycol [25,26]. The use of IC to monitor corrosion inhibitors was published before for amines in oil and gas industry [27] and in steam–water circuits [28] and in hydraulic fluids [29].

For many years the quantification of the anions like chloride, nitrite and nitrate in ethylene glycol based heat transfer media has been performed by IC in our laboratory using the IonPac AS14 separation column. However, the quantification of chloride and nitrite has become more difficult with the aging of the heat transfer fluids due to the interference of lower carboxylic acids. So an alternative method for the accurate determination of these anions at concentration levels below 100 ppm in degraded samples was required. In the present work this analytical problem was successfully solved by using an IonPac

AS9-HC column for an appropriate separation of the anions.

Another task was to find a more stable inhibitor for our problematic heating circuits. After testing some products, a molybdate-based inhibitor was selected for these heating circuits. This molybdate inhibitor showed sufficient corrosion protection as well as good stability at temperatures up to 150 °C. A photometric method was recommended for the determination of molybdate in aqueous solutions. Nevertheless, the application of photometric methods is not applicable due to the dark brown colour and turbidity of aged heat transfer fluids. Methods for monitoring the molybdate concentration using IC were therefore developed. Both tested columns, the IonPac AS14 and AS9-HC proved to be useful for this purpose together with a suppressed conductivity detection.

2. Experimental

2.1. Instrumentation

The equipment used for this work was a DX-120 isocratic IC system (Dionex, Sunnyvale, CA, USA). The separated anion components were detected by suppressed conductivity at 40 °C, using a DS4-1 conductivity cell. An anion self-regenerating suppressor ASRS-Ultra (Dionex) was used in the auto suppression recycling mode with a current setting of 100 mA. Integration and calibration were performed

Table 1
Method specific parameters

Parameter	Method 1	Method 2	Method 3	Method 4
Guard column	AG14	AG9-HC	AG14	AG9-HC
Analytical column	AS14	AS9-HC	AS14	AS9-HC
Eluent	3.5 mM Na ₂ CO ₃ – 1 mM NaHCO ₃	10 mM Na ₂ CO ₃	5 mM Na ₂ CO ₃	20 mM Na ₂ CO ₃
Eluent flow-rate (ml/min)	1	1	1	1
Expected conductivity (μS)	18–20	28–30	20–22	38–40
Injection volume (μl)	25	25	25	25

by PeakNet 5.1 software (Dionex). The chromatographic operating conditions used in these methods are summarized in Table 1.

Columns used for separation were IonPac AS14 and AS9-HC (250×4 mm) separator columns and IonPac AG14 and AG9-HC (50×4 mm) guard columns (all Dionex).

2.2. Reagents

All reagents used were of analytical-reagent grade (Merck, Darmstadt, Germany). Deionized water (18 MΩ) obtained from a Milli-Q water purification system (Millipore, Billerica, MA, USA) was employed throughout.

2.3. Calibration standards

Stock standard solutions for chloride, nitrite and nitrate (1 g/l) were from Merck. Molybdate standards were prepared by dissolving analytical-grade sodium molybdate dihydrate (Merck) in deionized water.

Anion working standard mixtures for calibration were prepared daily from the stock standard solutions. Evaluation was carried out by calibration curves up to 20 mg/l nitrite, nitrate and molybdate, respectively, up to 4 mg/l chloride.

2.4. Sample preparation

All samples were diluted with deionized water and

then filtered through 0.45-μm syringe filters Minisart SRP 25 (Sartorius, Göttingen, Germany).

3. Results and discussion

3.1. Method 1: Determination of nitrite with the IonPac AS14 separation column

The IonPac AS14 analytical column with carbonate–hydrogencarbonate eluents [30] has been efficiently used in our laboratory for many years for the determination of anions in aqueous samples with low matrix effects. This method is also applicable for the determination of chloride, nitrite, nitrate, sulfate and oxalate in MEG–water mixtures.

Fig. 2 shows chromatograms of samples taken from two different circuits. An efficient separation of chloride, nitrite and nitrate was achieved in less than 6 min. The samples were diluted 1:100. Sample CB was taken from a cooling circuit, containing 48% (v/v) MEG and 1350 mg/l nitrite. The content of carboxylic acids and chloride is low. Sample HB was obtained from a heater, containing 45% (v/v) MEG and 970 mg/l nitrite. The liquid sample was contaminated with chloride (224 mg/l) and contains organic acids in a concentration range typical for aged heat transfer fluids. In these kind of samples the anion detection and quantification can be reliably performed without any interference problems.

3.2. Method 2: Determination of nitrite with the IonPac AS9-HC separation column

In severely thermally degraded heat transfer fluids

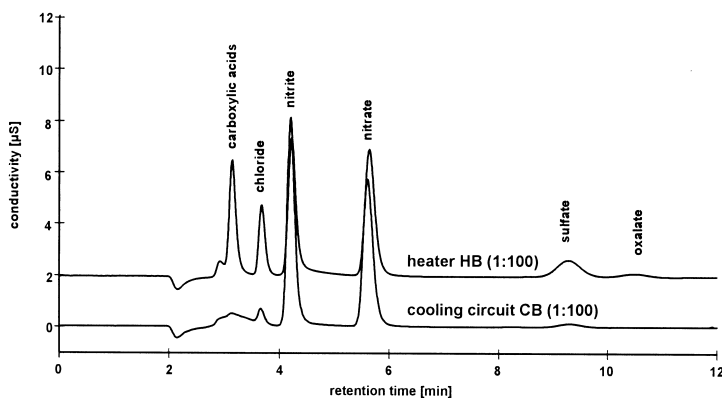


Fig. 2. Separation of anions in heat transfer fluids with AS14 and 3.5 mM Na_2CO_3 –1 mM NaHCO_3 .

the concentration of carboxylic acids can become very high, so that a baseline separation of the carboxylic acids, chloride and nitrite cannot be achieved, using the AS14 analytical column.

Looking for an alternative method with better separation, AS9-HC [31], a high-capacity column was also tested. Using 10 mM Na_2CO_3 as eluent, all anions of interest were baseline separated within 20 min. Even high concentrations of organic acids in the sample do not interfere in the quantification of the early eluted anions.

Fig. 3 shows chromatograms of a sample of heating circuit HA, where nitrite and glycol degradation occurs. HA contains 32% (v/v) MEG and 91 mg/l nitrite. The content of carboxylic acids in the

heat exchange medium exceeds 3 g/l. Sample dilution was 1:25.

3.3. Method 3: Determination of molybdate with the IonPac AS14 separation column

Weiss [32] described the determination of molybdate using different separation columns, among others the AS4A (Dionex). Many laboratories use the AS14, which has similar separation properties, for the determination of standard anions. Using 5 mM Na_2CO_3 as eluent, it was possible to separate molybdate within a short analysis time of 8 min (see Fig. 4). No analytical problems were detected.

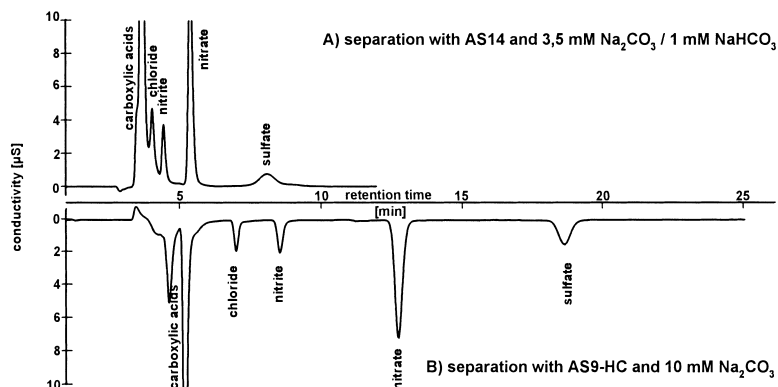


Fig. 3. Separation of anions in a sample from heating circuit HA (sample dilution was 1:25)—comparison of methods 1 and 2.

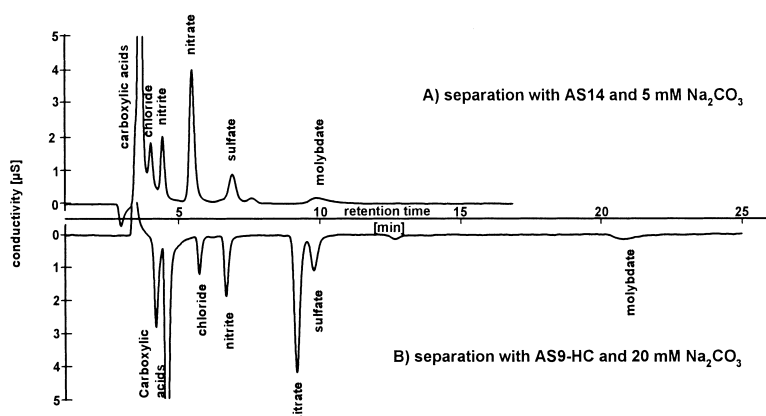


Fig. 4. Separation of anions in a molybdate spiked sample from heating circuit HA (sample dilution was 1:50)—comparison of methods 3 and 4.

3.4. Method 4: Simultaneous determination of nitrite and molybdate with the IonPac AS9-HC separation column

The AS9-HC separation column with 20 mM Na_2CO_3 as eluent offers the possibility to determine nitrite and molybdate simultaneously. Total analysis time is approximately 25 min. Fig. 4 shows a comparison of chromatograms obtained with a spiked sample collected from heating circuit HA. The sample was previously diluted 1:50. The analyte concentration in the diluted sample was 1 mg/l chloride, 3 mg/l nitrite and 4 mg/l molybdate.

Chromatograms for some commercially available

corrosion inhibitor samples for heating and cooling circuits containing different active components are shown in Fig. 5. Inhibitor N is a mixture of different salts containing nitrite and nitrate. Inhibitor P is based on nitrite and the inhibitor D contains molybdate as anti-corrosive component. Chromatographic separation was performed using method 4.

4. Conclusion

Monitoring of inorganic corrosion inhibitors, like nitrite or molybdate in heat transfer systems can be reliably performed by IC.

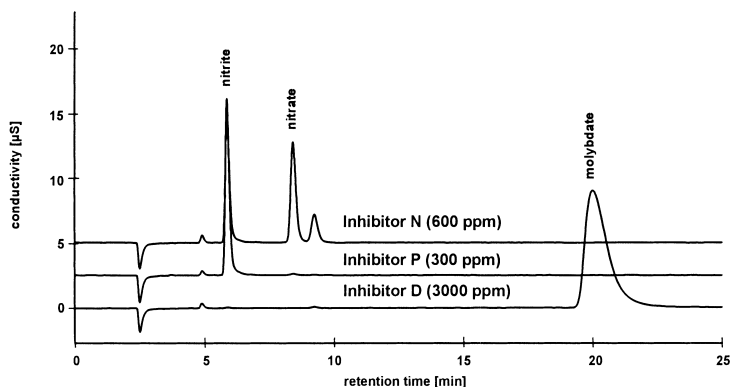


Fig. 5. Comparison of some commercial available inhibitors. Separation of anions with AS9-HC and 20 mM Na_2CO_3 .

Both analytical columns, AS14 and AS9-HC can be used for the efficient separation of the anions of interest. Using the AS14 under standard conditions, the correct quantification of chloride and nitrite may be more time consuming, if enhanced amounts of small carboxylic acids (several g/l) are present in the sample.

The use of AS9-HC extends the analysis time, but the separation of all anions of interest is good. This column enables the simultaneous determination of nitrite and molybdate, even in severely degraded heat transfer fluids.

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