Journal of Chromatography A, 1229 (2012) 223–229

Contents lists available at SciVerse ScienceDirect

Journal of Chromatography A

journal homepage: www.elsevier.com/locate/chroma

Ultra-trace level analysis of morpholine, cyclohexylamine, and diethylaminoethanol in steam condensate by gas chromatography with multi-mode inlet, and flame ionization detection

J. Luong[a,b], R.A. Shellie[a,*], H. Cortes[a,c], R. Gras[b], T. Hayward[b]

[a] Australian Centre for Research on Separation Science (ACROSS), University of Tasmania, Private Bag 75, Hobart, Tasmania 7001, Australia
[b] Dow Chemical Canada ULC, Highway 15, Fort Saskatchewan, Alberta T8L 2P4, Canada
[c] HJ Cortes Consulting LLC, Midland, MI 48642, USA

ARTICLE INFO

Article history:
Received 5 December 2011
Received in revised form 16 January 2012
Accepted 16 January 2012
Available online 24 January 2012

Keywords:
Gas chromatography
Water treatment process
Morpholine
Cyclohexylamine
Diethylaminoethanol
Amine

ABSTRACT

Steam condensate water treatment is a vital and integral part of the overall cooling water treatment process. Steam condensate often contains varying levels of carbon dioxide and oxygen which acts as an oxidizer. Carbon dioxide forms corrosive carbonic acid when dissolved in condensed steam. To neutralize the harmful effect of the carbonic acid, volatile amine compounds such as morpholine, cyclohexylamine, and diethylaminoethanol are often employed as part of a strategy to control corrosion in the water treatment process. Due to the high stability of these compounds in a water matrix, the indirect addition of such chemicals into the process via steam condensate often results in their presence throughout the process and even into the final product. It is therefore important to understand the impact of these chemicals and their fate within a chemical plant. The ability to analyze such compounds by gas chromatography has historically been difficult due to the lack of chromatographic system inertness at the trace level concentrations especially in an aqueous matrix. Here a highly sensitive, practical, and reliable gas chromatographic approach is described for the determination of morpholine, cyclohexylamine, and diethylaminoethanol in steam condensate at the part-per-billion (ppb) levels. The approach does not require any sample enrichment or derivatization. The technique employs a multi-mode inlet operating in pulsed splitless mode with programmed inlet temperature for sample introduction, an inert base-deactivated capillary column for solute separation and flame ionization detection. Chromatographic performance was further enhanced by the incorporation of 2-propanol as a co-solvent. Detection limits for morpholine, cyclohexylamine, diethylaminoethanol were established to be 100 ppb (v/v), with relative standard deviations (RSD) of less than 6% at the 95% confidence level ($n = 20$) and a percent recovery of 96% or higher for the solutes of interest over a range of 0.1–100 ppm (v/v). A complete analysis can be conducted in less than 10 min.

1. Introduction

Steam condensate water treatment is a vital and integral part of the overall industrial cooling water treatment process. For example, the treatment is employed in conventional and nuclear power generation plants where large quantities of water need to be processed on a daily basis to ensure operational safety. Another example is the use of the treatment in acute care medical facilities where the monitoring of the agents used for water treatment are conducted to safeguard the health of the patients at the facilities.

1.1. Background in cooling water treatment process

Finding ways to operate a large cooling water system economically while maximizing heat transfer is a complex and challenging task. Typically, problems encountered in doing so involve:

1.1.1. Corrosion

Most metals used in cooling water systems are very susceptible to corrosion. Keeping the vessel surface clean is the most important aspect of preventing corrosion, since under-deposit corrosion can take place resulting in very serious damage. Corrosion can be either localized or wide spread and leads to severe pitting and rapid equipment failure. Anti-corrosive chemicals such as zinc-phosphonates, molybdenate, and tolyltriazol are often used to suppress or eliminate corrosion [1–3].

---

[*] Corresponding author. Tel.: +61 3 6226 7656; fax: +61 3 6226 2858.
E-mail address: Robert.Shellie@utas.edu.au (R.A. Shellie).

0021-9673/$ – see front matter
doi:10.1016/j.chroma.2012.01.041

1.1.2. Scale

Minerals such as magnesium and calcium are relatively insoluble in water and can form scale deposits when exposed to conditions such as those commonly encountered in cooling water systems. A thin layer of scale can reduce heat exchanger efficiency. Scale formation can be controlled by inhibitors such as threshold inhibition chemicals and scale control polymers. Some examples of these include phosphonate blends and polyphosphates, which prevent scale formation by keeping the scale-forming minerals in solution [4].

1.1.3. Fouling

Solid material such as airborne debris, corrosion products, biofouling process in-leakage, and suspended solids accumulate in the system and lead to a loss in efficiency and equipment deterioration. Synthetic polymers and dispersants are used to prevent foulants from setting and to remove fouling deposits that have already been formed [4].

1.1.4. Corrosion mechanism

Steam condensate treatment is an integral and vital part of the overall water treatment process. Carbon dioxide and oxygen cause most condensate system corrosion. Oxygen acts as an oxidizer, while carbon dioxide, upon dissolving in water, forms corrosive carbonic acid, causing both weakening and failure of metal and formation of corrosion products which add to the boiler deposits. Oxygen enhances the corrosion rate and tends to produce localized pitting. Ammonia, combined with oxygen, attacks copper alloys [1–8].

Carbonic acid is the most common source of acidity in water. Carbon dioxide enters the water through equilibrium with the atmosphere:

$$CO_2(aq) \leftrightharpoons CO_2(g)$$

CO_2 (aqueous) then undergoes an important inorganic equilibrium reaction:

$$CO_2(aq) + H_2O(l) \leftrightharpoons H_2CO_3(aq) \quad K_c = 1.3 \times 10^{-3}$$

Only a small fraction of H_2CO_3 exists as carbonic acid.

Dissolved carbon dioxide, in the form of H_2CO_3, may lose up to two protons through the acid equilibria:

$$H_2CO_3(aq) + H_2O(l) \leftrightharpoons H_3O^+(aq) + HCO_3{}^-(aq) \quad K_{a1} = 4.46 \times 10^{-7}$$

$$HCO_3{}^-(aq) + H_2O(l) \leftrightharpoons H_3O^+(aq) + CO_3{}^{2-}(aq)$$

$$K_{a2} = 4.69 \times 10^{-11}$$

The protons liberated to the water decrease the pH which accounts for the low pH of 5.65 of any unbuffered and untreated water in equilibrium with the atmosphere.

The presence of carbonic acid lowers the pH of the water causing weakening and failure of metal and formation of corrosion products. If oxygen is present along with the carbon dioxide, the corrosion rate is much greater and localized pitting or even widespread corrosion can easily occur [9–11].

To remove oxygen, sulfites such as sodium metabisulfite, sodium bisulfite, or sodium sulfite are often used [10]. To neutralize the carbonic acid, volatile amine compounds such as morpholine (CAS 110-91-8), cyclohexylamine (CAS 108-91-8), and diethylaminoethanol (CAS 100-37-8) are often added to the steam condensate as part of a strategy to control corrosion in the water treatment process. The stability of these amines in water, however, often results in the indirect addition of such compounds into the process streams. If the concentrations of the amines are high enough, these compounds can often work their way through the process and even into the final product. Therefore, it is important to understand their effect and movement throughout the process streams.

The aforementioned compounds of interest can be analyzed by an array of analytical techniques such as high-pressure liquid chromatography [12–14], ion chromatography [15,16], or spectrophotometry [17] with detection limits in the low part-per-million (ppm) range. Some issues encountered with the methods cited include the constraints that not all the target compounds can be analyzed by the techniques in one single analysis. Further, sample enrichment or derivatization might be required which can add another level of complexity to method development and implementation. The ability to analyze said compounds by gas chromatography has historically been difficult at the detection limits similar to the techniques cited due to the lack of overall chromatographic system inertness like solute adsorptivity/absorptivity within the inlet liner, chemical reactivity between solutes and stationary phase used, and particularly the matrix effects involved in aqueous samples [18–21].

A practical gas chromatographic method without the need for sample enrichment or derivatization for measuring part-per-billion levels of morpholine, cyclohexylamine, and diethylaminoethanol in steam condensate samples has been successfully developed. The method was found to be reliable and suitable for field implementation in water treatment facilities. This paper summarizes the development and analytical performance of the methodology described herein.

2. Experimental

An Agilent 7890 gas chromatograph (Agilent Technologies, Wilmington, Delaware, USA) was used for the development of this analytical technique. This gas chromatograph was equipped with an Agilent G-4513A autosampler and an Agilent G-4514A tray, an Agilent Multi-Mode Inlet, and a flame ionization detector. A 30 m × 0.32 mm i.d. × 5 μm Rtx-Volatileamines (Restek Corporation, Bellefonte, PA, USA) capillary column was used for all analyses. An Ultra-Inert splitless inlet liner from Agilent (PN#5190-3163) was also used. Chromatographic data was collected using Agilent ChemStation B.03.01 Service Pack 1. Instrument operating conditions are reported in Table 1.

Reagent Plus grade cyclohexylamine, ACS grade morpholine, GC grade diethylaminoethanol, and ACS grade 2-propanol were all obtained from Aldrich Chemical Company Inc. (Oakville, ON, Canada). Deionized water was generated on site. Samples were prepared by first filtering with a 0.2 μm Teflon particle filter for the removal of suspended particles and subsequently diluted at a 1:1 ratio with 2-propanol for analysis.

Statistical data treatment was conducted using Microsoft Excel 2010. Relative standard deviation at the 95% confidence level was calculated by multiplying %RSD (standard deviation/mean × 100) with a *t*-value of 2.09 ($n = 20$, $d_f = 19$).

3. Results and discussion

When analyzing for anti-corrosion agents like morpholine, cyclohexylamine, and diethylaminoethanol in an aqueous matrix by gas chromatography, two main concerns must be addressed. The first is the adsorptivity of the solutes of interest by the gas chromatographic system. The second involves the interaction of the solute with the water matrix. Both matters are addressed below:

3.1. Adsorptivity

3.1.1. Column selection

The column selected for the analysis of said solutes by gas chromatography was the recently commercialized Rtx-Volatileamines.

Table 1

Analytical conditions for the analysis of ultra-trace part-per-billion level of morpholine, cyclohexylamine, and diethylaminoethanol by pulsed splitless, multi-mode inlet, GC/FID.

Instrument	Agilent 7890 GC										
Multi-mode inlet	Mode Pulsed splitless	Temperature	120 °C (0.3 min) to 250 °C @ 600 °C/min, hold 2 min							Liner	Ultra-trace, splitless P/N 5190-3163
GC conditions	Carrier gas Helium, 30 psig inlet pressure	Temperature	40 °C (2 min) to 250 °C @ 20 °C/min, hold 5 min							Column	30 m × 0.32 mm i.d. × 5 µm Rtx-Volatileamines
FID	Hydrogen 35 mL/min	Air	350 mL/min							Nitrogen (auxiliary)	25 mL/min
Autosampler	Mode Fast injection	Injection volume	5 mL	Rinse solvent	2-Propanol	Pre-rinse	3	Sample rinse	3	Pump times	3

The column offers a high degree of resistance to hydrolysis, often caused by the aqueous matrix and shows good stability as well as inertness in continuous use over a period of more than nine months. It is critical to select an inert stationary phase that aids in minimizing column adsorption activity towards amine compounds to achieve the lowest level of detection limit possible [22,23].

3.1.2. *Liner selection*

Initially, a SGE Focusliner PN# 092219 was used (SGE Analytical Science, Australia). However, the chromatogram obtained with this liner, while adequate at first, showed asymmetric peak shapes after fifty injections over a course of one-month period. This is likely due to adsorption of the amines on the hydrolyzed quartz wool surface. A number of other liners were investigated in an attempt to find one that would show less adsorptivity towards amines with an acceptable reproducibility of less than 5% RSD. The Cyclosplitter (RK20706, Restek Corporation, USA), split/splitless with glass wool (P/N 19251-60540, Agilent Technologies, USA), cup splitter (P/N RK20709, Restek Corporation, USA), base deactivated liner (P/N RK 20782-211.5, Restek Corporation, USA), and the newly introduced Ultra-inert Liner (P/N 5190-3163, Agilent Technologies, USA) were evaluated.

The Ultra-inert liner was found to deliver the best overall and sustained performance for the application described. According to the manufacturer, the Ultra-inert liner was treated with a proprietary surface deactivation process for both the quartz wool used and the inner surface of the liner, thereby, offering a high degree of inertness towards reactive compounds and resistance to hydrolysis for aqueous matrix [24]. Fig. 1 shows an overlay of chromatograms of every tenth analysis of 100 analyses performed at a rate of three analyses per day, over approximately one-month period of 25 ppm (v/v) each of morpholine, cyclohexylamine, and diethylaminoethanol in a 1:1 2-propanol/water matrix obtained under the conditions described. The RSD obtained for all solutes was less than 0.005% for retention time and less than 2% for area counts, highlighting the reliability of the analytical system.

Clearly, the liner and column selected contributed to the overall chromatographic performance of the methodology developed.

3.1.3. *Impact of mass of solute injected*

With amine compounds, regardless of how inert the chromatographic system is, there will be some degree of adsorption/absorption [22,23]. This can cause non-linear response behavior for the solute of interest, particularly at the ppb concentration level. Increasing the mass of solutes delivered can aid in overcoming this effect as long as the adsorptivity of the analytical system remains relatively constant between system maintenance schedules. Large-volume injection (LVI) and cool on-column techniques were considered, but not implemented since their performance are negatively impacted by the presence of water soluble inorganic salts such as calcium carbonate, magnesium sulfate, known to be present in reactor cooling water, and steam condensate. The approach chosen for this method to ensure adsorption effect can be minimized is the use of a recently commercialized multi-mode inlet to deliver sufficient amount of solute to overcome any adsorption that might exist in the chromatographic system. The multi-mode inlet is a temperature programmable inlet for gas chromatography, capable of attaining a heating rate of 900 °C/min with a maximum inlet temperature of 450 °C. Further, the inlet is capable of conducting pulsed splitless injection, where the initial pressure of the inlet can be set at a much higher level than operating conditions to minimize the expansion volume produced from the injected sample. Unlike cool-on column, LVI, or Programable Temperature Vaporizer (PTV) inlets, the multi-mode inlet's consumables are interchangeable with standard split/spliless inlets often found in contemporary gas

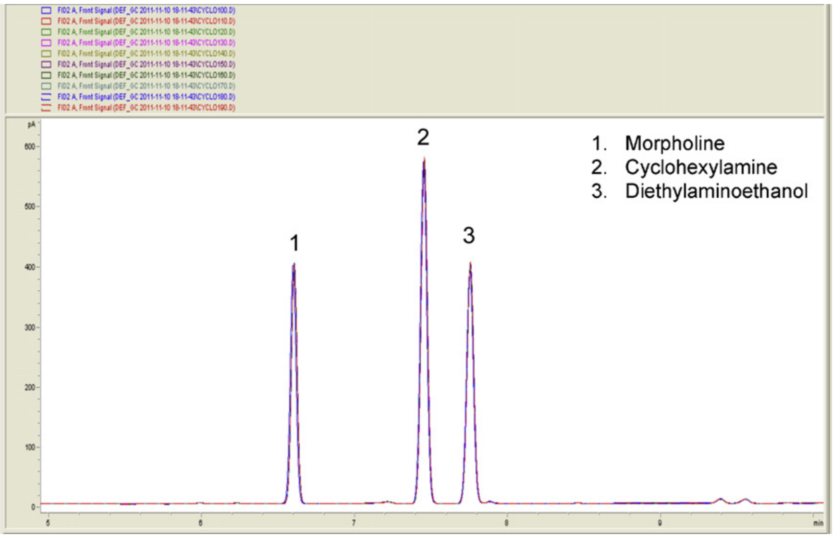

Fig. 1. Overlay of chromatograms of every tenth analysis of 100 analyses performed at a rate of three analyses per day, over approximately one-month period of 25 ppm (v/v) each of morpholine, cyclohexylamine, and diethylaminoethanol in a 1:1 2-propanol/water matrix.

chromatographs. This can improve field operation efficiency and lower cost of long term ownership.

With extensive method optimization, the combination of varying the inlet temperature during sample introduction and the pulsing of inlet pressure of up to 60 psig for a period of 1 min affords the delivery of up to 5 μL of the sample without overloading the volume of the liner. In terms of varying the inlet temperature during sample introduction, the strategy involved using a relatively cold temperature at first, sufficient to transfer the matrix of 2-propanol/water mix at 120 °C without causing a large expansion of vapor volume that can overload the liner capacity, then rapidly heating the inlet to the desired temperature of 250 °C at a rate of 600 °C/min to ensure the solutes could be vaporized and transferred effectively.

The oven temperature was held at 40 °C during the entire period of solutes and solvent transfer to maximize the focusing effect for the solutes and solvents involved at the head of the analytical column.

Unlike the liners used with the commercially available cool on-column or PTV inlets, the liner of the multi-mode inlet has a substantially higher internal volume, by at least a factor of four to five times, making the multi-mode inlet ideal for the implementation of the injection concepts proposed. The liner also aids in preventing the accumulation of inorganic salts like calcium carbonate in the column which can degrade chromatographic performance over extended use. Fig. 2 shows a chromatogram of 100 ppm (v/v) of morpholine, cyclohexylamine, and diethylaminoethanol in a 1:1 2-propanol/water matrix obtained under the conditions described. Note the respectable peak symmetry obtained for the solutes of interest.

3.2. Water matrix and the co-solvent approach

The co-solvent technique has been successfully utilized to decrease the effect of water on volatile polar solutes in gas chromatography [25,26]. The use of a co-solvent results in a reduced flood zone of the water matrix and alters the vaporization process of the sample. This results in improved peak symmetry. The co-solvent used should be volatile, polar and miscible with water [26]. 2-Propanol was used for this application in a 1:1 ratio with water. 2-Propanol was chosen for its small vaporization volume.

3.3. Analytical performance

Using the conditions outlined in Table 1, the technique was evaluated for analytical performance. Fig. 3 shows a chromatogram of a

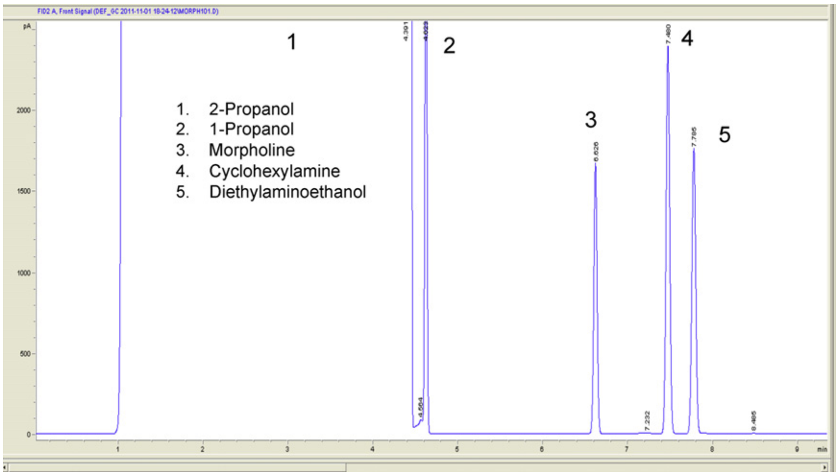

Fig. 2. Chromatogram of 100 ppm (v/v) of morpholine, cyclohexylamine, and diethylaminoethanol in a 1:1 2-propanol/water matrix.

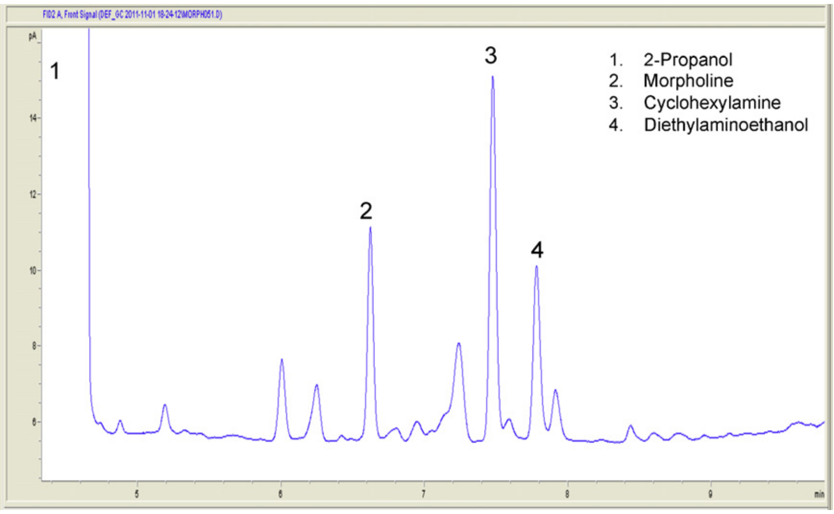

Fig. 3. Chromatogram of a 500 ppb (v/v) each of a mixed standard in 1:1 2-propanol/untreated steam condensate.

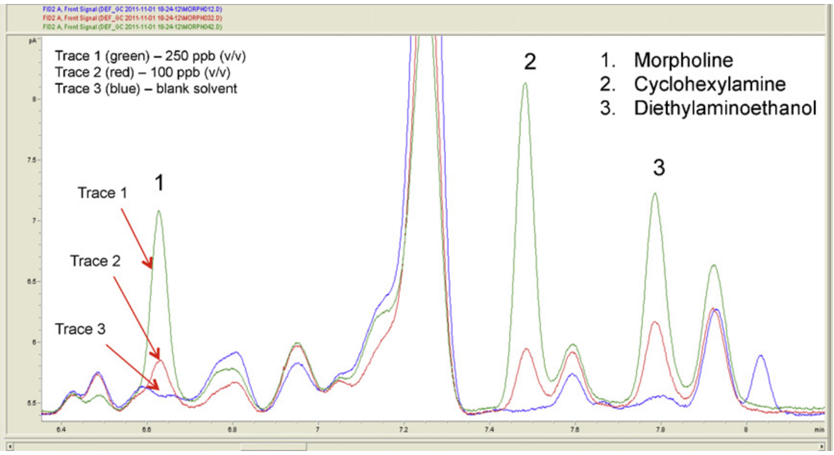

Fig. 4. Overlay of blank, 100 ppb (v/v) and 250 ppb (v/v) each of morpholine, cyclohexylamine, and diethylaminoethanol in a 1:1 2-propanol/water matrix.

500 ppb (v/v) each of a mixed standard in 1:1 2-propanol/untreated steam condensate using the procedure described. Total analysis time was determined to be less than 10 min.

The practical detection limits obtained were 100 ppb (v/v) for all solutes involved, as depicted in an overlay shown in Fig. 4. This is 20 times more sensitive than results reported by the American Society Testing Material's reference gas chromatographic method ASTM-D-4983-89 [13] and by other GC practitioners [10–12]. The method has approximately five times more sensitivity than that of HPLC [5,6] and two to three times more sensitivity than

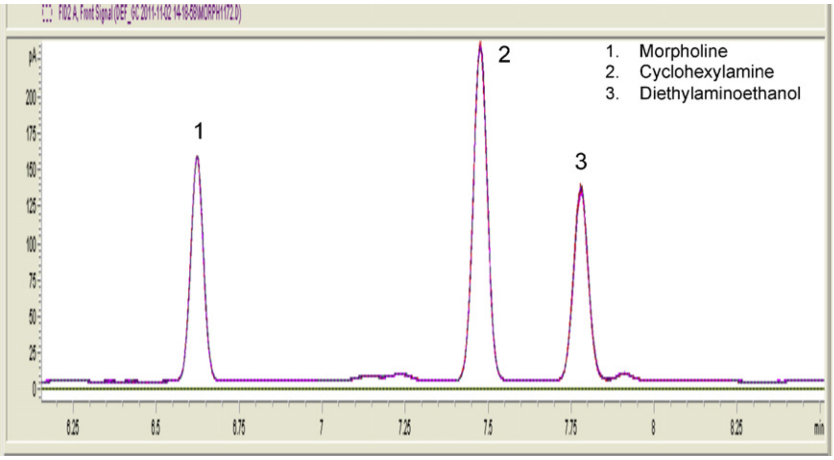

Fig. 5. Overlay of ten consecutive analyses of 10 ppm (v/v) each of morpholine, cyclohexylamine, and diethylaminoethanol in a 1:1 2-propanol/water matrix.

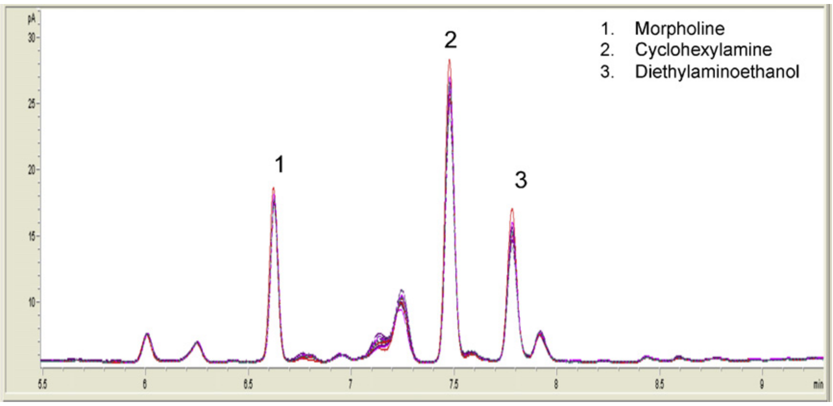

Fig. 6. Overlay of ten consecutive analyses of 1 ppm (v/v) each of morpholine, cyclohexylamine, and diethylaminoethanol in a 1:1 2-propanol/water matrix.

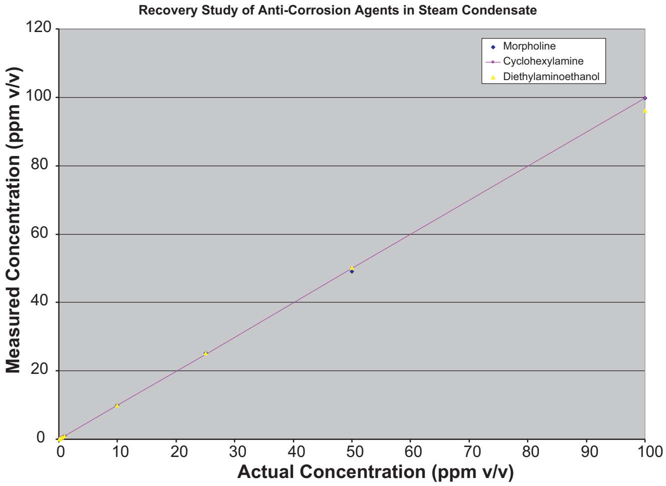

Fig. 7. Recovery study over a range from 100 ppb (v/v) to 100 ppm (v/v) each of morpholine, cyclohexylamine, and diethylaminoethanol in a 1:1 2-propanol/water matrix.

spectrophotometric method [9] and ion chromatographic method [7,8]. Also, not all the techniques can monitor all three solutes of interest in one single analysis.

As stated earlier, a practical limit of detection was established for this method. The practical limit of detection was based on a signal-to-noise level of twenty-to-one instead of three-to-one as conventional methodology would propose. This is to ensure that the method performance can be met over a period of six months under constant use as the chromatographic system components changes such as the aging of the capillary column, and any minor variations in the level of impurities of the co-solvent used would not create false positive reading for the solutes of interest at the level cited.

Using the technique described, an even lower detection limit is possible by selecting a 2-propanol diluent with fewer organic impurities in the area of interest; albeit the cost for such ultra-pure

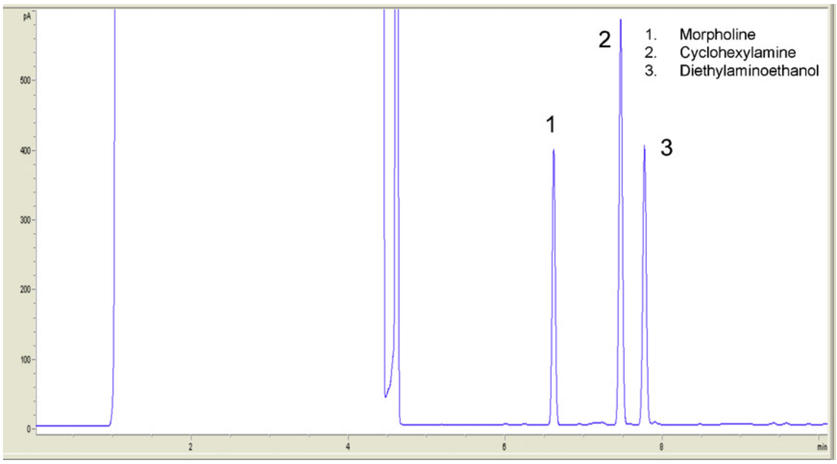

Fig. 8. Chromatogram of typical treated steam condensate sample from a water. Treatment process.

grade of diluent will increase exponentially. An alternative to achieve even lower detection limit would be to substitute the flame ionization detector with a mass selective detector operating in selective ion monitoring mode. This should yield detection limits for said solutes in the single digit ppb range.

A precision study was conducted at two different concentration levels for the three compounds of interest. At a concentration of 10 ppm (v/v), the RSD at the 95% confidence level was less than 1.1% ($n = 20$). At the 1 ppm (v/v) concentration level, the RSD at the 95% confidence level was less than 3% ($n = 20$) for all solutes of interest. Figs. 5 and 6 show overlays of some of the results obtained. To be expected, as the concentration of the solutes approach the practical detection limits of the method of 100 ppb (v/v), a wider RSD was observed. At the 250 ppb (v/v) concentration level, the RSD at the 95% confidence level was less than 6% ($n = 20$).

Linearity was also found to be acceptable for all three compounds. Linearity data was collected between 100 ppb (v/v) and 100 ppm (v/v) for morpholine, cyclohexylamine, and diethylaminoethanol. R^2 values of greater than 0.999 were obtained for all three components.

A recovery study was conducted by preparing a 100 ppm (v/v) stock standard of morpholine, cyclohexylamine and diethylaminoethanol into an industrial steam condensate sample. Various amounts of this stock standard were then spiked into the additional steam condensate to give eight samples ranging from 0.1 to 100 ppm (v/v) of amines. A recovery of more than 96% was attained over the concentration studied as shown in Fig. 7. Fig. 8 shows a typical treated steam condensate sample from a water treatment process.

4. Conclusions

The analysis of low level amines used as anti-corrosion agents in steam condensate by gas chromatography has been challenging due to the adsorptivity of these compounds in the chromatographic system and the interference of the water matrix.

By combining a recently innovated multi-mode inlet which offers fast programmable temperature of up to a maximum rate of 900 °C/min and pulsed splitless capability, and newly commercialized inert inlet liner and base-deactivated capillary column, ultra-trace ppb levels of volatile amines such as morpholine, cyclohexylamine, and diethylaminoethanol can be successfully analyzed by gas chromatography. This technique has demonstrated a high degree of reliability and is sufficiently rugged for implementation in production facilities.

Acknowledgement

Special thanks to Dave Walter of Dow Analytical Technology Center for his support and encouragement.

References

[1] A. Banweg, Shreir's Corrosion – Boiler and Feedwater Treatment, vol. 4, 2009, p. 2971.
[2] New Logic Research Inc., Feed Water Treatment for Industrial Boilers and Power Plants, Filtration and Separation, vol. 40, 2003, p. 28.
[3] A. Turnbull, S. Zhou, G. Hinds, Corros. Sci. 46 (2004) 193l.
[4] L. Baxter, T. Miles, T. Miles Jr., B. Jenkins, T. Miine, D. Dayton, R. Bryers, L. Oden, Fuel Process. Technol. 54 (1988) 47.
[5] A. Turbull, Corros. Sci. 23 (1983) 833.
[6] A. McMinn, F. Lyle, G. Leverant, Corrosion 41 (1985) 493.
[7] S. Nasrazadani, J. Diaz, J. Stevens, R. Theimer, Corros. Sci. 49 (2007) 3024.
[8] A. Turnbull, S. Zhou, Corros. Sci. 53 (2011) 503.
[9] K. Sung, C. Jeong, K. Lee, Proceedings of Japan Atomic Industrial Forum (JAIF) International Conference in Water Chemistry in Nuclear Power Plant, JAIF, Fukui City, Japan, April, 1991.
[10] H. Huss, Analysis of Steam and Condensate Circulation in a Paper Mill, Ph.D. Thesis, Technical University of Graz, Institut fur Warmetechnik, 1998.
[11] R. Soniassy, P. Sandra, C. Schlett, Water Analysis, Organic Micropollutants, Hewlett-Packard Co., 1994, p. 141 (HP part N 5962-6216E).
[12] M. Joseph, V. Kadiyal, Chromatographia 35 (1993) 173.
[13] R. Lindhal, A. Wasterby, J. Levin, Analyst 126 (2001) 152.
[14] F. Nordmann, Proceedings of 14th International Conference on the Properties of Water and Steam in Kyoto, Kyoto, Japan, 2004.
[15] R. Gilbert, R. Rioux, Anal. Chem. 56 (1984) 106.
[16] Dionex Corporation, Determination of Morpholine, Ethanolamine and Hydrazine in Simulated Nuclear Power Plant Wastewater, 2010 (Application Note 247).
[17] A. Kumbhar, S. Narasimhan, P. Mathur, Talanta 47 (1998) 421.
[18] M. Malaiyandi, M. Goddard, J. Test. Eval. 18 (1990) 11.
[19] M. Malaiyandi, H. Gord, M. Meek, J. Environ. Sci. Health 14 (1979) 609.
[20] S. Vtasala, V. Bansal, D. Tuli, Chromatographia 34 (1994) 456.
[21] American Society Testing Material, ASTM Method D4983-89, 2002, subcommittee: D19.06.
[22] J. Luong, R. Gras, B. Winniford, J. deZeeuw, 35th International Symposium of Capillary Chromatography, San Diego, CA, USA, May, 2011.
[23] G. Yang, J. Luong, R. Gras, T. Hayward, 18th National Symposium and Exhibition on Chromatography, Dalian, China, October, 2011.
[24] L. Zhao, D. Mao, M. Hastings, A. Vickers, A. Broske, L. Miller, Application of Agilent Ultra Inert Liners with Wool for the Analysis of Active Analytes by GC/MS and GC/MS–MS, Pittcon 2011, Atlanta (2011), Poster 1200-1P.
[25] J. Roeraade, Proceedings of the 26th International Symposium on Capillary Chromatography, Las Vegas, May, 2003.
[26] J. Petterson, J. Roeraade, Anal. Chem. 77 (2005) 3365.