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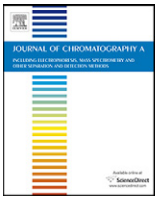

Ultra-trace level analysis of morpholine, cyclohexylamine, and diethylaminoethanol in steam condensate by gas chromatography with multi-mode inlet, and flame ionization detection

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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].

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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.