

Determination of Diethanolamine and Triethanolamine in Surface Finishing, Wastewater and Scrubber Solutions

Thermo Fisher Scientific Inc.

Introduction

Alkanolamines are important in the chemical and pharmaceutical industries for production of emulsifying agents and the manufacturing of laundry additives and dyes. The analysis of alkanolamines is also important in metal surface finishing and in wastewater effluents. They are commonly used in acid gas removal systems (scrubbers) in both oil refineries and natural gas plants. Hydrogen sulfide and carbon dioxide are two of the primary acid gases formed in a refinery. When the gases are dissolved in an aqueous medium, they dissociate to form weak acids. Amines, weak bases, combine chemically with the weak acids to form salts, thus removing the acid gases from the process stream. When the amine solution becomes overloaded with salts, the efficiency of the scrubbing process is adversely affected. Thus, continuous monitoring of the amine solution can improve amine makeup, improve final product performance, and decrease system maintenance, Figure 1. Monitoring soil and water samples in and around a refinery can identify sources of scrubber leaks before any serious losses or environmental contamination occurs, Figure 2. Alkanolamines are also used in surface finishing as shown in Figure 3 to control the etching process of aluminum and aluminum alloys in the aerospace industry.¹⁻⁴

Several alternatives are currently available for the determination of alkanolamines, including wet chemistry, gas chromatography and traditional high performance liquid chromatography. However, these methods are time consuming, with sample preparation and analysis times as long as two hours. Because these compound lack natural



chromophores or fluorophores, derivatization of the alkanolamines is required prior to detection. As a result, the data collected by these alternate methods are prone to numerous matrix interferences and shortened column life. Ion chromatography (IC) works particularly well for separations of alkanolamines. The sensitivity by conductivity detection, however, is poor because of the low equivalent conductance of alkanolamines.

Recommended Equipment

Thermo Scientific Dionex Series 4500i* with a Pulsed Amperometric Detector (PAD II) or a Pulsed Electrochemical Detector (PED)

**Equivalent or improved results can be achieved using the Thermo Scientific Dionex ICS-5000* system.*

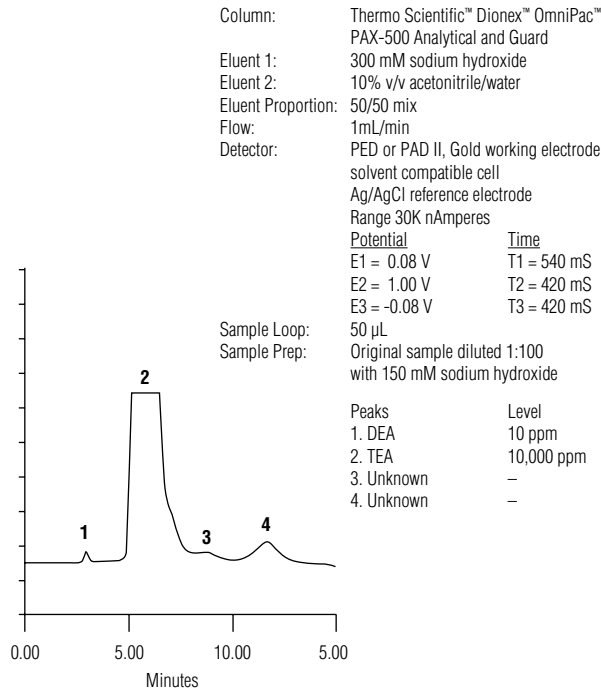


Figure 1. Diethanolamine determination in an oil refinery triethanolamine scrubber solution.

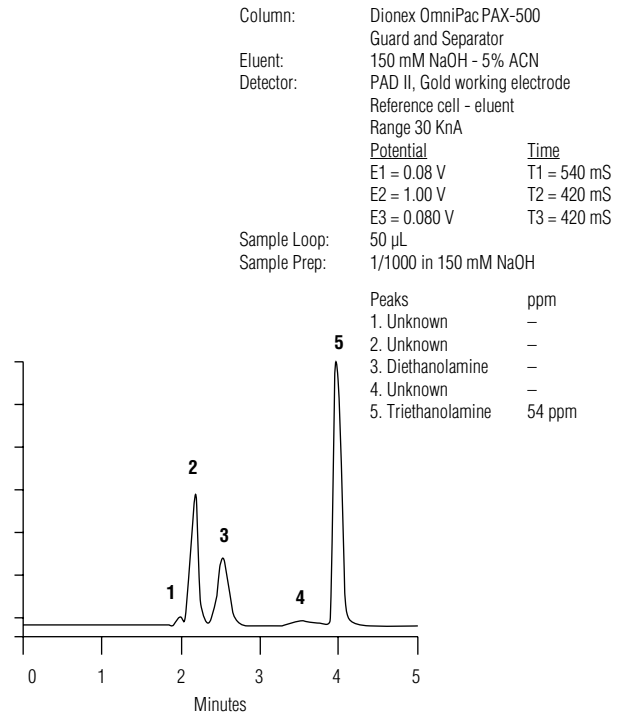


Figure 3. TEA determination in an operational alkaline etch solution.

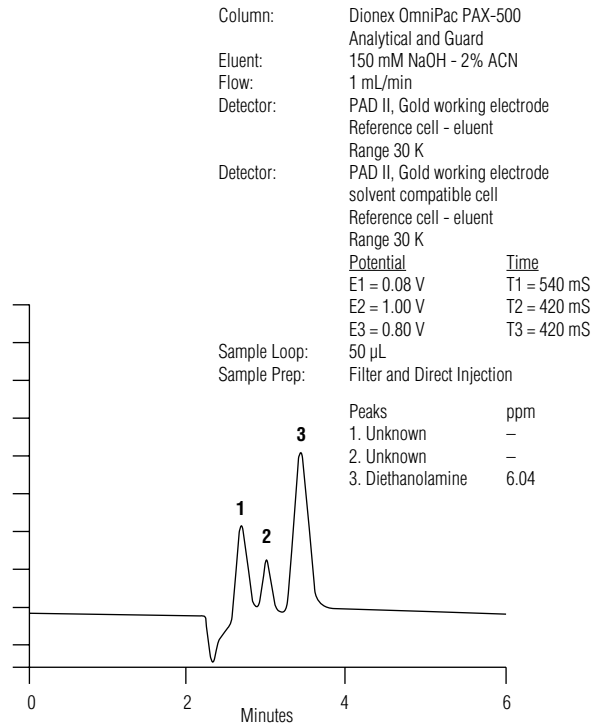


Figure 2. Oil refinery pond water for diethanolamine.

Preparation of Reagents and Standards

Conditions

Column:	Dionex OmniPac PAX-500 Analytical and Guard	
Eluent 1:	300 mM sodium hydroxide	
Eluent 2:	10% v/v acetonitrile/water	
Eluent Proportion:	50% E1/50% E2	
Flow Rate:	1 mL/min	
Detector:	PED or PAD II, Gold working electrode Solvent compatible cell Ag/AgCl Reference electrode Range 30K nA	
	<u>Potential</u>	<u>Time</u>
	E1 = 0.08 V	T1 = 540 mS
	E2 = 1.00 V	T2 = 420 mS
	E3 = -0.08 V	T3 = 420 mS
Sample Loop:	50 μ L	
Sample Prep:	Dilute in 150 mM sodium hydroxide	

It is recommended that all standards and samples be prepared and stored in 150 mM sodium hydroxide. Alkanolamines are not stable at low pH and quickly degrade. Standards and samples prepared in deionized water also degrade but more slowly.

Results and Discussion

Determination of total alkanolamines in this method is accomplished using liquid chromatography on Dionex OmniPac columns and Pulsed Amperometric Detection (PAD). The blended isocratic eluent is 150 mM sodium hydroxide solution containing 5% acetonitrile. The sodium hydroxide in the eluent maintains a high pH thus suppressing ionization of the alkanolamines. Under these conditions the alkanolamines are retained and separated by a reverse phased mechanism on the Dionex OmniPac PAX-500 analytical column. The acetonitrile present in the eluent controls the retention of the alkanolamines. Increasing the acetonitrile concentration reduces the retention times.

Standards were prepared in 150 mM sodium hydroxide at the 0.1, 1, 10, 50, 75, and 100 ppm levels. Linearity over the range of 0.1 to 100 ppm using a 50 μ L sample exhibited a coefficient of determination (r^2) greater than 0.998 for each alkanolamines. Precision, expressed as percent relative standard deviation (%RSD) for 374 replicate analyses of the alkanolamines at the 70 ppm level was better than 3% in an operational alkaline etch solution. The method detection limit by direct injection using a 50 μ L loop has shown to be 10 parts-per-billion in an alkaline etch solution. Peak areas were used in preference to peak height for quantification of the alkanolamines.

Precautions

The eluent used in this method contains sodium hydroxide and acetonitrile. Acetonitrile in a high pH solution decomposes to weak organic acids and other compounds. These decomposition products, when present, interfere with the electrochemical detector's response. The acetonitrile decomposition reaction is not rapid, and small amounts of the breakdown components have no immediate effects upon the analysis. To avoid this decomposition reaction, on line low pressure mixing using the Thermo Scientific Dionex Gradient Pump is recommended to blend separate sodium hydroxide and acetonitrile solutions together.

References

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2. Burwell, K.F.; Dubek, D.J.; Sigmund, P.W., *Hydrocarbon Processing*, March 1982, 108–116.
3. Keaton, M.M.; Bourke, M.J., *Hydrocarbon Processing*, August 1983.
4. Campbell, D.C.; Carson, S.; Heberling, S.; Bramer, D.V., Improved Separation and Detection of Alkanolamines using Liquid Chromatography and Electrochemical Detection, Submitted to: *Journal of Chromatography*.

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