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Improved determination of alkanolamines by liquid chromatography with electrochemical detection

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ABSTRACT

The determination of alkanolamines has traditionally been difficult due to the complexity of the detection methods and the difficulty of the separation. Wet chemistry, gas chromatography and high-performance liquid chromatography methods all require time-consuming, complex sample treatments which are prone to numerous interferences.

This paper will describe the use of a liquid chromatography method using a polymer based reversed-phase column coupled to a pulsed amperometric detector. This method provides simple, direct quantitation of triethanolamine. Evaluation of this method for linearity, reproducibility and detection limits in an alkaline etch process will be presented.

INTRODUCTION

The determination of alkanolamines is currently of great interest, as these compounds are used widely in chemical and pharmaceutical industries. Alkanolamines are used in the production of emulsifying agents, the manufacturing of laundry additives and dyes, and are commonly used in metal surface finishing [1]. The analysis of alkanolamines is important in the purification of gases and in waste water effluents [2].

Several traditional methods have been used for the determination of alkanolamines. These include wet chemistry, high-performance liquid chromatography with spectroscopic detection, ion chromatography with conductivity detection and gas chromatography. Gas chromatography (GC) is almost eliminated as an analytical technique because of the high polarity which alkanolamines exhibit. Precolumn derivatization is required prior to analysis to achieve an acceptable separation. The GC columns tend to degrade rapidly resulting in poor performance [3]. Ion chromatography has worked well for the separation of individual alkanolamines. Still, the sensitivity by suppressed conductivity detection is poor due to the low equivalent conductance of alkanolamines relative to the hydrogen ion [4]. Liquid chromatography

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techniques for amines have shown highly efficient separations, however, the effect of the amine functionality on some silica-based gels can result in serious tailing of the chromatographic peak. Because the alkanolamines lack natural chromophores or fluorophores, derivatization of these compounds with nitroaromatic chromophors is required prior to spectroscopic detection. The reagents available for derivatization result in poor sensitivities and have been shown to be unreliable due to numerous interferences [5].

This paper will describe the use of a polymeric column coupled with pulsed amperometric detection (PAD) for the determination of alkanolamines. Specifically, triethanolamine (TEA) in an aluminum and aluminum alloy chemical etching process will be presented.

The original work for this paper began as a joint project with the Boeing Commercial Airplane Group, Seattle, WA, U.S.A. In an effort to improve the quality control and production performance of their aluminum products for commercial airplanes, Boeing identified the need for improved monitoring of important chemical additives and bath constituents in their Aluminum Finishing Process Line. TEA was identified as a primary additive responsible for maintaining proper operation of the alkaline etch bath. A properly controlled TEA alkaline etch bath is maintained at 4.2–5.3 oz/l sodium hydroxide, 0.4–1.3 oz/l sodium sulfide, 1.1–2.1 oz/l TEA and 0.7–2.6 oz/l dissolved aluminum at an operational temperature of 60–90°F [6]. Improved monitoring of the TEA may allow for the development of tighter specifications in control and product integrity. The data generated and reported in this paper is believed to be accurate and correct for the conditions and processes developed at Boeing.

EXPERIMENTAL

All chromatography was performed on a Dionex system 4000i ion chromatograph consisting of a pump, a chromatography module and a pulsed amperometric detector. A gold working electrode, a stainless-steel counterelectrode and a silver/silver chloride (1 *M* NaCl) reference electrode were used in the amperometric flow-through detector cell. The applied potentials (V) and pulse durations (ms) were the following: $E1(t1)$, 0.08(540); $E2(t2)$, 1.0(420); $E3(t3)$, −0.80(420). The sample volume for all injections was 50 μl unless otherwise noted. The column was a Dionex OmniPac PAX-500 with the anion-exchange resin in the hydroxide form. The eluent was 150 m*M* NaOH and 5% (v/v) acetonitrile at a flow-rate of 1 ml/min. All chemicals used in methods development were reagent grade.

RESULTS AND DISCUSSION

Pulsed amperometric detection

In 1981, Hughes *et al.* introduced pulsed amperometric detection [7]. By using strongly basic solutions, alkanolamines could be detected [8]. Pulsed amperometric detection uses an automated repeating sequence of three potentials. The analyte molecules are oxidized at the first potential ($E1$), and the current is measured. The potential is then stepped to a more positive value ($E2$), and a gold oxide layer is formed on the electrode surface. The third potential ($E3$) is a negative potential at which the

oxide layer is reduced to produce the bare metal. This sequence is repeated several times per second and one point on the chromatogram is acquired during each cycle. The pulsed sequence is an advantage since the electrode is cleaned during the alternating positive and negative pulsing. When only a single potential is used, peak response from a series of injections will quickly decrease as the electrode becomes coated by the products of the oxidation reaction.

Separation

Pulsed amperometric detection at a gold electrode in a basic solution is specific for small oxidizable molecules. These include alkanolamines, sulfides and metals. Detecting these individual species in a complex matrix such as an aluminum etch solution can be a difficult task. Therefore the selectivity for the quantitative analysis must be provided for by the chromatography. Separation was achieved on a Dionex OmniPac PAX-500 using a sodium hydroxide–acetonitrile eluent. The PAX-500 is a solvent-compatible anion exchange, reversed-phase column. The core is a macroporous polymer substrate. Attached to this surface is a cationic latex coating upon which a layer of anion-exchange material is covalently bonded.

A chromatogram of a standard solution of TEA is shown in Fig. 1. Complete baseline separation occurs between diethanolamine and TEA. Other oxidizable species do not interfere. Alkanolamines at the pH of the eluent, pH = 3, have little or no ion-exchange characteristics and their retention is unaffected by the anion-exchange portion of the PAX-500 column. The alkanolamines, therefore, are retained and separated by the reversed-phase mechanisms on the PAX-500 analytical column. The acetonitrile present in the eluent controls the retention mechanisms of the alkanolamines.

Acetonitrile in high pH solutions is decomposed to acetic acid and other nitrogen containing compounds [9]. These decomposition products interfere with the electrochemical detector's response and stability as the contaminates build up with time.

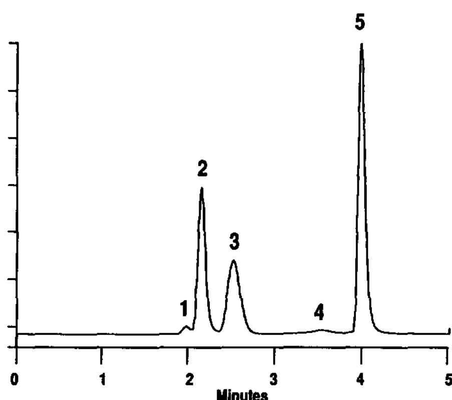

Fig. 1. TEA determination in an operational alkaline etch solution. Column, PAX-500 guard and analytical; eluent, 150 m*M* NaOH–acetonitrile (95:5, v/v); detector, pulsed amperometric detection, range 30 μA; loop, 50 μl; sample preparation, 1/1000 in 150 m*M* NaOH. Peaks: 1 = unknown; 2 = unknown; 3 = diethanolamine; 4 = unknown; 5 = triethanolamine (54 ppm).

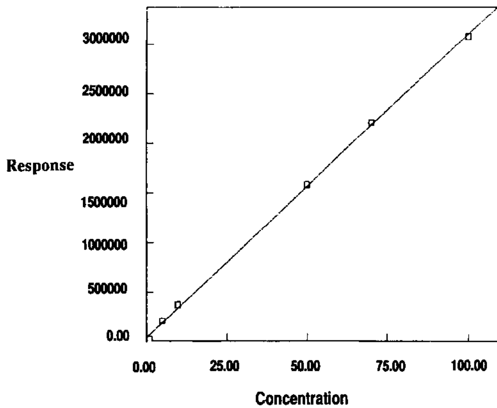

Fig. 2. Linearity of TEA. Correlation coefficient r = 0.9996. TEA range, 1.0–100 ppm (50 μl injection).

The reaction of acetonitrile in sodium hydroxide is not rapid, and the breakdown components have no immediate effects upon the analysis. Eluents should be made fresh every 8 h to ensure optimum performance of the instrument. It is not recommended to store the sodium hydroxide and the acetonitrile in the same bottle.

One way to ensure optimum eluent performance would be the use of a proportioning pump for blending two or more separate solutions together. Individual sodium hydroxide and acetonitrile solutions can be metered together by on-line mixing at the proportioning valve in the eluent pump. This ensures that no degradative chemical reaction takes place prior to the analysis of the alkanolamines and results in reliable long term stability of the analysis.

Low concentrations of alkanolamines are not stable in neutral or low pH matrices. It is recommended that all standards and samples be prepared and stored in 150 mM NaOH. When the standards and samples are diluted in the sodium hydroxide, no stability problems were observed over normal sampling times of 8 h.

The alkanolamines were quantified by automatic measurements of peak areas. A comparison of peak height *vs.* peak area data showed better linearity and reproducibilities by peak area calculations. All calculations in this paper are based upon peak area calculations and not peak height.

TABLE I

REPRODUCIBILITY OF TEA IN A SINGLE ALKALINE ETCH SAMPLE SOLUTION BY PEAK AREAS

	Dionex	Boeing
Observations	374	44
Minimum (ppm)		37.8
Maximum (ppm)		42.1
Mean (ppm)	71.2	40.1
Standard deviation (ppm)	0.954	0.937
Relative standard deviation (%)	1.34	2.3

Fig. 2 shows the linearity of TEA in a standard alkaline etch bath. Standards of TEA were prepared at the 1, 10, 50, 75, and 100 ppm levels. Seven duplicate measurements were made for each standard and the resultant average plotted. The linearity for TEA over the range of 1–100 ppm showed a coefficient of determination (r^2) equal to 0.9992. No overloading of the analytical column was observed over this entire analytical range. Detection limits are approximately 1 part-per-billion for TEA and the other alkanolamines.

Reproducibility data, reported in Table I, was studied under similar conditions at both Dionex and Boeing. At Dionex the relative standard deviation (R.S.D.) for 374 replicate analyses of TEA in a diluted single-concentration alkaline etch sample at the 70 ppm level was 1.34%. A similar sample analyzed at Boeing provided similar reproducibility results. Forty-four replicate analyses of TEA in a diluted single-concentration alkaline etch sample at the 40 ppm level showed a 2.3% R.S.D. All samples were diluted 1 to 1000 for this study.

CONCLUSION

In summary, liquid chromatography using a polymer resin coupled to pulsed amperometric detection is a sensitive and selective technique for the simultaneous determination of TEA and other alkanolamines. This new technique has been adopted as the standard method for the determination of TEA at Boeing. It is believed to be a more rapid, reliable and accurate method for alkanolamines than former wet chemistry or spectroscopic methods. The choice of an OmniPac PAX-500 analytical column and electrochemical detection results in a rugged, simple and reliable method for the analysis of alkanolamines in complex matrices and environmental samples.

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