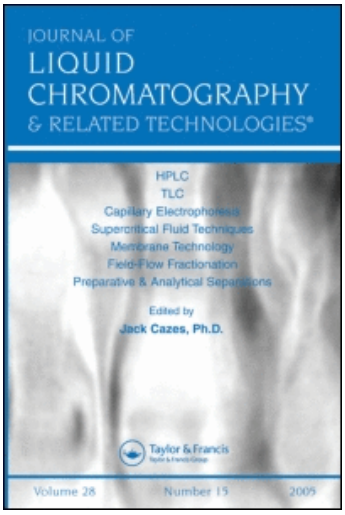

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ANALYSIS OF CATIONIC SURFACTANTS IN HOUSEHOLD PRODUCTS BY HIGH PERFORMANCE LIQUID CHROMATOGRAPHY WITH NITROGEN CHEMILUMINESCENCE DETECTION

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ABSTRACT

For compounds containing less than 10% (wt./wt.) nitrogen, the sensivity of nitrogen chemiluminescence detection is limited to concentrations of greater than 0.1 mg/mL under typical operating conditions. For determinations of nitrogen containing surfactants in household products, such sensitivity is not prohibitive due to the high levels of surfactant added to the formulations and is potentially offset by the advantage of the detector's specificity towards nitrogen containing compounds. Lauryl/myristyl monoethanolamide is detected without interfence in a variety of dishwashing liquids and n-methyl glucosamides are detected in liquid laundry detergents. Replicate injections of a single dishwashing liquid preparation indicate a quantitative

reproducibility of 8% rsd for lauryl/myristyl monoethanolamide. Performance comparable to HPLC with UV detection has been achieved for methyl neodecanamide in an all purpose cleaner.

INTRODUCTION

Lauryl/myristyl monoethanolamide (LMMEA), methyl neodecanamide (MNDA) and n-methyl glucosamides are used in a variety of household products, along with quarternary ammonium compounds, ethoxylated alcohol sulfates, alkyl benzene sulfonates and other anionic, cationic, amphoteric and nonionic surfactants. The use of HPLC for the analysis of cationic surfactants was recently reviewed[1] and it was noted that for the analysis of non-aromatic surfactants, refractive index detection is used most frequently. Due to its lack of specificity, such an approach is not ideally suited for the analysis of LMMEA, MNDA or glucosamides in the presence of compounds with similar hydrophobicity, especially when it is desirable that the separation method is applicable to multiple formulations which may vary considerably in composition. To address this issue, various other approaches to the analysis of nitrogen containing surfactants, including derivatization[2-3] and post-column reaction procedures[4] have been developed. Evaporative light scattering detection has been used to allow for the use of solvent gradients.[5]

Nitrogen chemiluminescence detection (NCD),[6-8] is based on the pyrolysis of chemically bound nitrogen compounds. Specifically, column effluent is swept into a pyrolysis furnace by streams of oxygen and helium, and nitrogen containing compounds are converted to nitric oxide. The effluent is subsequently swept into a splitting tube where it is divided between a heated membrane dryer and waste.

The part of the effluent which enters the membrane dryer is pulled by vacuum into a reaction chamber, where nitric oxide reacts with ozone to form nitrogen dioxide in the excited state. Decay to the ground state, causes light emission which is measured using a photomultiplier tube and provides the basis for quantitation. An ozone generator (using oxygen as the feed gas) is used to produce the necessary flow of ozone into the reaction chamber.

Since the detector is specific to nitrogen containing compounds, it should be ideally suited for the analysis of cationic surfactants and structurally related compounds. This work describes the applicability of the detector to the analysis of LMMEA in dishwashing liquids, n-methyl glucosamides in liquid laundry detergent and MNDA in all purpose cleaner (APC), as well as the influence of detector operating variables on performance.

MATERIALS AND METHODS

Instrumentation and Methods

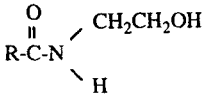
An Antek Model 7000 HPLC CLND detector (Antek Instruments, Inc., Houston, TX) was connected to a Gast DOA oil-less diaphragm vacuum pump (Gast Manufacturing Corp., Benton Harbor, MI). The CLND photomultiplier was set at 700 V for all analyses and the ozone generator to a temperature of -15°C, although this temperature was never actually achieved. The actual temperature averaged approximately -4°C. The ozone flow, the pyrolysis oxygen flow and the helium flow were set to 1.8, 3.0 and 5.5 (arbitrary units), respectively, for all analyses. For LMMEA and glucosamides, the pyrolysis temperature was 1100°C and the membrane temperature was 125°C; for MNDA the pyrolysis and membrane temperatures were set to 1050°C and 97°C, respectively.

For LMMEA analyses, chromatography was performed using a Waters model 590 pump (Waters, Milford, MA), a Rheodyne model 7520 injection valve with a 1 µL internal volume (Rheodyne Inc., Cotati, CA), and a 150 x 1mm Inertsil ODS(2) column (Phenomenex, Torrance, CA). The mobile phase was 80/20 (v/v) methanol/water at a flow rate of 0.0625 mL/min. (methanol was obtained from J. T. Baker, Phillipsburg, NJ; 15 Mohm-cm water was obtained from a Milli-Q Reagent Water System (Millipore Corp., Milford MA)). Data were collected using PE Nelson Access Chrom. Software (Perkin-Elmer, Norwalk, CT). Similar conditions were used for glucosamides except that injections were performed using a Rheodyne model 7125 valve with a 10 µL loop and a mobile phase of 75/25 (v/v) methanol water. MNDA analyses were conducted using flow injection analysis (no column). To reduce pump pulses an Upchurch Scientific 500psi BPR (Upchurch Scientific, Oak Harbor, WA) was placed between the pump and the 1 µL injection valve. Methanol, at a flow rate of 0.0625 mL/min, was used to transfer the sample from the injector to the detector.

Sample Preparation

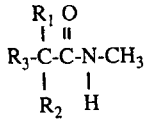
All standards and samples were obtained in-house. For LMMEA, standards were prepared to operating concentrations of 0.5 - 2 mg/mL in 80/20 (v/v) methanol/water. Dishwashing liquid samples were prepared by dissolving 5g / 50 mL. The glucosamide standard and samples were prepared by dissolving 50mg of lauryl/myristyl n-methyl glucosamide in 50 mL and 2.5g of liquid laundry detergent in 100 mL of 70/30 (v/v) methanol/water. MNDA standards were prepared in methanol to operating concentrations of 0.1 - 1.0

LMMEA (6.03% N)



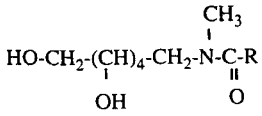
$R = C_{12}H_{25}$ or $C_{14}H_{29}$

MNDA (8.00% N)



$R_1 + R_2 + R_3 = C_8H_{19}$

GLUCOSAMIDE (3.46% N)



$R = C_{12}H_{25}$ or $C_{14}H_{29}$

Figure 1. Chemical structures and % nitrogen of LMMEA, MNDA and glucosamides.

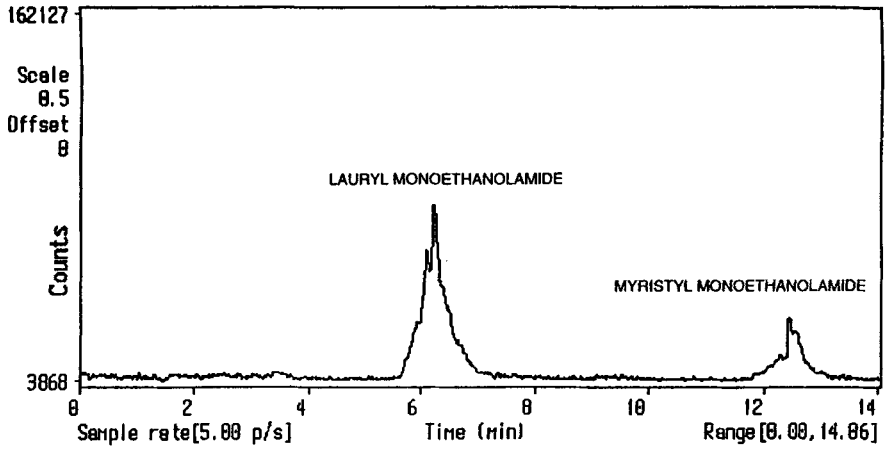


Figure 2. Chromatogram of an LMMEA standard. Pyrolysis temperature = 1050°C, membrane temperature = 97 C. For additional conditions see text.

mg/mL. Samples were prepared by dissolving 2.5g of APC in 50 mL of methanol. All samples were filtered prior to injection using 0.45 μm Autovial syringeless filters (Whatmann, Clifton, NJ).

RESULTS AND DISCUSSION

A primary advantage of nitrogen chemiluminescence detection is selectivity, potentially making it possible to analyze for nitrogen containing compounds in the presence of coeluting compounds. However, several limitations exist: The effluent entering the detector must be less than 200 µL/min., which requires the use of microbore columns or the use of post-column splitters; acetonitrile cannot be used as a mobile phase constituent; and the sensitivity of the detector is limited to approximately 0.4ng of nitrogen under favorable chromatographic conditions.[7]

Surfactants are typically added to cleaning formulations at fairly high levels (>0.25% wt/wt). As a result, the sensitivity should not be a limiting factor despite the low nitrogen content of the compounds of interest (Figure 1). The substitution of methanol for acetonitrile in reverse phase HPLC changes selectivity and increases solvent viscosity, but by virtue of the better specificity of the detector, the increased back pressure generated using methanol is offset by the lower separation efficiency required. For simpler separations, it is possible to use shorter columns or columns packed with larger particles to separate the analyte from the matrix.

To evaluate NCD for the analysis of LMMEA in dishwashing liquids, manufacturer recommended settings[8] were used as a starting point for method development. Specifically, the pyrolysis tube temperature was set at 1050°C, the membrane dryer temperature at 97°C and the ozone flow, the pyrolysis oxygen flow and the helium flow to 1.8, 3.0 and 5.5 (arbitrary units), respectively. Under these conditions (Figure 2) poor peak shapes were observed. Variation in the membrane dryer temperature was insignificant over the range studied (97 -150°C), and variations in the gas flows either had no effect or decreased the signal to noise ratio. The effect of increasing the pyrolysis temperature to 1100°C was, however, pronounced. Using the latter conditions, both the peak shapes and the sensitivity are acceptable (Figure 3). While the concentration of LMMEA in the standard shown in Figure 3 is 2 mg/mL, the mass of nitrogen injected is approximately 120 ng.

The conditions of Figure 3, were used for the analysis of several different dishwashing liquids. Despite variations in the formulations, both LMMEA peaks were resolved from the matrix, showing the applicability of the method for qualitative analysis. A typical chromatogram is shown in Figure 4. To investigate the reproducibility of the method, 6 replicate injections of a prepared sample were performed and an rsd of 8% was observed. Since the influence of LMMEA concentration on product efficacy is critical, it is important to reduce this variability.

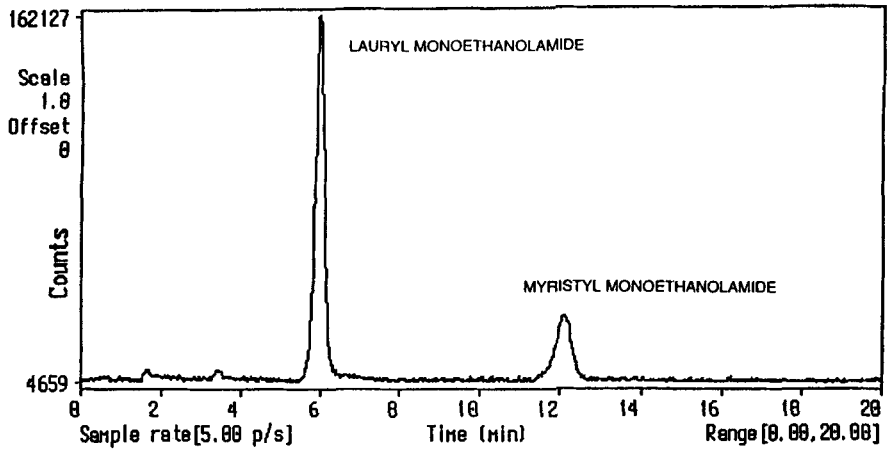


Figure 3. Chromatogram of an LMMEA standard. Pyrolysis temperature = 1100°C, membrane temperature = 125 C. For additional conditions see text.

Table 1

Comparison of Flow-Injection - NCD with HPLC-UV for the Analysis of MNDA in APC

	HPLC-UV	FI-NCD
RSD of 6 determinations	1.5%	2.0%
Analysis of 0.25% sample	0.260%	0.243%
Analysis of 0.50% sample	0.500%	0.480%
Analysis of 0.75% sample	0.780%	0.770%
Regression (r)	0.9961	0.9996

The poor reproducibility observed for LMMEA was not observed for MNDA in an all purpose cleaner using flow injection analysis. Table I, compares the results to those obtained using an HPLC method with UV detection described previously.[9] As shown, the performance of the CND method is comparable to that of the HPLC-UV method with respect to accuracy and precision.

As a result of the performance of the detector with MNDA, it was concluded that the large rsd, observed for LMMEA samples, was due to the nature of the analyte and/or the sample matrix. Notably, after the analysis of

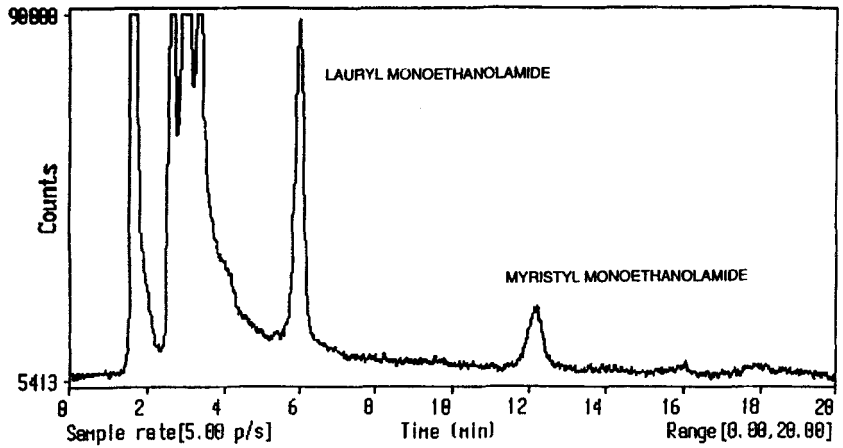


Figure 4. Chromatogram of LMMEA in a commercially available dishwashing liquid. Conditions are as for Fig. 3.

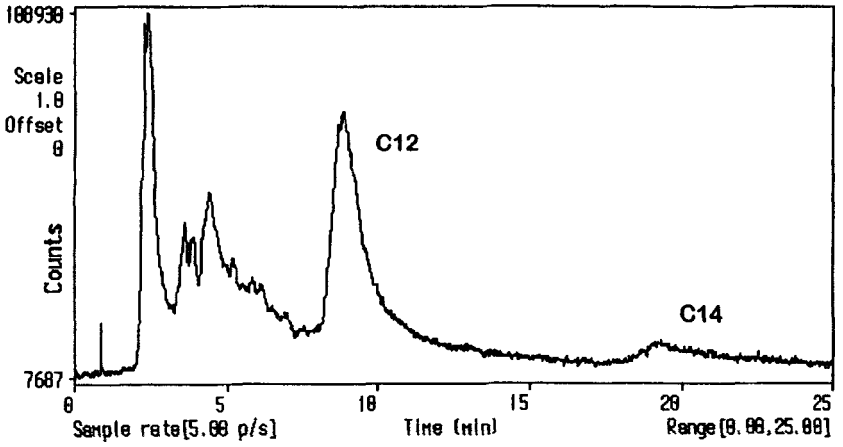


Figure 5. Chromatogram of lauryl/myristyl n-methyl glucosamide in liquid laundry detergent. For conditions see text.

several dishwashing liquid samples, it was noted that the waste outlet on the splitter, which controls the amount of material entering the membrane dryer, was partially clogged. Variability in the back pressure of the outlet should directly influence the split ratio and, therefore, the amount of analyte entering the ozone reaction chamber. Most likely, the problem is due to incomplete

pyrolysis of dishwashing liquid matrix components and could possibly be minimized by sample clean-up procedures prior to chromatography. As a more general solution, we are currently investigating means of modifying the splitter design to minimize deposition at the waste outlet.

While additional research is required to improve reproducibility and ruggedness, CND is currently useful for qualitative analysis. As an example, the detector has been used to screen liquid laundry detergents for glucosamides (Figure 5). In addition, several products previously screened for LMMEA content using refractive index detection and retention time for identification, have been shown to have provided false positives.

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