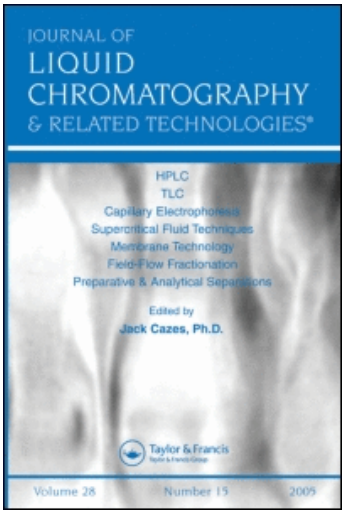

Journal of Liquid Chromatography & Related Technologies
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597273

Determination of Octadecylamine in Water by Quantitative High Performance thin Layer Chromatography

Joseph Sherma[a]; Karen Chandler[a]; Julie Ahringer[a]
[a] Department of Chemistry, Lafayette College Easton, PA

To cite this Article Sherma, Joseph , Chandler, Karen and Ahringer, Julie(1984) 'Determination of Octadecylamine in Water by Quantitative High Performance thin Layer Chromatography', Journal of Liquid Chromatography & Related Technologies, 7: 14, 2743 — 2749
To link to this Article: DOI: 10.1080/01483918408067042
URL: http://dx.doi.org/10.1080/01483918408067042

JOURNAL OF LIQUID CHROMATOGRAPHY, 7(14), 2743-2749 (1984)

DETERMINATION OF OCTADECYLAMINE IN WATER BY QUANTITATIVE HIGH PERFORMANCE THIN LAYER CHROMATOGRAPHY

Joseph Sherma, Karen Chandler, and Julie Ahringer
Department of Chemistry
Lafayette College
Easton, PA 18042

ABSTRACT

Octadecylamine (ODA) was isolated from water by solvent extraction with ethylene dichloride or trapping on a micro Chromosorb column. The ODA in the extract or column eluent was chromatographed on a high performance silica gel layer, detected by spraying with ninhydrin, and quantified by reflectance densitometry. Recovery at 3 ppm averaged 81.3% using extraction and 94.0% with the column. Recovery at 0.3 ppm was 94.2% using the column procedure.

INTRODUCTION

Octadecylamine (ODA) is a corrosion-inhibiting boiler water additive used in the preparation of steam that will contact food. The Code of Federal Regulations for Food and Drugs (21:173.310) limits its level in steam to 3 ppm. Currently used analytical methods for the determination of ODA in steam condensate are usually based on extraction with an organic solvent followed by reaction of the amine with methyl orange or salicylaldehyde and colorimetry (1-3). These methods are not selective for ODA in the presence of other amines and bases. ODA has also been determined in boiler water by an indirect method involving formation

 0148-3919/84/0714-2743$3.50/0

of an amine-chromate complex, extraction into nitrobenzene, and atomic absorption spectrometry of the Cr in the extract (4).

The method reported in this paper is direct and selective since it includes resolution of ODA by thin layer chromatography. Isolation of ODA from water was achieved by solvent extraction and by a more simple micro-column trapping/elution procedure patterned after work by Schwartz (5). Adequate recoveries from spiked water were demonstrated at the tolerance level (3 ppm) for the extraction and column procedures and also at 0.3 ppm for the latter. Other permitted boiler water additives were shown not to interfere with the analysis.

EXPERIMENTAL

Materials and Solutions

Octadecylamine (stearylamine) was purchased from the Life Sciences Group of ICN Pharmaceuticals, Inc., Plainview, NY, and recrystallized from absolute ethanol. A stock spiking solution was prepared in absolute ethanol at a level of 3.00 mg ODA/ml (heating was required). Dilutions with ethanol were made to give a spiking solution containing 0.500 mg/ml and a TLC standard of 60.0 ng/µl.

Procedures

TLC analyses were carried out on 10 x 20 cm Whatman LHPK pre-adsorbent high performance silica gel TLC plates scored into 19 channels. The plates were prewashed by development with methanol-methylene chloride (1:1) before use.

Standards (5.00 to 20.0 µl; 300 to 1200 ng) and samples (5.00 or 20.0 µl) were applied by streaking broadly across the preadsorbent areas of the lanes using a 25 µl Drummond Dialamatic microdispenser. The spotting area was completely air-dried, and

plates were developed for a distance of 5.5 cm beyond the preadsorbent-silica gel interface in a paper-lined, vapor-saturated rectangular glass HPTLC chamber with the mobile phase n-butanol-glacial acetic acid-water (3:1:1). Development required about 1 hour.

Plates were dried with a stream of warm air from a hair dryer for 5 minutes, sprayed uniformly (but not heavily) with a 2 mg/ml ninhydrin solution in acetone, and heated for 5 minutes at 100° C in a ventilated chromatography oven.

ODA zones were measured with a Kontes Model 800 filter optics scanner in the single beam, reflectance mode using the white phosphor disk (440 nm peak, 300 nm band width) and the 8 mm source beam length to match the lane width of the divided plates. Peak areas were integrated with a Hewlett Packard Model 3390A calculating integrator/recorder coupled to the scanner. Calibration curves were calculated and samples on the same plate interpolated by means of a linear regression program run on a Commodore 64 minicomputer.

Deionized water was fortified at 3.00 ppm by adding 6.00 ml of the 0.500 mg/ml ODA solution to 994 ml of hot (50-60° C) deionized water and shaking vigorously for 5 minutes. One hundred ml (containing 0.300 mg of ODA) was placed in a 250 ml separatory funnel, and 2 ml of acetate buffer solution was added. The buffer was prepared by mixing 3.7 g of sodium acetate, 6.3 g of potassium chloride, and 12.5 ml of glacial acetic acid and diluting to 50 ml with water. ODA was extracted with three 10 ml portions of ethylene dichloride by shaking vigorously for 5 minutes and allowing the layers to separate for 10 minutes each time. The three extracts were combined in a 50 ml beaker and reduced to a volume of about 10 ml on a warm hot plate under a stream of nitrogen gas. The solution was quantitatively transferred to a calibrated 13 ml centrifuge tube and the volume further reduced to a value between 7 and 8 ml. Duplicate 20 µl aliquots were applied to a plate along with the series of bracketing standards. The theoretical amount of ODA in the sample zones for 100% recovery was 750 to 857 ng, depending upon the exact volume of extract in the tube. Percentage recovery was calculated by comparing the actual and theoretical ODA concentrations.

To prepare fortified samples for evaluation of column extraction, 100 µl of the 3.00 mg/ml ethanolic ODA stock solution (measured with a syringe) was dissolved in 100 ml and 1000 ml of hot distilled water. The resultant solutions were 3.00 ppm and 0.300 ppm, respectively. A "large volume" Pasteur pipet (Fisher No. 13-678-8) was plugged with a 0.25-0.3 g wad of glass wool and 2 ml of a water slurry of Chromosorb 102 styrene-divinylbenzene polymer (80-100 mesh) (20 g/100 ml water) was added followed by a layer of sand. The resin was purified by washing with methanol and acetone before suspending in water.

A funnel was attached to the top of the column by 2 cm of 5/16 in. id Tygon tubing, and the 100 ml or 1000 ml water sample passed through by gravity. The funnel was removed and nitrogen gas blown through from the top until the column was totally dry. ODA was eluted into a small vial with 2 ml of acetone, the acetone was evaporated under a stream of nitrogen and the residue dissolved in 3.00 ml of acetone by pipet. Duplicate 5.0 µl portions were applied to a plate with the bracketing standards. The theoretical amount of ODA in the sample zones for 100% recovery was 500 ng for both fortification levels.

RESULTS AND DISCUSSION

ODA appeared as a tight red band with an R_F value of 0.70 after development with the butanol-acetic acid-water mobile phase and detection with ninhydrin. An orange-yellow band formed across the entire width of the layer at R_F 0.50 (probably due to solvent demixing), but this did not interfere with scanning of the ODA zones. After exposure to the atmosphere for 24 hours, the ODA bands faded and the background acquired a yellow or purple tint. Many other mobile phases were evaluated, but all caused diffuse or non-linear (bell-shaped) zones. Fluorescamine gave equal visual sensitivity (ca. 250 ng) for detection of ODA, but peak areas were not as large for the fluorescent zones produced by this reagent.

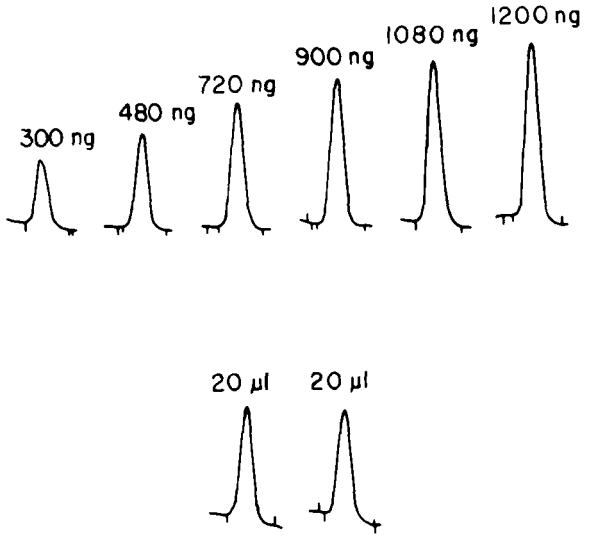

Figure 1. Scans of 300-1200 ng of octadecylamine and duplicate 20 µl extract samples representing a recovery of 71.5% using the Kontes Model 800 scanner and Hewlett Packard Model 3390A integrator with attenuation X7.

Figure 1 illustrates typical scans of a series of ODA standards and duplicate 20 µl solvent extract samples on the same plate. The calibration curve calculated from the standard peak areas had a linearity correlation coefficient of 0.996. Although slope and y-intercept (area) values were relatively consistent from plate to plate, samples and standards were always chromatographed in parallel to correct for variations in these parameters. Reflectance scanning produced larger peaks with more even baselines compared to scanning in the transmission mode.

Recoveries of ODA from eight separate samples fortified at 3.00 ppm and analyzed using the ethylene dichloride extraction procedure (1) ranged from 68.3 to 103% with a mean of 81.3%. The reproducibility (percent difference) of the duplicate samples in each analysis averaged 4.20% with a range of 0.66 to 10.8%. Addition of 20 g of sodium chloride to a water sample before extrac-

tion in order to increase the partition coefficient of ODA in favor of the organic solvent compared to water resulted in a recovery of 85%, an insignificant improvement compared to the results without salt.

Five other boiler water additives that are permitted to be used in combination with ODA under FDA regulations were tested for possible interference in the analysis in case they might be co-extracted with ODA. The compounds were spotted separately at the 1 μg level and chromatographed and detected as described above. Neither trisodium nitriloacetate nor diethylaminoethanol were detected with ninhydrin. Hydrazine produced a light purple zone with R_F 0.53, morpholine a purple-brown streaking zone with R_F 0.57, and cyclohexylamine a very faint purple-brown zone with R_F 0.38. None of these would interfere with scanning of ODA.

The main purpose of this research was to improve the published (1) FDA analytical procedure for ODA in water by substituting a more selective TLC determination for solution spectrometry. However, in the course of this work the Chromosorb column trapping/elution procedure described above was found to be simpler and give better recovery and sensitivity compared to solvent extraction. Two samples fortified at 3.00 ppm gave average recoveries of 92.8 and 95.3%, and a single sample fortified at 0.300 ppm gave a recovery of 94.2%. Columns eluted with blank (nonfortified) samples gave no TLC spots. A larger column with more capacity combined with a greater acetone elution volume might be required to analyze samples containing sorbable organic impurities in addition to ODA by the method. The pH of the water sample must be high enough to assure that the ODA is not in its salt form. This general approach, as devised by Schwartz (5), should be applicable to the recovery of a variety of unionized organic compounds from water samples.

ACKNOWLEDGEMENTS

We thank Dr. Daniel Schwartz of the USDA Eastern Regional Research Laboratory, Philadelphia, PA, for suggesting the column

isolation approach and helping with preliminary experiments to demonstrate its applicability to the analysis of water for ODA. Dr. Charles Warner of the FDA, Washington, DC, provided advice and information on boiler water analysis.

REFERENCES

1. Food Additives Analytical Manual, Field Service Branch, Division of Field Operations, Food and Drug Administration, Washington, DC, revised edition, December 1, 1973.

2. Silverstein, R. M., Am. Chem. Soc., Div. Water Waste Chem., Preprints, p. 15, March (1962).

3. Larrick, R. M., Anal. Chem., 35, 1760 (1963).

4. Glaeser, E. and Bartholome, L., Chem. Tech. (Leipzig), 30, 33 (1978).

5. Schwartz, D. P. and McDonough, F. E., J. Assoc. Off. Anal. Chem., 67(3), 563 (1984).