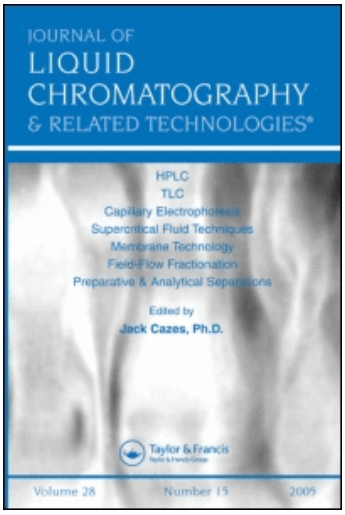

Journal of Liquid Chromatography & Related Technologies
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597273

Determination of Cyclohexylamine in Water by Solid Phase Extraction and Quantitative High Performance Thin Layer Chromatography

Joseph Sherma[a]; Linda Dallasta[a]
[a] Department of Chemistry, Lafayette College, Easton, Pennsylvania

To cite this Article Sherma, Joseph and Dallasta, Linda(1986) 'Determination of Cyclohexylamine in Water by Solid Phase Extraction and Quantitative High Performance Thin Layer Chromatography', Journal of Liquid Chromatography & Related Technologies, 9: 16, 3439 — 3446
To link to this Article: DOI: 10.1080/01483918608077794
URL: http://dx.doi.org/10.1080/01483918608077794

JOURNAL OF LIQUID CHROMATOGRAPHY, 9(16), 3439-3446 (1986)

DETERMINATION OF CYCLOHEXYLAMINE IN WATER BY SOLID PHASE EXTRACTION AND QUANTITATIVE HIGH PERFORMANCE THIN LAYER CHROMATOGRAPHY

Joseph Sherma and Linda Dallasta
Department of Chemistry
Lafayette College
Easton, Pennsylvania 18042

ABSTRACT

Cyclohexylamine (CHA) was isolated from water by solid phase extraction on a C_{18} microcolumn. The CHA in the column eluate was chromatographed on a high performance preadsorbent silica gel layer, detected with ninhydrin reagent and exposure to UV light, and quantified by reflectance scanning. Recovery from fortified distilled water samples at 10 ppm averaged 95.0% and at 1 ppm averaged 94.9%. Quantitative recoveries from tap water at 10 ppm and from lake water at 1 ppm were also demonstrated. Other boiler water additives permitted by FDA do not interfere.

INTRODUCTION

Cyclohexylamine (CHA) is permitted for use as a corrosion-inhibiting boiler water additive in the preparation of steam that will come in contact with food (code of Federal Regulations for

 0148-3919/86/0916-3439$3.50/0

Food and Drugs, 21:173.310). The concentration in steam is limited to 10 ppm. The Food Additives Analytical Manual (1) describes a gas chromatography method for determination of CHA as an impurity in foods and artificial sweetners, but no method is included for CHA in condensed steam. The previous edition of the FDA Food Additives Analytical Manual (1973) states that "there is no analytical method for determining cyclohexylamine in steam at present." The ASTM standard method (D2909-74) for CHA in water is a nonspecific colorimetric procedure based on diazotization of p-nitroaniline.

Other procedures that have been reported for the determination of CHA in water include the following: direct titration for measurement of total alkalinity, which is also nonspecific for CHA (2); flame ionization detector gas chromatography with direct aqueous injection (3); flame thermionic detector GC after isolation of CHA by distillation and extraction and acetylation (4); and ion chromatography (HPLC) (5).

CHA and other primary amine standards were separated by thin layer chromatography (TLC) and measured by in situ fluorometric scanning after derivatization to salicylaldehydeazomethine-diphenylboron chelates, but no real samples were analyzed (6). The following quantitative TLC method does not require prior derivatization of CHA and is applicable to its determination in condensed steam after concentration on a C_{18} microcolumn. Adequate recoveries from spiked water were demonstrated at the tolerance level (10 ppm) and also at 1 ppm. Other FDA-permitted boiler water additives were shown not to interfere with the analysis.

EXPERIMENTAL

Materials and Solutions

Cyclohexylamine was purchased from Aldrich (No. 24,064-8, Gold Label quality). A stock spiking solution was prepared in distilled water at a concentration level of 10.0 mg/ml. Dilutions with absolute ethanol were made to give the standards containing 100 and 500 ng/µl.

Procedure for TLC

Quantitative TLC analyses were carried out on Whatman laned preadsorbent high performance silica gel plates using procedures for initial zone application, development, and data handling that were described earlier (7). For detection of CHA, the developed chromatogram was irradiated for 6 minutes with a longwave (366 nm) ultraviolet light source, after spraying with ninhydrin and oven drying as described previously (7). The plate was positioned 2-3 inches below the UV tube inside of a dark box. The detected zones were scanned immediately with a Kontes Model 800 densitometer in the single beam, reflectance mode using the white phosphor disk (7).

Procedure for Sample Preparation and Analysis

Fortified samples were prepared by dissolving 100 µl of the 10.0 mg/ml standard (measured with a Hamilton GC syringe) in 100 ml or 1000 ml of water. The resulting solutions were 10.0 and 1.00

Acetone was added to the vial to adjust the volume to exactly 4 ml. Triplicate 4.00 µl aliquots of sample were applied to separate lanes of a plate alongside of triplicate aliquots of standard containing the theoretical weight of CHA for 100% recovery (1000 ng; 2.00 µl of the 500 ng/µl standard), using a 10 µl Drummond microdispenser. Recovery was calculated by comparing the average areas of the sample and standard scans.

RESULTS AND DISCUSSION

After development with butanol-acetic acid-water (3:1:1) mobile phase, spraying with ninhydrin, and exposure to longwave ultraviolet (UV) light, CHA appeared as a dark pink flat, oval-shaped zone with an R_F value of 0.62. A golden yellow band also formed across the entire width of the layer at R_F 0.59 (probably due to solvent demixing), but this did not interfere with scanning of the CHA zones. Exposure to UV light was necessary to intensify the color of the CHA zones, which were very faint pink after application of ninhydrin and heating. Upon exposure to the atmosphere, the CHA zones faded to a light rose color and the layer background became light pink-purple. Therefore, plates were scanned immediately after exposure to UV light. The time required for mobile phase development was 50 minutes.

Linearity of absorption with concentration was established by spotting 300 to 3000 ng standards of CHA. The linearity correlation coefficient (R) was 0.98 when peak area was plotted against

ng/zone (Figure 1). Figure 2 illustrates typical scans of triplicate 1000 ng standards and four microliter aliquots of column eluate. Samples and standards representing 100% recovery were always chromatographed in parallel on the same layer in order to correct for any minor variations in parameters such as R_F, detection intensity, and time of scanning.

Quantitative sorption of CHA from aqueous solution by the C_{18} column was found to occur only when the compound was in its fully unionized form. To achieve this, the sample was adjusted to pH 12.5, two units above the 10.56 pKa of CHA. Passage of 1000 ml of water through the column required approximately 22 minutes, and 100 ml samples required proportionately less time.

Recoveries of CHA from six separate 100 ml distilled water samples fortified at the FDA-permitted concentration level 10.0 ppm ranged from 88.7 to 101% with a mean of 95.0%. The reproducibility (CV) of the triplicate samples in each analysis averaged 7% with a range of 4 to 10%. To test the method at a lower concentration, three 1000 ml water samples fortified at 1.00 ppm were analyzed. Average recoveries were 89.3, 96.1, and 99.4%, and precision was 3.0% (CV). A 100 ml sample of Easton, PA tap water was fortified at 10.0 ppm and gave a 97.5% recovery. A blank tap water sample yielded no zone at the R_F of CHA, nor were any other zones evident on the blank or sample chromatograms. Duplicate 1000 ml natural (lake) water samples fortified at 1.00 ppm gave recoveries of 98.8 and 100.6%. Additional purple-pink zones were detected near the origin and above the CHA, but neither of these interfered

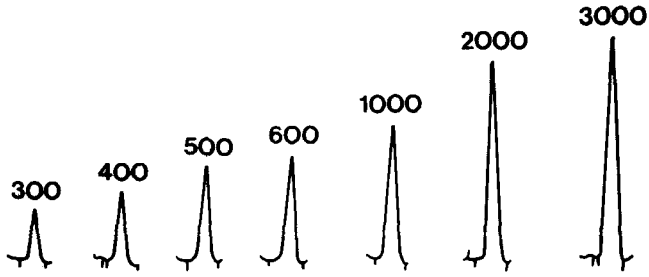

Figure 1. Typical scans of 300-3000 ng of CHA applied by spotting 3 to 6 µl of a 100 ng/µl standard and 2 to 6 µl of a 500 ng/µl standard. The attenuation setting on the HP 3390A integrator/recorder was X6.

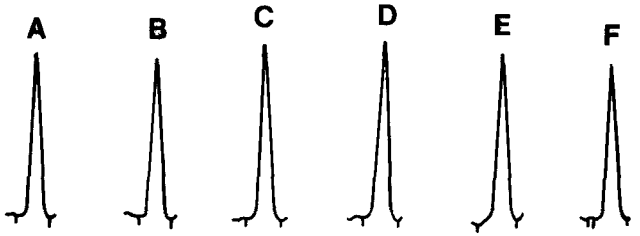

Figure 2. Scans of triplicate 1000 ng CHA zones (2 µl of a 500 ng/µl standard (A, B, C) and triplicate 4 µl aliquots of the C_{18} column eluate from a 10.0 ppm fortified water sample (D, E, F), representing 95.3% recovery.

with its measurement by scanning. Both of these extra zones were also present in a blank lake water analysis, but no zone was found with the R_F of CHA.

The recoveries of the other five FDA-permitted boiler water additives on the C_{18} column were not tested, but even if they were present in samples and co-extracted, they would not interfere in the CHA determination. Trisodium nitrilotriacetic acid and diethylaminoethanol are not detected by ninhydrin, and octadecyl-

amine, hydrazine, and morpholine migrate with higher R_F values and are separated from CHA.

Several preliminary experiments indicated that CHA could also be recovered from aqueous solutions with neutral or acidic pH by use of a strong acid cation exchange SPE column followed by elution with methanol containing base. This approach was not seriously pursued but might prove advantageous for certain impure samples containing unionized compounds that would co-extract with CHA on C_{18} columns and interfere during TLC analysis. Cyclohexyl-bonded silica gel SPE columns are also available from Baker and may be more-or-less selective for unionized CHA, but were not tested.

This paper describes a simple and selective method with high sample throughput that is suitable for the determination of CHA in condensed steam and other aqueous samples. Accuracy, precision, and sensitivity are adequate for routine monitoring of CHA at low ppb concentrations.

ACKNOWLEDGEMENT

The authors appreciate the advice and support of Joseph M. Patterson of J. T. Baker Chemical Company and Fred Rabel of Whatman Chemical Separation, Inc.

REFERENCES

1. Sherma, J., technical editor, FDA Food Additives Analytical Manual, Volume I, published by the Association of Official Analytical Chemists, Arlington, VA, pp. 112-120 (1982).

2. Przybylenski, J. L., Mater. Perform., 18, 49 (1979).

3. Malaiyandi, M., Thomas, G. H., and Meek, M. E., J. Environ. Sci. Health, Part A, A14, 609 (1979).

4. Murayama, H., Mukai, H., Ozaki, K., and Tominga, T., Niigata-ken Kogai Kenkyusho Kenkyu Hokoku, 7, 16 (1983).

5. Gilbert, R., Rioux, R., and Saheb, S. E., Anal. Chem., 56, 106 (1984).

6. Hohaus, E., Fresenius' Z. Anal. Chem., 310, 70 (1982).

7. Sherma, J., Chandler, K., and Ahringer, J., J. Liq. Chromatogr., 7, 2743 (1984).