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## SELECTIVE CONCENTRATION OF AMINES FROM AQUEOUS SOLUTIONS BY A GAS PURGING TECHNIQUE

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### SUMMARY

Amines are removed from heated, basic solutions saturated with salt by inert gas stripping and selectively trapped as coordination complexes on columns containing copper(II) salts coated on an inert support. An estimate of the amine concentrations at ppm levels can be made by measuring the length of the trapping column colored by the complexes. Concentrations of amines in ppb\* can be determined by eluting this column with potassium hydroxide and determining the amines in the effluent directly by gas chromatography. The procedure allows amines to be concentrated by a factor of 200 and removes potentially interfering substances from the sample.

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### INTRODUCTION

Simple methods for determining amines at ppb\* concentrations in aqueous samples such as waste water and biological fluids are not presently available. Direct gas chromatographic (GC) methods<sup>1,2</sup> are not applicable to amine concentrations much below the ppm level, and other organic contaminants in water can overlap the chromatographic peaks of amines. Pre-concentration of amines by solvent extraction or other techniques prior to their GC determination will allow more sensitive determinations, but interfering substances will also be concentrated. If available, nitrogen-specific GC detectors may be used to reduce or eliminate non-amine interferences. In this work techniques for selectively concentrating amines from aqueous solutions as a prelude to their GC determination were investigated.

Cation-exchange resins have been used for retaining amines from aqueous solutions<sup>3</sup>. We have found, however, that amine recoveries are not quantitative using this technique at concentrations below the ppm level. Walton and co-workers<sup>4,5</sup> have successfully separated compounds containing the amine functional group by ligand exchange chromatography. Investigations of the feasibility of using this technique for the pre-concentration of amines revealed that amines can be quantitatively retained on the copper, nickel and zinc forms of cation-exchange resins. Unfortunately no

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\* Throughout this article the American billion (10<sup>9</sup>) is meant.

sufficiently simple technique was discovered whereby amines could be quantitatively eluted from the resin in a form amenable to their GC determination.

Several workers<sup>6,7</sup> have reported the isolation of different organic compounds from aqueous solutions by gas purging techniques (also referred to as headspace techniques), coupled with trapping of the volatilized substances on materials such as Tenax GC. In previous work we have shown that amines can be selectively removed from gas streams using a support phase coated with copper(II) salts as an abstractor material<sup>8</sup>. By combining the gas stripping techniques with selective trapping of amines on columns containing copper(II) salts, an extremely simple and effective method has been developed for concentrating amines by a factor of up to 200-fold and simultaneously eliminating interfering substances. Amines are purged from a heated, basic solution saturated with salt and trapped on a column packed with Chromosorb W AW DMCS coated with copper(II) chloride. The amines are subsequently eluted with potassium hydroxide and determined directly in the potassium hydroxide solution by GC.

In addition to its utility as a selective method for concentrating ppb levels of amines prior to their GC detection, the gas purging method also provides an extremely simple method for determining ppm levels of amines. By merely measuring the lengths of trapping columns colored by the copper-amine complexes, estimates of amine concentrations as low as 0.5 ppm can be made.

## EXPERIMENTAL

### *Chemicals and apparatus*

A Hewlett-Packard Model 5711A gas chromatograph equipped with dual flame ionization detectors was used for determining amines. Amines were separated on 6- or 10-ft.  $\times$  1/8 in. O.D. stainless-steel columns packed with 28% Pennwalt 223 and 4% potassium hydroxide on 80-100 mesh Gas-Chrom R. Amines were purged from water using a modified 500-ml gas wash bottle. A coarse mesh gas diffusion tip was attached to the immersion tube, the exit tube was bent upward to prevent water condensation in the trapping tube, and the exit arm was drawn out to 1/4 in. O.D. to accommodate the use of Swagelok unions. The amine trapping material was prepared by dispersing (9 g of Chromosorb W AW DMCS in a minimal amount of methanol containing 1 g of dissolved copper chloride dihydrate (0.37 g Cu(II)). The mixture is heated to evaporate most of the methanol leaving a paste-like material that is then air dried until free flowing. The coated support is packed into glass tubes (1/8 or 1/4 in. O.D.) to give 2-5-in. bed volumes, and is retained with glass wool plugs.

### *Determination of amines in water by GC*

Add a sample of water containing amines to a gas wash bottle and bring the total volume to 100-200 ml with distilled water. Add 75 g potassium chloride and 1 g potassium hydroxide to the solution. Attach a 1/8-in. trapping column containing a 2-in. bed of coated Chromosorb to the exit arm of the gas wash bottle using a Swagelok union with PTFE ferrules. Seal the system and start purge gas flow at a rate of ca. 300 ml/min. Heat the water to a temperature of 60°. After stripping is completed (1½ h) remove the trapping tube and attach to an unused inlet of a gas chromatograph and allow carrier gas to flow through the tube at a temperature of 100°

for 5 min to volatilize any interfering organic substances that may have condensed on the trapping material. Remove the tube and attach to a syringe and slowly force 1 ml of 1 *M* potassium hydroxide through the column. Collect the effluent, allow any copper hydroxide precipitate to settle (*ca.* 5 min), and chromatograph a 2- $\mu$ l aliquot of the solution, using a 6-ft. Pennwalt column and a flow-rate of 25 ml/min. Acceptable chromatograms have been obtained at an isothermal oven temperature, 30° below the boiling point of the least volatile amine in a sample.

#### *Method for estimating amine concentrations*

Estimate ppm concentrations of amines using the same stripping procedure described above. Use 1/8-in. trapping columns containing 5 in. of sorbent for amine concentrations up to 10 ppm in 200 ml samples; use 1/4-in. trapping columns for higher concentrations. Mark the top of the colored amine band after 30 min and then at 15 min intervals until lack of movement indicates that all amines have been purged from the sample. After stripping is completed, measure the length of the colored amine band and determine the amine concentration from a calibration curve. In some cases the distinction between the copper-amine complex (generally blue) and the copper-aqua complex (light blue) covering the rest of the column may be difficult. In such cases heat the column with gas flowing through it. This will destroy the copper-aqua complex and leave a brown color without affecting the blue copper-amine complex.

## RESULTS AND DISCUSSION

#### *Recovery of amines added to water*

The GC method gives nearly quantitative recovery of most amines added to water at 100 ppb ( $\mu$ g/l) concentrations (Table I). Of the amines tested only morpholine gave unacceptable results. Based on 40 determinations all other amines tested gave an average recovery of 98.2% with a relative standard deviation of 7.6%. Morpholine cannot be efficiently purged from water because it is both very water soluble and relatively non-volatile. More volatile water-soluble amines, such as diethylamine, can be readily stripped from water. Less volatile amines that are sparingly soluble in water,

TABLE I

#### RECOVERY OF AMINES BY THE GAS CHROMATOGRAPHIC METHOD

Amines tested in mixtures containing 3 to 6 components each at a concentration of 100 ppb, *N* = number of determinations.

<i>Amine</i>	<i>N</i>	<i>Average recovery (%)</i>	<i>Amine</i>	<i>N</i>	<i>Average recovery (%)</i>
Triethylamine	3	95	Octylamine	3	95
Tributylamine	3	102	Hexylamine	3	98
Dibutylamine	6	104	Piperidine	4	97
Butylamine	3	90	Pyridine	6	100
Cyclohexylamine	3	91	Aniline	3	100
Diethylamine	3	101	Morpholine	3	8

Average recovery (excluding morpholine), 98.2%. R.S.D., 7.6%.

such as tributylamine, can also be stripped from water. The gas stripping method fails however, when applied to amines that are both non-volatile and extremely water soluble.

#### *Gas stripping conditions*

The type of purge gas used, its flow-rate, and the method of dispersing it in water all affect the removal rate of amines from water. All preliminary work on this method was performed using air as a purge gas because it appeared as effective as other gases evaluated (helium, nitrogen, and methane) and less expensive. However, when the method was applied to piperidine, recoveries of only 50% were attainable and an unidentified peak appeared in the chromatograms. When helium was used as a purge gas the recoveries improved and the unidentified peak disappeared. It is reasonable to assume that piperidine and presumably other amines can be air oxidized and thus use of an inert gas is recommended. Stripping time decreases as gas flow-rate is increased. A flow-rate of 300 ml/min is used because amines can be stripped in a reasonable length of time and higher flow-rates lead to a pressure build-up in the system. Use of a gas dispersion tip on the immersion tube is essential for the rapid stripping of amines. Using an open tube di(*n*-butyl)amine, for example, cannot be stripped in 4 h. However, when a coarse mesh sparger tip is used purging is complete in less than 30 min.

The temperature and salt content of the solution affect the time required for complete removal of amines. At room temperature most amines cannot be purged to any appreciable extent. At 60° all amines tested can be stripped in less than 1 h. Saturating the solution with salt decreases the purging time significantly. As an example of its effect, diethyl amine requires 22 h for complete stripping from a solution containing no added salt but less than 30 min from a solution saturated with potassium chloride. Potassium hydroxide prevents ionization of amines and thus facilitates the sparging process.

#### *Amine trapping materials*

Prior work indicated that copper(II)chloride coated on Chromosorb W AW DMCS would be effective and selective for removing amines from gas streams<sup>8</sup>. No serious effort was made to discover if other combinations are as effective for this application. When zinc salts are used in place of copper salts, amine peaks do not appear in the chromatograms at their expected retention times. Instead, broad humps occur at longer retention times. Macroreticular resins were found to be effective as support phases, but other organic compounds are strongly retained on them. In previous work when copper-coated Chromosorb was used as an amine abstractor material for use in GC, a coating of 25% copper(II) chloride dihydrate was used<sup>8</sup>. For the present application a 10% coating has as high a capacity for removing amines and a more uniform coating is obtainable. Presumably at higher coating levels a large fraction of the copper is inaccessible to the amines.

#### *Elution and GC determination of amines*

Amines can be eluted from the sorbing material with alkaline alcohol solutions, with cyanide solutions, or with aqueous basic solutions. Alcohols are undesirable as eluting solvents because the alcohol peaks or their tailing edges obliterate the peaks

of early eluting amines. The use of cyanide to displace amines from copper complexes is effective, but offers no advantages that outweigh the hazards involved in its use. Since the Pennwalt columns used for separating amines can tolerate water and contain potassium hydroxide as a supplementary stationary phase, it was believed that aqueous potassium hydroxide would not adversely affect the column. Aqueous potassium hydroxide effectively elutes amines from the trapping column and offers the additional benefit that any copper washed off is precipitated as its hydroxide. Several hundred injections of potassium hydroxide solutions of amines into the Pennwalt column did not produce any significant changes in the chromatographic separations; thus the assumption that this eluting solvent would not adversely affect the column was borne out. No serious efforts were made to modify or improve previously reported GC methods for separating amines because the goal of this work was to develop techniques for applying existing methods for determining lower concentrations of amines after removal of interferences.

### *Interference studies*

Of the organic compounds studied, none was retained to a significant extent on the amine sorbent used (Table II). However, nearly all of these substances condense on the trapping column and the heating step is required to remove them. Only acetone and pentanone are retained on the column after the heating step and these only to an extent of about 1% of the amount added to the sample as an interference. It was anticipated that metal ions present in samples might complex amines and interfere with their removal from water. However, the potassium hydroxide added to adjust sample pH also serves to precipitate most transition metals and no interferences were encountered. One devious interference was encountered when the semi-quantitative method was applied to the determination of ammonia in urine. The standard stripping procedure hydrolyzes urea in urine to release ammonia. This problem is eliminated by omitting the heating step, although this lengthens the required stripping time considerably.

TABLE II

### SUBSTANCES NOT AFFECTING THE DETERMINATION OF AMINES

Mixture of all organic compounds each at a concentration of 10 ppm added to a mixture containing 100 ppb each of diethylamine, butylamine, pyridine, cyclohexylamine, and dibutylamine. Inorganic ions added singly to same amine mixture at concentrations, in ppm, indicated in parentheses.

<i>Organic</i>		<i>Inorganic</i>
Methanol	Benzene	Calcium (450)
Ethanol	Benzaldehyde	Magnesium (1000)
Propanol	Ethylene dichloride	Copper (1000)
Acetone	Carbon tetrachloride	Nickel (1000)
2-Pentanone	Phenol	Iron (1000)
Isopropyl ether	Benzyl alcohol	Chloride (1000)
Ethyl acetate	Dichlorobenzene	Sulfate (1000)
Octane	Cumene	Carbonate (1000)
Acetonitrile	Acetic acid	Zinc (1000)

*Semi-quantitative determination of amines*

The semi-quantitative method was applied to a variety of amines and was found to be reasonably sensitive and reproducible (Table III). The detection limits for amines established for this procedure are based on an arbitrarily chosen band length of 1 mm when 1/8 in. O.D. columns are used. Lower detection limits would be obtainable with smaller diameter columns, but such columns create excessive back pressure. Lower concentrations of copper coating on the Chromosorb also lead to greater sensitivities, but the use of significantly lower amounts of copper coatings usually makes the bands difficult to detect. Pyridine, aniline, and some other amines form extremely intensely colored copper(II) complexes and in such cases the coating could be reduced.

TABLE III  
SEMI-QUANTITATIVE METHOD PARAMETERS

<i>Amine</i>	<i>Amine/Cu(II) *</i>	<i>Detection limit**</i> (ppm)	<i>Calibration curve***</i> slope ( $\mu M/mm$ )
Trimethylamine	1.0	1.0	2.2
Dimethylamine	1.0	0.5	2.2
Butylamine	1.1	1.0	2.4
Cyclohexylamine	0.9	1.0	1.9
Aniline	0.9	1.0	1.9
Dibutylamine	1.5	2.0	3.2
Tributylamine	1.5	3.0	3.2
Pyridine	2.0	1.5	4.3
Ammonia	4.0	0.5	8.6

\* Known amount of each amine stripped from 200 ml of water and trapped on 1/8 in. O.D. column containing 2.16  $\mu$ moles Cu(II)/mm of length.

\*\* Calculated concentration of amine giving a 1-mm band length when purged from a 200-ml sample.

\*\*\* Slope obtained using 1/8 in. O.D. columns coated with 10%  $CuCl_2 \cdot 2H_2O$ .

The reproducibility of the method was tested on six replicates of 1.4 mg of di(*n*-butyl)amine purged from volumes of water ranging from 100 to 200 ml and trapped on different batches of the sorbent. Bands ranging from 14.5 to 16.0 mm were measured, with an average of 14.8 and an average deviation from the mean of 0.5 mm. The variability is primarily due to the non-planarity of the leading and tailing edges of the amine band which leads to an uncertainty in the measurement of length. This uncertainty is relatively independent of the length of the amine band; thus the relative uncertainty will increase as the amount of amine decreases.

Linear calibration curves were obtained when the semi-quantitative method was applied to a representative group of amines. The slopes of calibration curves (Table III) are, of course, influenced by the amount of copper coated on the support and the column diameter. Both of these variables, however, are readily controlled. The slope obtained for an individual amine is determined by the stoichiometry of the complex formed. Metal to ligand ratios for the copper-amine complexes were calculated by stripping a known amount of amine and trapping it on columns containing a known amount of copper(II) per unit length. The molar ratios obtained (Table III)

were quite reasonable in most cases which also indicates that practically all the copper is accessible to the amines. Because many amines form 1:1 complexes with the copper(II) under stripping conditions, it is possible in some cases to estimate the total amine concentration in a sample even if the identity of the amines is not known. Such an estimate may, however, be in error if a sample contains significant amounts of amines, such as ammonia or pyridine, that form higher order complexes.

Tubes containing 5 in. of sorbing material are used in the semi-quantitative method. In general this length of column is adequate for trapping at least 0.25 mmole of amines when 1/8 in. O.D. columns are used and 1.0 mmole when 1/4 in. O.D. columns are used. The larger columns were rarely used in developing the method, but the reproducibility is similar on both column sizes.

### *Applications*

The semi-quantitative method was used to determine ammonia in urine and in the effluent from a municipal sewage plant. With no heating the urine sample required 2 h for complete stripping and 28 ppm ammonia were found. A second sample was heated to 95° during the purging and gave 1300 ppm ammonia, due primarily to the hydrolysis of urea. The sewage plant effluent sample contained 45 ppm of ammonia. A sample of condensed steam from a power plant containing a proprietary mixture of amines as a corrosion inhibitor was analyzed using both the GC technique and the semi-quantitative procedure. The gas chromatographic method indicated the sample contained 1.3 ppm of cyclohexylamine plus four other unidentified amines having retention times less than that of diethylamine. The semi-quantitative method indicated a total amine concentration of 1.6 ppm based on a cyclohexylamine calibration curve.

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