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DETERMINATION OF LOW CONCENTRATIONS OF LOW-MOLECULAR-WEIGHT ALDEHYDES AND KETONES IN AQUEOUS SAMPLES

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SUMMARY

Low concentrations of aldehydes and ketones in aqueous samples are concentrated on a small column containing a zeolite known as ZSM-5. The carbonyl compounds are then eluted with a small volume of acetonitrile and converted to the 2,4-dinitrophenylhydrazones, which are then separated by liquid chromatography. Excellent recoveries are obtained for all of the carbonyl compounds studied with the exception of formaldehyde. The method has been used in the analysis of drinking water samples.

INTRODUCTION

The analytical technology for preconcentration of trace organic compounds from aqueous samples has improved tremendously in recent years. However, the determination of very low concentrations of volatile, hydropohilic organic compounds in water has been carried out only with great difficulty. The determination of polar organic compounds of low molecular weight in drinking water is of importance in order to understand better the complicated chemistry involved in the chlorination of water. Coleman *et al.*[1] believe that mutagenic organic compounds can be produced by chlorination of humic matter that occurs naturally in water. Chloroacetone was included in the list of compounds that might be produced.

Organic compounds in drinking water, except for humic matter, usually are found in such low concentrations that a concentration step is needed prior to analysis[2]. With recent advances in capillary columns used in gas chromatography (GC), direct injection of aqueous samples has become a viable method for trace analysis of some organic compounds with a favorable flame ionization detection (FID) response[3,4]. However, Richard and Junk[5] indicated that a concentration of at least 1 ppm is necessary for the direct injection of samples containing low-molecular-weight polar compounds.

The usual methods for preconcentration of organic compounds, such as concentration on XAD-2[6] or Tenax[7,8], do not work for small, polar molecules. These compounds can sometimes be sorbed on activated charcoal, but desorption has not been reproducible[9]. While compounds such as aniline and chlorophenols have been

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reported to be effectively sorbed by reversed-phase liquid chromatographic (LC) columns[10,11], many others are not taken up. Multiple fractional distillation[12] or steam distillation[13] has been used for certain specialized cases.

A novel method for accumulation of aldehydes and ketones was reported by Takami *et al.*[14] in which an ion-exchange column loaded with 2,4-dinitrophenylhydrazine (DNP) was employed. The authors were able to determine low concentrations of aldehydes and ketones in rain water and river water, although the method was not applied to drinking water.

The physical and chemical characteristics of a zeolite, ZSM-5, have been reported[15]. A unique property of ZSM-5 is that it has channels that are about 5–5.6 Å in diameter. Organic molecules of the proper size and shape are able to invade these channels and these organic molecules are retained due to the unusual hydrophobicity of ZSM-5. Recently, investigations with Silicalite[16,17], a member of the ZSM-5 substitutional series[18], have reported that Silicalite has high capacity for low-molecular-weight polar organic compounds.

The use of the zeolite, ZSM-5, for the preconcentration of polar organic compounds from aqueous samples is examined. Low-molecular-weight aldehydes and ketones, with the exception of formaldehyde, are strongly retained by the zeolite and can be subsequently eluted by a small volume of methanol or acetonitrile. The effluent is then reacted with DNP and the resulting derivatives are then separated by conventional LC.

EXPERIMENTAL

Solvents and reagents

Water was produced using the Barnstead Nanopure II System (Barnstead, Division of SYBRON, Boston, MA, U.S.A.). All organic solvents were distilled in glass UV-grade (Burdick & Jackson Labs., Muskegon, MI, U.S.A.). Unless specified, these solvents were used as received.

Acetonitrile, and pentane were further purified by adding 0.5 ml of a dilute solution of DNP and hydrochloric acid to 100 ml of acetonitrile or pentane and then distilling. In each case 75 ml of distillate was collected.

Test solutions

For breakthrough experiments, 100 μl of the aldehyde or ketone to be tested was dissolved in 100 ml of pure water. For accumulation experiments, a stock solution containing 1 μl of aldehyde or ketone in 10 ml of water was diluted to the desired concentration with pure water.

Preparation of ZSM-5 column

The zeolite, ZSM-5, was in the ammonium form and was used as received. However, classification of particle size was accomplished by slurrying 1 g of the zeolite with 60 ml of water and decanting the fine particles that had not settled after 15 min. This process was repeated twice. The remaining zeolite was collected and dried overnight.

For capacity experiments dry zeolite was added to a small glass tube and held in place by a plug of glass wool. For accumulation of carbonyl compounds from

aqueous samples, a 5 cm × 4.6 mm I.D. stainless-steel column was packed with about 0.5 g of the dry zeolite by the tap and fill method[19]. After use, the column was filled with methanol or acetonitrile for storage.

Chromatographic instruments

A Tracor 550 gas chromatograph (Austin, TX, U.S.A.) with FID was used. For aqueous injections a 6 ft. × 1 mm I.D. glass column (made by house glass shop) was packed with 50–80 mesh Porapak Q. (Supelco, Bellefonte, PA, U.S.A.). For hexane and methylene chloride solutions a 12.5 m × 2 mm I.D. dimethyl silicone capillary column (Hewlett Packard, Canoga Park, CA, U.S.A.) was used.

The loading apparatus used consisted of a Milton Roy minipump, pressure gauge, pressure relief valve, Valco injector and a 2-μm solvent filter. For high-performance liquid chromatographic (HPLC) analysis either a Spectra-Physics 8000 with a fixed-wavelength detector at 254 nm, or a Tracor 970A variable-wavelength UV–Vis absorbance detector was used. A 10-μl sample loop was used in conjunction with a 5 m × 4.5 mm column filled with 3-μm Spherisorb C_{18} packing (the "Little Champ").

Procedure for determination of capacity

Breakthrough curves were obtained by passing an aqueous solution containing 1 mg analyte/ml solution through 0.5 g of ZSM-5. Using gravity flow at ambient temperature, fractions at 1-ml intervals were collected and analyzed by GC on Porapak Q.

Procedure for determining aldehydes and ketones in aqueous samples

The ZSM-5 column was washed with 3 ml of purified acetonitrile, which was added by means of a hand-held syringe. Then 200 ml of pure water was pumped through the column to remove the acetonitrile. A water sample of appropriate volume (100 ml for recovery experiments, 1–3 l for drinking water) was passed through the column at a flow-rate of approximately 4 ml/min.

The ZSM-5 column was removed from the loading apparatus and eluted with 3 ml of purified acetonitrile directly into the bottom of a centrifuge tube containing DNP for derivatization. The tube contained 0.5–0.7 ml of a solution of 1.7 mg of DNP per milliliter of purified acetonitrile. Perchloric acid catalyst (0.02 ml of 1 *M* aqueous solution) was added just before the elution. The ZSM-5 column was immediately washed with water to avoid later plugging.

After 15–20 min reaction with the DNP reagent, 50 ml of water was added and the resulting solution was extracted twice with 10-ml portions of purified pentane. Each pentane layer was extracted twice with 15 ml of water to remove traces of unreacted DNP. The combined pentane extracts were dried over anhydrous sodium sulfate. The pentane solution was then concentrated in a Kuderna-Danish apparatus and then carefully evaporated to dryness.

The residue was dissolved in 1–2 ml of acetonitrile–water (50:50). Nitrobenzene or acenaphthene was used as an internal standard, by addition to the DNP solution used for derivatization. A 10-μl aliquot of the acetonitrile–water (50:50) solution of the residue was injected into the HPLC apparatus. Gradient elution was used, going from methanol–water (40:60) to methanol–water (70:30) over 30 min and continuing

to 100% methanol over the next 25 min. The temperature was 25°C and the flow-rate was 0.5 ml/min. Quantitation was based either on peak height or peak area at 254 nm, or at 331 nm if spectral interferences were encountered at 254 nm.

RESULTS AND DISCUSSION

Capacity experiments

Dilute aqueous solutions (1 mg/ml) of several aldehydes and ketones were passed through a column of ZSM-5 to ascertain the feasibility of using this material to accumulate carbonyl compounds. Each solution was passed through the ZSM-5 column at gravity flow until breakthrough occurred. Results are given in Fig. 1.

The capacity of the zeolite for aldehydes and ketones increased with higher molecular weight. ZSM-5 showed good retention for all of the carbonyl compounds tested with the exception of formaldehyde and acetaldehyde. From the data in Fig. 1, the estimated distribution coefficients ranged from 1.2 for formaldehyde to 100 for 2-pentanone. Exploratory experiments showed that smaller amounts of most aldehydes and ketones are well retained by the zeolite column, even after washing with rather large volumes of water.

Elution

Several investigators have selected derivatization with DNP and LC separation for quantitative determination of aldehydes and ketones[20,21]. We found the improved derivatization method of Lipari and Swarin[22] to be convenient and effective. An online derivatization and elution procedure was investigated first. The ZSM-5 column containing sorbed carbonyl compounds from an aqueous sample was connected to a LC column. An elution gradient beginning with 100% water and ending with 100% methanol was started. Immediately after starting the gradient, a DNP reagent with catalyst was injected to react with the carbonyl compounds on the zeolite column. However, this method gave unfavorable results, possibly because of insufficient reaction time of DNP with the sorbed carbonyl compounds.

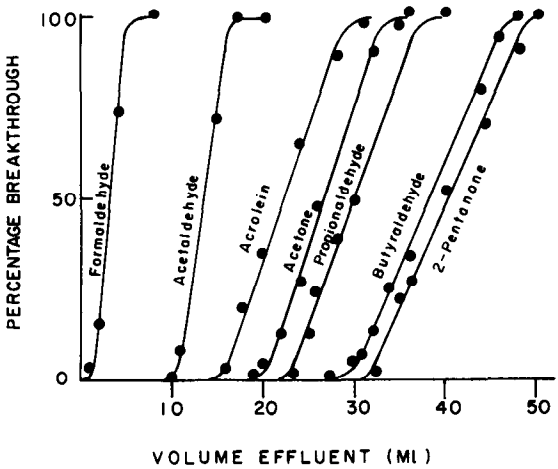

Fig. 1. Breakthrough curves for aldehydes and ketones. Aqueous solutions containing 1 mg/ml of carbonyl compounds were passed through a mini-column containing 0.50 g of ZSM-5.

The next approach was to elute the carbonyl compounds from the zeolite column with an organic solvent and then to form 2,4-dinitrophenylhydrozones in a post-column reactor. Experimental work demonstrated that all of the carbonyl compounds studied could be completely eluted from the ZSM-5 column with a small volume of either methanol or acetonitrile. Acetonitrile was selected because a smaller volume was required for elution and because acetonitrile was found to contain fewer carbonyl impurities than methanol.

Derivatization of carbonyl compounds and solvent extraction of DNP

Reaction of the aldehydes and ketones (eluted with acetonitrile) with DNP was complete within a few minutes. During the elution step it was found necessary to run the acetonitrile effluent directly into he DNP solution, which was contained in a small centrifuge tube. If this was not done, losses were sometimes noted for volatile compounds such as acetone.

When the derivatization reaction was complete, it was necessary to separate the derivatives from the acetonitrile and from the excess of DNP. Some concentration is also very desirable. These aims were accomplished by adding water, extracting twice with pentane, and carefully evaporating to dryness (Table I). The dinitrophenylhydrazones were then taken up in a small volume of acetonitrile–water (50:50) and aliquots injected into a liquid chromatograph for separation of the individual dinitrophenylhydrazones.

Chromatography and recovery studies

Some effort was needed to work out an effective combined procedure for derivatization, solvent extraction and subsequent separation by HPLC. Using the derivatization and extraction procedure described, LC on a very short column ("Little

TABLE I

EXTRACTION OF 2,4-DINITROPHENYLHYDRAZONES WITH PENTANE

Conditions: 10 μg of aldehyde or ketone added to 0.65 ml DNP reagent, then diluted with 50 ml of water and extracted with 10 ml of pentane.

Compound	*Recovery (%)*	
	First extraction with pentane	*Second extraction with pentane*
Formaldehyde	48.4 ± 3.2*	82.2 ± 2.6
Acetaldehyde	64.7 ± 3.9	93.4 ± 3.1
Acrolein	79.1 ± 6.0	75.6 ± 0.5
Acetone	73.0 ± 18.9	112.4 ± 0.4
1-Propanal	82.6 ± 5.0	98.4 ± 1.6
Crotonaldehyde	88.8 ± 6.1	101.4 ± 1.7
1-Butanal	85.7 ± 6.9	102.1 ± 1.2
2-Butanone	76.3 ± 21.3	103.3 ± 4.5
1-Pentanal	91.4 ± 6.9	101.2 ± 1.1
2-Pentanone	76.6 ± 19.8	101.3 ± 5.8
1-Hexanal	78.6 ± 13.7	101.0 ± 2.6
2-Hexanone	78.6 ± 13.7	101.0 ± 2.6

* Average deviation.

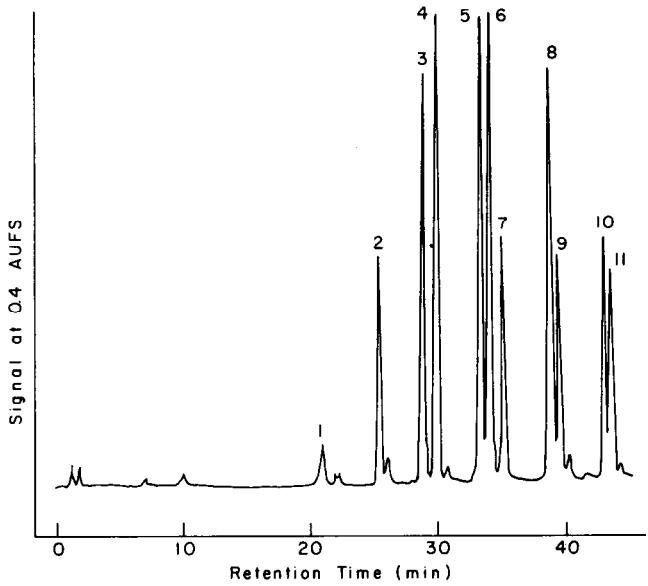

Fig. 2. Chromatogram of 2,4-dinitrophenylhydrazones. Conditions: "Little Champ" column, 25°C, detection at 254 nm, 0.4 A.U.F.S. Gradient elution methanol–water (40:60) to methanol–water (70:30) in 30 min, then to 100% methanol in 25 min. Flow-rate 0.5 ml/min. Peak identification: 1 = formaldehyde, 2 = acetaldehyde, 3 = acrolein, 4 = acetone + 1-propanal, 5 = crotonaldehyde, 6 = 1-butanal, 7 = 2-butanone, 8 = 1-pentanal, 9 = 2-pentanone, 10 = 1-hexanal, 11 = 2-hexanone.

TABLE II

RECOVERY OF MODEL COMPOUNDS

Compound	*1000 μg/l**	*100 μg/l***
Formaldehyde		1.2 ± 1
Acetaldehyde		90 ± 9***
Acrolein		98 ± 6
Acetone	43 ± 6	84 ± 6
1-Propanal		98 ± 4
Crotonaldehyde		98 ± 1
1-Butanal		103 ± 3
2-Butanone	100 ± 2	100 ± 4
1-Pentanal		96 ± 7
2-Pentanone	97 ± 3	97 ± 6
1-Hexanal		95 ± 6
2-Hexanone		95 ± 3

* A volume of 900–500 ml of 1000 μg/l solution was loaded on 0.5 g of ZSM-5. Analysis of effluent was by GC.

** A volume of 100 ml of 100 μg/l solution was loaded on 0.5 g of ZSM-5. Analysis of DNP derivative was by HPLC.

*** A volume of 50 ml of 100 μg/l solution was loaded on 0.5 g of ZSM-5. Analysis of DNP derivative was by HPLC.

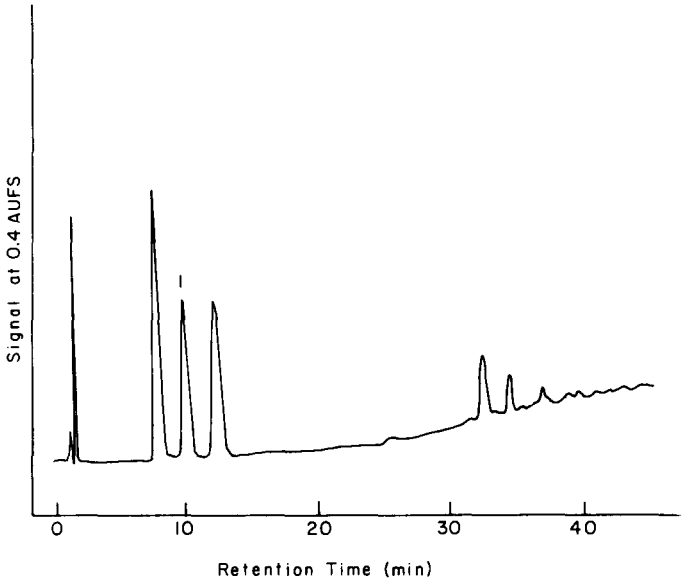

Fig. 3. Chromatogram of blank. Nitrobenzene added as internal standard.

Champ") with a methanol–water gradient was found to give good resolution of the derivatives studied. The chromatogram in Fig. 2 is for known carbonyl compounds added to acetonitrile and carried through the procedures described above.

Recoveries of test compounds were made by passing 100 ml of an aqueous solution containing 100 μg/l of aldehyde or ketone through the zeolite column and

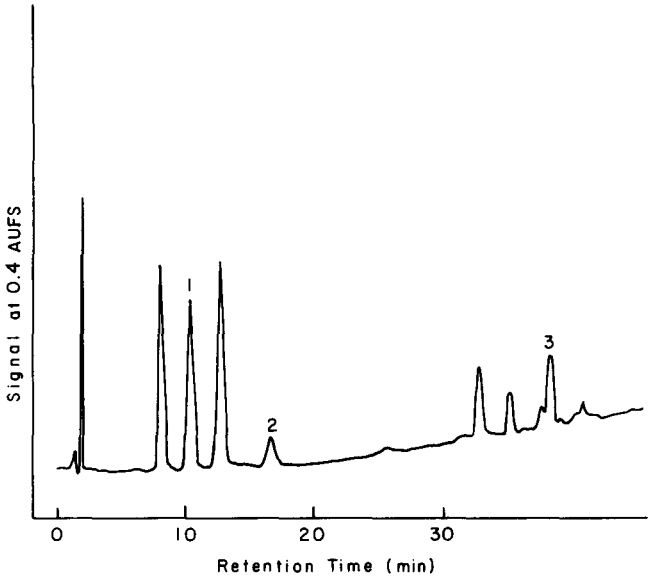

Fig. 4. Chromatogram of Des Moines water. Peak identification: 1 = nitrobenzene (internal standard), 2 = formaldehyde, 3 = 2-butanone.

following the procedure described. Only 50 ml of the aqueous solution containing acetaldehyde was used. The results in Table II show excellent recoveries for all compounds investigated with the exception of formaldehyde. A larger volume (500–900 ml) of a more concentrated solution (1000 μg/l) also gave good recoveries in two cases. The low recovery of acetone could be due to volatility losses from the collection technique that was in use at that time.

In these experiments the residue from the pentane extraction and evaporation was taken up in 2 ml of acetonitrile–water (50:50) and 10 μl was injected into the LC column, monitored at 254 nm at 0.4 A.U.F.S. A very conservative estimate of the detection limit is less than 10 ng of aldehyde or ketone.

Application to drinking water

Samples ranging from 1–3 l of both raw and finished drinking water were passed through a ZSM-5 column and analyzed for possible low-molecular-weight carbonyl compounds by the new procedure. A blank, carried out with pure distilled water, is shown in Fig. 3. Nitrobenzene was added as an internal standard. The other peaks are believed to come from residual DNP and accompanying impurities.

Fig. 4 shows the chromatogram obtained in the analysis of Des Moines, Iowa water. Peak 3 was identified as 2-butanone and peak 2 is believed to be the derivative of formaldehyde. The retention times differ somewhat from those in Fig. 2 owing to some deterioration of the LC column. However, the 2-butanone product was confirmed by GC–MS analysis. This water was estimated to contain 1.6 ppb (μg/l) of 2-butanone. No aldehydes or ketones were found in water samples from Ames, Iowa or from the nearby Skunk River.

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