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LIQUID CHROMATOGRAPHIC DETERMINATION OF ACETIC ACID TRAPPED IN CHARCOAL TUBES

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SUMMARY

A liquid chromatographic procedure suitable for the analysis of charcoal tubes containing as little as 0.03 mg acetic acid is described. Recovery of spiked acetic acid varied from 95 to 109% over the range of 0.03 to 0.50 mg with a precision of 1–3% relative. In the described procedure acetic acid trapped in charcoal packed tubes is desorbed with 0.1 *N* sodium hydroxide solution and then separated on a cation resin with a 0.02 *N* sulfuric acid mobile phase. This liquid chromatographic procedure overcomes many common limitations of trace-level gas chromatographic determinations of acetic acid such as peak ghosting, non-linear calibration, and inadequate detection limits. The ability to detect sub-milligram quantities of acetic acid trapped on charcoal allows use of significantly shorter sampling times in monitoring personal exposure to acetic acid vapors. The procedure is also suitable in other situations where low levels of acetic acid vapor can be trapped in charcoal tubes. In addition the described liquid chromatographic analysis is potentially applicable for any aqueous samples containing trace levels of acetic or other lower fatty acids at levels down to 1–2 ppm.

INTRODUCTION

Exposure to excessive levels of acetic acid vapor produces a number of nasal, eye, and respiratory disorders leading to problems such as pharyngitis and catarrhal bronchitis[1]. The Occupational Safety and Health Administration (OSHA) recommended permissible exposure limit value for acetic acid is 25 mg/m^3 in air. Atmospheric acetic acid determinations are normally performed by pumping a known volume of air through a trapping medium prior to analysis of the collected acetic acid vapors. For example, the standard National Institute for Occupational Safety and Health (NIOSH) procedure for monitoring personal exposure to acetic acid in the workplace employs charcoal tubes to trap and concentrate acetic acid that is later desorbed from the charcoal with formic acid (88%) and determined by gas chromatography[2]. This procedure has been validated for tubes containing 2–9 mg acetic acid. However, at lower levels traces of acetic acid present in the formic acid used to desorb tubes may contribute a significant blank value. An alternate approach recently de-

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scribed[3] utilizes aqueous sodium carbonate to trap acetic acid vapors prior to conversion of the acid to a methyl ester. This procedure suffers from the disadvantage of employing liquid traps which are awkward to use in personal monitoring.

In this report a liquid chromatographic procedure suitable for the analysis of charcoal tubes containing as little as 0.03 mg acetic acid is described. Determinations of acetic acid at this level by gas chromatography are subject to numerous drawbacks including ghost peaks, inadequate detection limits, inadequate accuracy, and non-linear calibration curves[4,5]. These difficulties were not encountered in the procedure described here where linear calibrations were obtained and peak ghosting was not observed. In this work charcoal tubes spiked with acetic acid were desorbed with 0.1 *N* sodium hydroxide solution for 30 min and the resulting solution was diluted and injected directly into a liquid chromatograph employing a cationic resin and a mobile phase of 0.02 *N* sulfuric acid. The eluting acids were detected by monitoring absorbance at 210 nm. This liquid chromatographic technique for the separation of organic acids has been referred to as ion-moderated partition chromatography[6].

The ability to analyze charcoal tubes containing low levels of acetic acid allows the use of significantly decreased sampling times in industrial hygiene personnel monitoring for exposure to acetic acid vapors at the OSHA limit. In addition, acetic acid concentrations far below the OSHA standard can be determined with reasonable sampling times. Thus the analysis of trace levels of acetic acid vapors generated from diverse sources such as microbiological metabolism or industrial emissions could be rapidly monitored.

In addition the described liquid chromatographic method is applicable to the analysis of any aqueous sample containing ppm levels of acetic or other lower fatty acids. Acetic acid present in non-aqueous solutions could be determined following extraction with sodium hydroxide.

EXPERIMENTAL

All charcoal tubes employed in this study were spiked directly with known amounts of acetic acid. Previous reports[2] have demonstrated that charcoal tubes are effective in trapping acetic acid vapors from air with breakthrough limits in excess of 10 mg. In our studies standard size charcoal tubes, 70 × 6 mm, were spiked by slowly adding 1–8 μl of aqueous acetic acid solution to the center of the front section of a charcoal tube with a 10-μl syringe. In cases where more than 3 μl were added, the syringe was slowly pushed deeper into the charcoal bed as the spike was deposited. In some comparative studies acetone replaced water as the spiking solvent while in other studies methyl acetate was spiked in place of acetic acid. All charcoal tubes were capped immediately after spiking and allowed to equilibriate at room temperature for at least 24 h.

Prior to analysis the charcoal and associated glass wool and foam plugs were transferred from the glass tubes into a small vial and 1 ml of 0.1 *N* sodium hydroxide solution was pipeted into the vial. The desorption was allowed to proceed for 30 min with occasional shaking of the vial. After this time a 0.5-ml aliquot was removed and placed in a 5-ml volumetric flask which was diluted to the mark with water thus diluting the samples ten-fold and reducing the sodium hydroxide concentration to 0.01 *N*. This solution was directly analyzed. Thus acetic acid is initially injected as the acetate, however in the pH 1.7 mobile phase, it is rapidly converted to the acid.

Liquid chromatographic separations were performed on a system consisting of a Waters Assoc. Model 6000A pump, a Rheodyne Model 7010 fixed-loop injector, and a Varian UV-50 variable-wavelength detector. A detection wavelength of 210 nm and an injection volume of 100 μl were employed. Separations were performed on a Bio-Rad HPX-87 liquid chromatographic column (300 $\times$ 7.8 mm) at room temperature. The mobile phase, 0.02 N sulfuric acid, was pumped at a volumetric flow-rate of 0.6 ml/min. Water used to prepare the mobile phase was purified by passage through a Millipore Milli-Q water treatment system. The mobile phase was degassed by rapid stirring while under vacuum. Peak height measurements were employed in all quantitative calculations.

RESULTS AND DISCUSSION

The liquid chromatographic column employed in these studies, Bio-Rad HPX-87, contains a strong cation resin consisting of totally porous sub-10-μm particles[6]. Two retention mechanisms, ion exclusion and "reversed-phase" adsorption are reported to primarily influence retention behavior of organic acids on cation resins[7–10]. Ion exclusion is similar to size exclusion or gel permeation chromatography except ionic repulsion at the stationary phase surface rather than molecular size is responsible for the exclusion of molecules from the intraparticle volume.

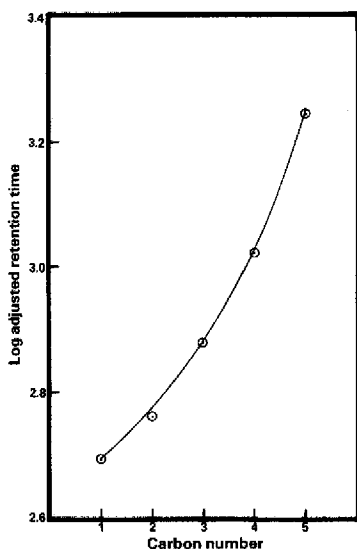
Organic acids with low pK_a values are separated on this type of column principally by an ion-exclusion mechanism while organic acids with higher pK_a values such as acetic acid, which exists predominantly as a undissociated acid at the mobile phase pH, are separated by adsorption on the relatively non-polar styrene–divinylbenzene resin backbone. The data in Table I demonstrate that acetic acid retention on this cation resin is essentially independent of mobile phase pH over the pH range examined. Retention, as measured by the capacity factor, k', shifted by only 4% as the mobile phase pH was changed from 3 to 1.7. Acetic acid retention shifted to slightly lower values as the pH decreased.

TABLE I

ACETIC ACID RETENTION AS A FUNCTION OF MOBILE PHASE COMPOSITION

Mobile phase (N H_2SO_4)	*pH*	*k' acetic acid*
0.001	3.0	1.84
0.002	2.7	1.84
0.004	2.4	1.79
0.008	2.1	1.80
0.020	1.7	1.77

Fig. 1 contains a plot of log adjusted retention time against carbon number for formic through valeric acids. Note that this plot appears to approach linear behavior as carbon number increases. This plot is similar to those obtained in gas–liquid chromatography and in reversed-phase liquid chromatography with octadecyl-bound silica columns for homologous series. Fig. 2 is a chromatogram of an aqueous solution containing roughly 200 μg/ml each of formic through valeric acids. Retention



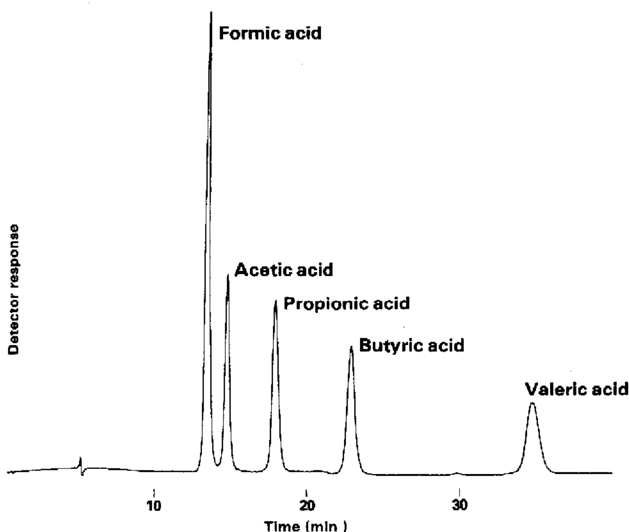


Fig. 1. Log adjusted retention time for formic through valeric acids as a function of carbon number. Bio-Rad HPX-87 column with 0.02 *N* sulfuric acid mobile phase.

Fig. 2. Chromatogram of formic through valeric acids. Bio-Rad HPX-87 column, 0.02 *N* sulfuric acid mobile phase at 0.6 ml/min, detection at 210 nm, 0.2 absorbance units full scale.

times vary from 14 min for formic acid to 35 min for valeric acid. Although the discussion in this report is focussed upon the determination of acetic acid, any of these five acids could be examined under the specified chromatographic conditions.

A linear calibration curve passing through the origin was obtained by chromatographing in duplicate a series of five aqueous acetic acid standards ranging from 2.0 to 107 μg/ml. A linear least-squares fit of the data gave a correlation coefficient exceeding 0.999. A chromatogram of the 107 μg/ml standard is provided in Fig. 3. The concentration range spanned by this calibration would correspond to roughly 20 to 1000 μg acetic acid present on a charcoal tube. Peak height measurements were selected for this calibration over peak area measurements for convenience. Similar results were obtained with either method of quantitation.

The precision and accuracy of the liquid chromatographic analysis were evaluated by running a series of standard solutions each five times. The standards were prepared in 0.01 *N* sodium hydroxide at concentrations varying from 2.4 to 60 μg/ml. Table II summarizes the results of these analyses. Relative standard deviations were typically 1–2 % and ranged from 0.6 % for the highest concentration standard to 4.4 % for the lowest. Solution recoveries varied from 95 to 108 %. From these results both the precision and relative error of the liquid chromatographic analysis are expected to normally be less than ± 5 % over the entire calibration range even at the 2 μg/ml level.

Three desorption solvents, water, 0.01 *N* sodium hydroxide and 0.1 *N* sodium hydroxide were evaluated as potentially useful materials for the desorption of trapped acetic acid from charcoal. This study was conducted by spiking known amounts of acetic acid dissolved in either acetone or water onto the tubes and allowing them to

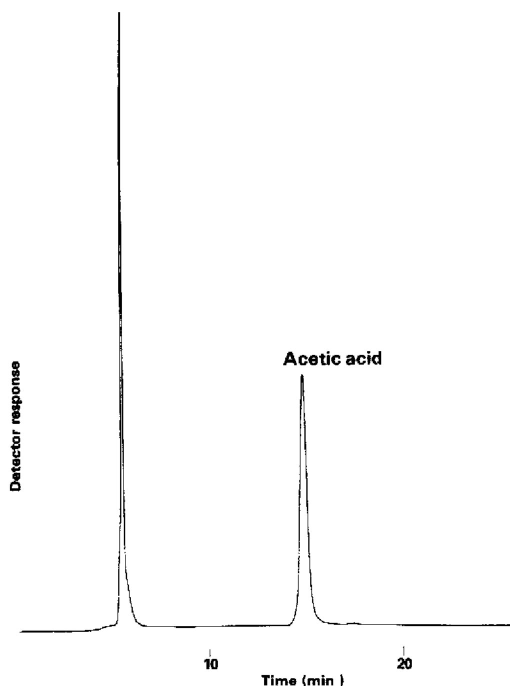


Fig. 3. Chromatogram of 107 μg/ml acetic acid standard. Bio-Rad HPX-87 column, 0.02 *N* sulfuric acid mobile phase at 0.6 ml/min, 100-μl injection.

equilibriate 24 h. The results of these experiments, provided in Table III, indicate that only 0.1 *N* sodium hydroxide is able to quantitatively desorb the spiked acetic acid from the charcoal. No significant differences were observed between results obtained with either acetone or water spikes. Therefore, in all later studies water was used as spiking solvent.

In order to establish the recovery of acetic acid trapped on charcoal, a series of tubes spiked with 30–500 μg acetic acid were analyzed. These results are provided in

TABLE II

ACCURACY AND PRECISION OF THE LIQUID CHROMATOGRAPHIC ANALYSIS OF ACETIC ACID CALIBRATION SOLUTIONS

Prepared concentration (μg/ml)	*Analyzed concentration (μg/ml)**	*Relative standard deviation (%)*	*Recovery (%)***
2.39	2.33	4.3	97
5.98	5.92	2.0	99
14.1	13.4	1.4	95
44.0	47.5	1.8	108
59.8	57.3	0.6	96

* Average of five determinations.

** Recovery = (analyzed/prepared) × 100%.

TABLE III

EVALUATION OF SOLVENTS FOR THE DESORPTION OF ACETIC ACID FROM CHARCOAL

Desorption solvent	*Spiking solvent*	*Recovery (%)**
Water	Water**	83, 79
Water	Acetone***	74, 80
0.01 *N* NaOH	Water	87, 87
0.1 *N* NaOH	Water	104, 100
0.1 *N* NaOH	Acetone	98, 100

* Results of duplicate spikes.
** 102 μg added for all water samples.
*** 196 μg added for all acetone samples.

Table IV. In two cases, at 100 and 200 μg, five tubes were spiked at each level in order to obtain precision data. Recoveries from charcoal of spiked acetic acid ranged from 109% at 32.5 μg spiked to 95% at 498 μg. In general higher recoveries were obtained at the lower spike levels. The average recovery of acetic acid from charcoal was 101%.

Relative standard deviations for the two sets run five times were in the 1–3% range. In each case average recoveries were close to 100%. Relative standard deviations obtained here are very similar to those obtained for the chromatographic analyses reported in Table II. A chromatogram obtained from analysis of a charcoal tube containing 260 μg acetic acid is provided in Fig. 4. A few additional peaks are apparent in the chromatogram but these do not interfere with the acetic acid determination.

In the described procedure desorbed samples are diluted tenfold prior to analysis. This practice was adopted because peak distortion problems had been occasionally encountered in the analysis of samples dissolved in 0.1 *N* sodium hydroxide solution. In order to circumvent potential problems all desorbtion solutions in this study were diluted such that NaOH concentrations were reduced to 0.01 *N*. A tenfold increase in the detection limit of the charcoal tube analysis could be achieved by eliminating this dilution step.

TABLE IV

RECOVERY OF ACETIC ACID SPIKED ONTO CHARCOAL TUBES

Acetic acid spiked (μg)	*Acetic acid analyzed (μg)*	*Relative standard deviation (%)*	*Recovery (%)**
32.5	35.4	–	109
65.0	66.9	–	103
97.5	98.6	–	101
99.6	99.3**	2.7	100
199	200**	1.2	100
260	249	–	96
498	475	–	95

* Recovery = (analyzed/spiked) × 100%.
** Average of five separate determinations.

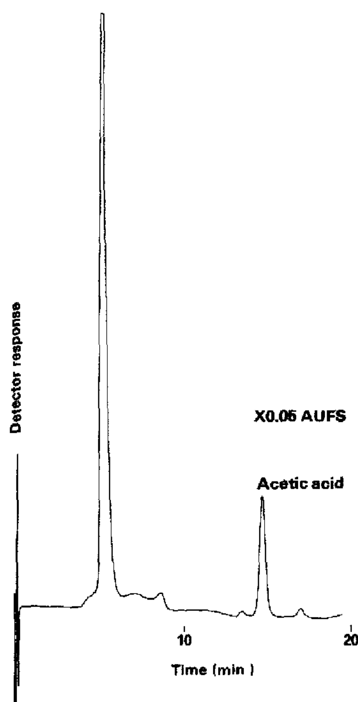


Fig. 4. Chromatogram of charcoal tube sample spiked with 260 μg acetic acid. Bio-Rad HPX-87 column, 0.02 *N* sulfuric acid mobile phase at 0.6 ml/min, 100-μl injection.

In some applications methyl acetate could potentially interfere in this analysis since desorbed methyl acetate might rapidly hydrolyze to acetic acid in 0.1 *N* sodium hydroxide. In order to assess this problem, three charcoal tubes were spiked with 500 μg methyl acetate. These tubes were analyzed in the normal manner. No detectable quantities of acetic acid were observed in any of the three cases. Apparently methyl acetate is not rapidly desorbed from the charcoal surface by 0.1 *N* sodium hydroxide solution.

ACKNOWLEDGEMENT

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