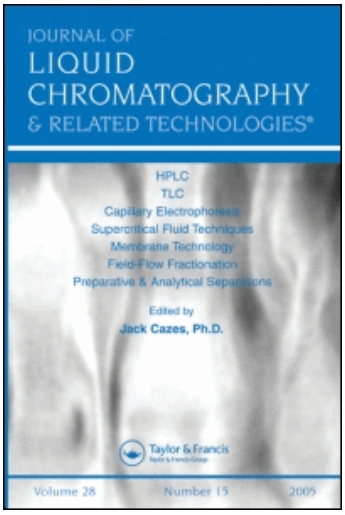

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DETERMINATION OF FUMARIC ACID, MALEIC ACID, AND PHTHALIC ACID IN GROUNDWATER AND SOIL

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ABSTRACT

When present at > 1 μg/mL, each title compound was determined in groundwater by ion-exclusion chromatography after sample acidification and filtration. For groundwater with one or all analyte concentrations of < 1 μg/mL, the acid anions were first concentrated from a 100-mL sample using a quaternary amine anion-exchange cartridge. The acids were recovered by eluting the cartridge with 1 mL of 1 N H_2SO_4 and two 2-mL deionized water washes; this solution then was examined by anion-exclusion chromatography. For soil, the acids were extracted from a 10-g sample with 20 mL of 1 N H_2SO_4 and two 15-mL water washes. This extract was filtered then analyzed by anion-exclusion chromatography. All analyses used 25-μL injections into the HPLC column which was maintained at 60°C and eluted with a 0.6 mL/min. flow of 0.02 N H_2SO_4. Analytes were monitored with a UV detector operated at 200 nm. The analysis procedures for groundwater were validated with solutions which were fortified with from 50 ng/mL to 200 μg/mL of each analyte; recoveries ranged from 90 to 110%. The soil method was validated using fortified samples which contained each acid at concentrations of from 5 to 160 μg/g. Recovery values were between 81 and 120%. For samples exhibiting minimal detector response from compounds other than the acids of interest, 100-μL injection volumes provided an estimated detection limit of 1 μg/g for soil and 10 ng/mL for groundwater.

INTRODUCTION

For an investigation of a landfill site, procedures for the determination of fumaric acid, maleic acid, and phthalic acid in soil and groundwater samples were needed. Detection limits of 10 μg/g for soil and 1 μg/mL for groundwater were required; however, estimating analyte concentrations at one tenth these levels was a goal. Since many organic acids have been quantitated by gas chromatography after derivatization (1-3), similar methodology was considered. For the dicarboxylic acids of interest here, bis(trimethylsilyl) esters have been prepared and their chromatographic behavior studied (4,5). However, developing a procedure for isolating the acids in a matrix suitable for derivatization and conducting the derivatization was not felt to be the preferred route. Therefore, liquid chromatography was investigated.

Chromatography literature abounds with HPLC methods for determining aliphatic and aromatic acids with mono- and dicarboxylate functionalities. For example, physiological fluids have been analyzed for organic acids using reversed-phase, ion-exchange, and ion-exclusion techniques as discussed by Bulusu et.al.(6). Ion-exclusion chromatography (IEC) has been applied in many areas (7) using various detection systems (8). Thus, IEC has been used to quantitate organic acids in sugar cane process solutions using refractive index detection (8) and, by incorporating an anion-exchange suppressor column, conductivity detection was possible (9). For anions which exhibit UV absorption spectra, the most direct approach is single-column IEC with UV detection. Grosjean et.al. pointed out the advantages of this technique and demonstrated its application in the measurement of atmospheric carboxylic acids (10). We were able to apply a similar approach to soil and water by developing sample preparation methods that resulted in aqueous H_2SO_4 solutions for the acids of interest. These solutions were conveniently analyzed by anion-exclusion HPLC with UV

detection. This paper presents our sample preparation and chromatographic procedures along with results from validation studies.

EXPERIMENTAL

Instrument and Operating Conditions

The liquid chromatograph was a Hewlett Packard Model 1090L equipped with a PV5 solvent delivery system, column oven, an automatic liquid sampler with variable-volume injector, and a model 1040A photodiode array detector. The instrument was operated with revision 5.22 software using a 79994A ChemStation which was linked to a 9153C disk drive and a 2225A ThinkJet printer. The column was a 300 x 6.5 mm ORH-801 preceded by an ion Guard™ GC-801 guard column. These were packed with a cation-exchange resin in the hydrogen form and were purchased from Interaction Chromatography. Injection volumes were 25-μL and analyses were conducted at 60°C with a 0.6 mL/min flow of 0.02 N H_2SO_4. For quantitation, the detector signal was monitored at 200 nm (10 nm bandwidth) relative to a reference wavelength of 550 nm (100 nm bandwidth). Analysis run times usually were 40 min (extended to 55 min for samples with numerous late-eluting components); during this time the detector signal was recorded/integrated from 4.5 to 25 min.

Special Supplies

Fumaric Acid	-	Aldrich, 99+% (Cat. 24,074-5)
Maleic Acid	-	Aldrich, 99% (cat. M15-3)
Phthalic Acid	-	Aldrich, 99+% (cat. 24, 022-2)
Sulfuric Acid	-	Baker, Ultrex®, Ultrapure Reagent (Cat. 4802-05)
Water	-	Deionized, from Millipore, Milli-Q purifier system.

Extraction Cartridges	-	3-mL, Baker-10 SPE disposable columns (Cat. 7091-3). These contained 500 mg of 40 μm, 60A silica gel with a quaternary amine (N+) anion exchange functionality.
Glass Fiber Filters	-	Whatman, grade GF/B (Cat. 1821-042) and GF/D (Cat. 1823-042) with 4.25 cm diameters.
Buchner Funnels	-	Coors (Cat. 60239), 43 mm i.d.
Microparticulate Filters	-	Gleman #4187, 3-cm diameter, Acrodisc PF which has a 0.8 μm prefilter and a 0.2 μm membrane filter.
Centrifuge Tubes	-	Nalgene, 50-mL, Oak Ridge FEP (#3114-0050)

Preparation of Instrument Calibration Solutions

Stock solution A which contained 4000 μg/mL of each acid was prepared by combining and dissolving 4.000 g of each acid in 1000 mL of water. Stock solution B was prepared to contain 1000 μg/mL of each acid by diluting stock solution A with water. Calibration solutions with acid concentrations of 200 or 100 μg/mL were prepared by diluting either 20 or 10 mL of stock solution B with 20 mL of 1 N H_2SO_4 and sufficient water to give 100-mL solutions. Other calibration solutions (0.25 to 50 μg/mL) were made by appropriately diluting the 100 μg/mL solution with 0.2 N H_2SO_4.

Preparation of Fortified Samples

Deionized water was fortified with from 50 ng/mL to 50 μg/mL of each acid by serially diluting stock solution B. Groundwater was fortified with analytes (50 ng/mL to 1 μg/mL) by diluting 5 mL of fortified deionized water to 100 mL with sample water; for concentrations from 1 to 200 μg/mL, 250

μL of water was removed from a 5-mL sample aliquot and replaced with 250 μL of an appropriate fortified deionized water solution to provide the required fortification level.

For soil samples, a 10 $\pm$ 0.05 g portion (not dried) of screened (8 mesh) and mixed soil was weighed into a 50-mL beaker or 50-mL centrifuge tube. Fortification concentrations of 5, 10, 20, 40, 80 and 160 μg/g were obtained by respectively dispersing 50, 100, 200, 400, 800 and 1600 μL of stock solution B onto the soil surface. These samples were not analyzed until they had air dried for at least one hour.

Sample Preparation for Groundwater

For samples with >1 μg/mL of each analyte, a 5-mL aliquot was acidified with 25 μL of conc. H_2SO_4, then a few mL of this solution was filtered with a 5-mL syringe fitted with an Acrodisc PF membrane filter. HPLC analysis then was conducted.

The following procedure was used to determine analytes whose concentrations were <1 μg/mL. A SPE extraction cartridge was inserted into a 250-mL vacuum filtration flask which was attached to an adjustable vacuum manifold (set to 15 inches Hg). Each column was conditioned by eluting with 3 mL of methanol followed by two 3-mL deionized water washes. The wash liquids were discarded then a 125-mL feed reservoir was attached to the cartridge. To the reservoir 100 mL of sample was added after it was first filtered through a Buchner funnel with a GF/B filter. With application of vacuum a 4-5 mL/min flow of sample through the cartridge was observed. The eluted groundwater was discarded and a 16 x 125 mm collection tube was placed inside the vacuum flask. The cartridge was eluted with 1 mL of 1 N H_2SO_4, followed by two 2-mL deionized water washes. The volume of the resulting extract was adjusted to 5.0 mL with deionized water. This extract then was ready for HPLC analysis.

Sample Preparation for Soil

Into a 50-mL beaker, 10 $\pm$ 0.05 g of screened (8 mesh) and mixed soil (not dried) was weighed, then 20 mL of 1 N H_2SO_4 was added. This mixture was thoroughly blended and allowed to stand for 20 minutes. The resulting slurry was vacuum filtered using a Buchner funnel which held a GF/D filter. While the soil cake was still moist, it was washed with 15 mL of water which first was used to rinse the extraction beaker. After a second 10-mL water wash, the combined filtrate volume was adjusted to 50 mL with water. For HPLC analysis, a 3-mL aliquot of extract solution was filtered using a 5-mL syringe fitted with an Acrodisc PF membrane filter.

For soils containing high concentrations of clay, the 10-g sample was weighed into a 50-mL centrifuge tube to which 25 mL of 1.0 N H_2SO_4 was added. The mixture was blended, allowed to stand for 20 minutes, then centrifuged for 5 minutes at 5000 RPM. The clarified acid solution was decanted into a 50-mL volumetric flask. To the centrifuge tube, 25 mL of water was added and the soil cake slurried. This mixture was centrifuged at 5000 RPM for 5 minutes then the liquid layer was transferred to the 50-mL volumetric flask. After adjusting the sample volume to 50.0 mL with water, an aliquot was filtered (Acrodisc PF membrane filter) and examined by HPLC.

Calculation of Results

Area responses for analyte peaks in the analyzed solutions were compared to areas produced by analytes in calibration solutions. The following equation was used to calculate analyte concentrations in samples:

$$\frac{\text{Analyte Area from Sample Soln.}}{\text{Analyte Area from Calib. Soln.}} \times \text{Calib. Conc.} \times F = \text{Sample Conc.}$$

where F is the dilution/concentration factor. F is 1.0 for water samples with no analyte concentration step and 0.05 when the 20-fold enrichment process was used. For soil, F was 5 due to a factor of 5 dilution from sample preparation.

RESULTS AND DISCUSSION

Chromatography

Ion-exclusion chromatography provided excellent separation of the acid analytes. The retention times followed the order: maleic acid < fumaric acid < phthalic acid. Elution ordering for organic acids usually is explained by their respective acid strengths (pK_a values) and hydrophobic adsorption effects from the ion-exchange resin (7, 11-13). In general, increased compound acidity results in shorter retention time; therefore, from their acidity values (14), maleic acid (pK_a = 1.8) should elute first followed by phthalic acid (pK_a = 2.9) and then fumaric acid (pK_a = 3.0). However, the aromatic function of phthalic acid strongly interacts with the aromatic resin lattice so an extended retention time is noted. Retention is also a function of temperature and concentration of the eluting sulfuric acid. Increasing temperature causes shorter retention especially for phthalic acid (Table 1). Elution of each acid is retarded by increases in concentration of H_2SO_4 eluent (Table 2). We chose 60° to speed the analysis and to reduce column operating pressure. For rapid analyses, the concentration of H_2SO_4 in the eluent should be minimized; however, we selected 0.02 N H_2SO_4 for all analyses. This was necessary because some soil extracts exhibited a large tailing response just prior to the maleic acid peak (see Figure 1 for example). Part of that response was from the H_2SO_4 which was present in all extracts. For most soil analyses the early-eluting peak was not a problem (see Figure 2) and was never a concern for water samples. However, to assure adequate resolution for quantitation of maleic acid, the high-strength eluent was employed.

Respective UV maxima occur at 205, 210 and 200 nm for maleic acid, fumaric acid and phthalic acid. Best overall responses for all acids was obtained at a wavelength setting of 200 nm. This low value was possible since the isocratic eluent of 0.02 N H_2SO_4 produced minimal background absorbance resulting in high signal-to-noise ratios. Figure 3 is a

TABLE 1
Effect of Temperature on Retention*

Temperature (°C)	Retention Time (minutes)		
	Maleic Acid	Fumaric Acid	Phthalic Acid
40	5.88	11.43	21.94
50	5.78	10.70	19.49
60	5.69	10.10	17.43

* Using 0.01 N H_2SO_4 eluent

TABLE 2
Effect of Eluent Strength on Retention*

H_2SO_4 (N)	Retention Time (minutes)		
	Maleic Acid	Fumaric Acid	Phthalic Acid
0.005	5.14	9.51	15.99
0.010	5.70	10.06	17.40
0.015	6.05	10.28	17.98
0.020	6.31	10.38	18.28
0.030	6.71	10.49	18.63
0.050	7.18	10.63	19.02

* Elution temperature was 60°C

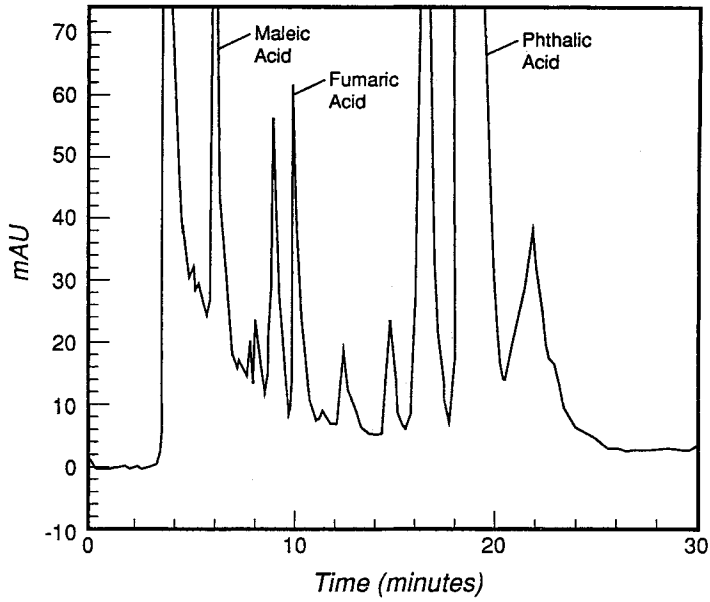

FIGURE 1. Chromatogram from 25-μL injection of extract from contaminated soil which produces a large tailing response prior to maleic acid.

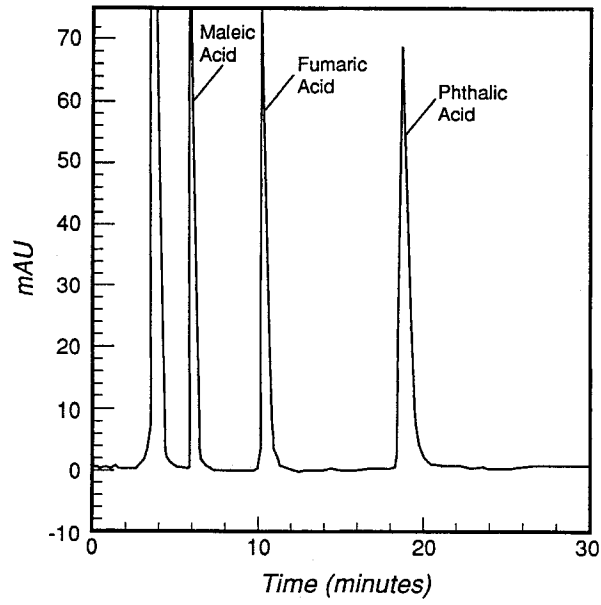

FIGURE 2. Chromatogram from 25-μL injection of extract from uncontaminated soil that had been fortified with 50 ppm of each acid.

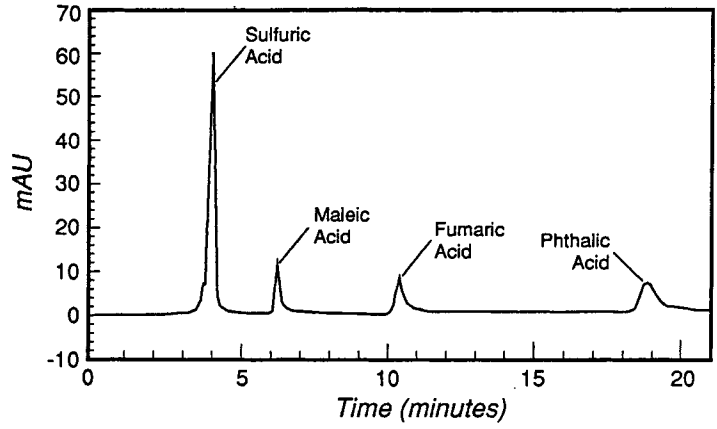

FIGURE 3. Chromatogram from 25-μL injection of a calibration solution which contained 1 ppm of each acid.

chromatographic trace for a calibration solution containing 1 μg/mL of each acid. Even with responses of only about 10 mAU, the peaks were accurately integrated by the data system. Detector linearity was maintained with up to 5 μg of each component being injected into the column. Thus, with 25-, 50- and 100-μL injection volumes, respective ranges for detector linearity were found to be 1-200 μg/mL, 0.5-100 μg/mL and 0.25-50 μg/mL. In all cases, correlation coefficients of >0.999 were calculated. Although component responses were linear with 50 and 100 - μL injections, peak broadening was noted so large injections were only used in special situations (see later discussion) to achieve detection limits below 5 μg/g with soils and below 50 ng/mL with water samples.

Typically, HPLC analyses give best results when calibration solutions are similar to sample solutions. For water analyses this criteria was met. For soils the extract acidity was about twice the concentration present in calibration solutions, but this had no observable impact on the chromatography. In fact, calibration solutions in 0 to 0.8 N H_2SO_4 were

tested. For maleic acid, retention gradually increased with higher H_2SO_4 levels; in 0.8 N H_2SO_4 only a 0.1 minute shift was seen. The other analytes exhibited no changes.

Water Analyses

For analyte concentrations >1 μg/mL, samples only need to be acidified and filtered prior to HPLC examination. Filtration was demonstrated not to cause loss of target acids by comparing analyte responses from calibration solutions (1, 25 and 50 μg/mL) before and after filtration. In all cases, the response differences were < 2%. Using a groundwater sample from a landfill well, no problems due to filtration or sample matrix were found. This was shown by recovery tests with samples fortified with analytes to 1, 10, 50 and 200 μg/mL. For these, recovery values ranged from 96 to 102% (single test per level).

To achieve lower detection limits an analyte concentration step was needed prior to HPLC analysis. Anion exchange has been used to isolate organic acids from various aqueous samples such as sugar cane process juices (8), urine samples (5,6,15), beer (16), and precipitation (17). Using a similar approach, the analyte acids were conveniently extracted from a 100-mL groundwater sample onto an anion-exchange cartridge. The acids then were recovered in a 5-mL solution (20-fold enrichment) by eluting the cartridge with H_2SO_4 and deionized water. No prior sample treatment was carried out other than filtration to remove any particulates that might have plugged the extraction cartridge. Table 3 presents method validation data from recovery studies using fortified deionized water and fortified groundwater. Concentrations tested were from 50 ng/mL to 50 μg/mL; recoveries ranged from 89 to 110%. The 50 μg/mL test demonstrates sufficient cartridge capacity to handle samples that need to be concentrated but have one or two of the acids at > 1 μg/mL.

TABLE 3
Recovery Results from Fortified Water Samples After Using Anion-Exchange Isolation/Enrichment of Analytes

A - Deionized Water B - Groundwater

Fortification Conc. (ppm)	Average % Recovery*		
	Maleic Acid	Fumaric Acid	Phthalic Acid
A-0.05	90 (1.1)	95 (2.6)	96 (2.4)
B-0.05	89	91	91
A-0.25	97 (3.6)	99 (2.6)	99 (3.6)
B-0.25	102	101	103
B-0.50	92	93	96
A-1.00	95 (6.8)	95 (5.3)	95 (7.4)
B-1.00	100	100	101
A-2.00	96 (2.3)	96 (2.6)	94 (2.5)
A-10.0	108 (3.3)	109 (3.5)	104 (4.3)
A-50.0	89 (10.4)	96 (11.7)	100 (13.3)

* Values in parentheses for A samples are % relative standard deviation for 4 tests; for 50 ppm there were eight tests. For B samples only one test done at each concentration.

TABLE 4
Recovery Results from Fortified Soil Samples

Fortification Conc. (ppm)	Average % Recovery[a] Maleic Acid	Fumaric Acid	Phthalic Acid
5	92 (1.8)	99 (8.2)	88 (1.9)
10	82 (3.9)	97 (2.1)	93 (6.6)
20	87 (6.5)	95 (4.8)	101 (2.5)
40	102 (9.3)	105 (8.1)	111 (11.3)
80	90 (9.7)	92 (10.3)	98 (11.6)
160	107 (4.1)	108 (3.5)	115 (1.3)
5[b]	87	100	90
15[c]	83	90	92

a Values in parentheses are % relative standard deviation for three tests; for 5 ppm there were four tests.

b Using centrifugation procedure with sandy/clay soil (one test).

c Using centrifugation procedure with clay soil (one test).

The recovery data of Table 3 verifies a 50 ng/mL method detection limit. However, for samples exhibiting minimum background HPLC response,a detection limit estimated at 10 ng/mL can be attained with 50 or 100-μL injection volumes.

Soil Analyses

Sulfuric acid is very effective in extracting the analytes from soil. Filtration of the soil slurry usually resulted in some suspended material in

extracts so a final clarification with a membrane filter is recommended. Recovery values for a sandy/clay soil which was fortified with from 5 to 160 μg/g of each acid are given in Table 4; results from 81 to 120% were obtained. For this specific sample (local farm soil) and with many of the submitted landfill soils, the filtration process took about 20 minutes. However, a few samples were mostly clay and formed a very sticky mass that was virtually unfilterable. To handle these samples, extractions had to be conducted in centrifuge tubes. The clay slurry centrifuged so well that all the resulting clarified extract could be poured off the clay layer. Isolating the extract by this method also worked with other soil types that typically would be filtered. The centrifugation procedure takes about as long as for filtration; therefore, choice of technique is not an issue since either gives comparable results (see Table 4).

The recovery data in Table 4 show that a 5 μg/g method detection limit can be reached. An estimated detection limit of 1 μg/g is possible when the background HPLC responses are minimal and 50 or 100-μL injection volumes are used.

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