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Note

Ion-suppression reversed-phase liquid chromatographic determination of acetate in brine

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With the chemical industry ever increasingly going to closed-loop plants, recirculation of aqueous streams, including brine, is practiced. Build-up of organic impurities such as acetate in recycle streams, frequently must be closely monitored. There is a lack of methodology for the measurement of acetate, as acetic acid, in such a matrix. The determination of acetic acid in rainwater was accomplished by gas chromatography[1] and by isotachophoresis[2] in silage. Other methods employ steam distillation followed by titration[3] and column chromatography with titration[4]. Ion chromatography[5] can also be applied; however, the high salt concentration limits sensitivity. Richards[6] chromatographed acetate and other weak organic acids using an eluent of dilute sulfuric acid and an ion-exchange column. However, the system required long analysis time and is complicated by the soft resin settling in the column. Therefore, a rapid and specific method requiring no sample treatment was needed.

EXPERIMENTAL

Acids were obtained from either Eastman Organic Chemicals or J. T. Baker, and used without further purification. Whenever ACS reagent requirements were applicable, compounds of that quality were employed.

Equipment

The liquid chromatograph consisted of an LDC UV III Monitor (1203) with a 214-nm source; a Waters Assoc. M-45 pump; a Rheodyne 7120 injection valve with 20-μl loop; a Sargent-Welch SRG recorder; a Systems I (Spectra-Physics) computing integrator; and a Whatman Partisil 5 ODS-3 RAC 10 cm × 9.4 mm I.D. column (minimum 90,000 plates per meter) protected with a 5 cm × 2.1 mm I.D. precolumn containing Waters Assoc. pellicular μBondapak C_{18}/Corasil.

Calibration solution

A 20% (w/w) aqueous solution of a sodium chloride brine was prepared. With a 100-μl syringe, 100 μl of glacial acetic acid (density 1.049) was added to 105 g of the brine solution. This gave a standard solution containing 1000 ppm acetic acid (983 ppm as acetate ion).

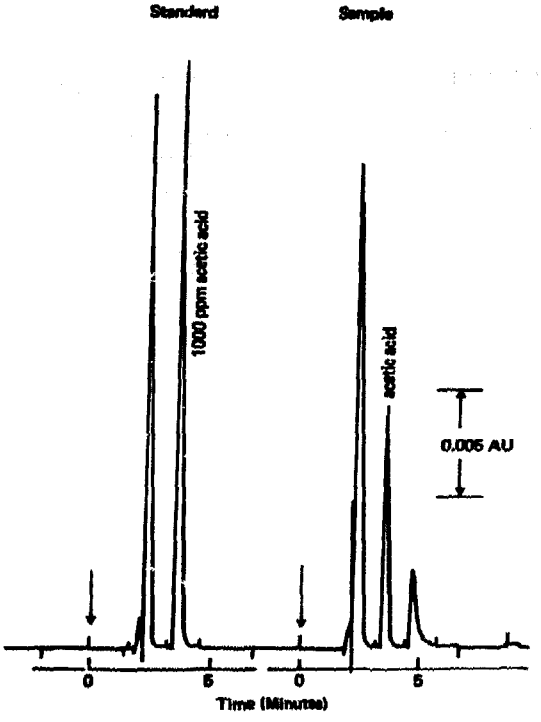

Fig. 1. Liquid chromatogram of sample and standard for the determination of acetate in brine according to the liquid chromatographic conditions described in the text.

Chromatographic conditions

The mobile phase was 0.01 *N* aqueous sulfuric acid prepared with water from a Milli-Q water purification system. The flow-rate was 2 ml/min (400 p.s.i.g.); injection volume, 20 μl; detection wavelength, 214 nm; and attenuation, 0.064 a.u.f.s. for typical analyses, and 0.008 to obtain high sensitivity.

Procedure

Without any sample pretreatment, 20 μl of the brine is injected and chromatographed as described above.

RESULTS AND DISCUSSION

Fig. 1 illustrates the measurement of acetate, as acetic acid, in a commercial 20% sodium chloride brine. The sodium chloride emerges at the column void volume.

This analysis has been carried out over an eight-month period using the same column. Minimal column degradation has been observed as indicated by less than a 10% decrease in peak height. Eluent was pumped continuously five days a week, 24 hours a day, on recycle. Fresh eluent was prepared monthly.

Because of the high polarity of the acetic acid molecule, it is important that the columns have an efficiency of > 90,000 plates/meter. Also, adsorption effects must be at a minimum; therefore, column packings having significant amounts of free hydroxyl sites cannot be tolerated.

TABLE I

RETENTION TIMES AND SENSITIVITIES FOR VARIOUS WEAK ACIDS BY ION-SUPPRESSION REVERSED-PHASE LIQUID CHROMATOGRAPHY

	t_R (min)	Sensitivity (ng)*
Void volume	2.0	
Oxalic acid	S.F.**	
Lactic acid	2.6	0.2
Glycolic acid	2.6	0.1
Formic acid	2.8	0.2
Pyruvic acid	3.1	0.02
Malonic acid	3.3	0.04
Acetic acid	3.6	0.1
Monochloroacetic acid	4.8	0.5
Dichloroacetic acid	4.9	0.1
Maleic acid	5.0	0.006
Fumaric acid	5.9	0.004
Acrylic acid	6.1	0.06
Propionic acid	6.8	0.4
3-Chloropropionic acid	8.5	0.2
Trichloroacetic acid	8.9***	0.1
2-Chloropropionic acid	10.9***	1.0
2,3-Dichloropropionic acid	11.6***	0.5
2,2-Dichloropropionic acid	12.4***	0.5
Methacrylic acid	18.5	0.04

* Amount in a 20-μl injection and 3 times signal-to-noise ratio.
** Excessive tailing.
*** Moderate tailing.

In Table I are the retention times and sensitivities for a number of weak acids. Fig. 2 illustrates the separation of a select number of these acids.

Retention times for the more strongly retained acids can be shortened by the addition of 5% acetonitrile to the mobile phase.

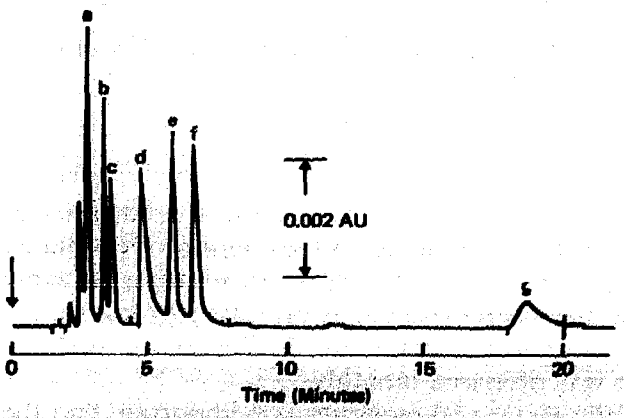

Fig. 2. Liquid chromatogram of weak acids according to conditions described in the text. Sample: 20 μl of a solution containing (a) 200 ppm glycolic acid, (b) 100 ppm malonic acid, (c) 190 ppm acetic acid, (d) 85 ppm dichloroacetic acid, (e) 1 ppm fumaric acid, (h) 320 ppm propionic acid and (g) 1 ppm methacrylic acid.

TABLE II

PRECISION OF ACETATE IN BRINE MEASUREMENT

	Amount acetate (ppm)
Day 1	417
	416
	419
	416
	416
Day 2	414
	416
	413
	416
	414
Mean	415.7
Standard deviation	1.7
Coefficient of variation	±0.4%

Lactic and glycolic acids, because of their proximity to the solvent front, are not measurable in 20% brine. For this same reason and because of excessive tailing, oxalic acid cannot be measured under these conditions.

Acids other than acetic have not been specifically measured in the presence of brine. However, it should be entirely possible to make such measurements.

Acetic acid was found to be linear from 10 to 5000 ppm in both area and peak height.

The column efficiency for acetic acid was studied as a function of eluent pH. With the 0.01 *N* sulfuric acid eluent (pH 2.2), the column gave 5048 theoretical plates; for a buffer of pH 3.5, it was 4986; and at pH 5.15, it fell to 822. As expected with an eluent buffer of pH 7.1, the acetic acid was not retained and came off at the column void volume.

The precision of the analysis was determined by measuring the acetate concentration five times on each of two consecutive days. Results are given in Table II.

This method can also be applied to calcium chloride brines. However, bromide containing brines cannot be analyzed for acetate because bromide is a strong ultraviolet absorber, and does not sufficiently clear the column before emergence of the acetate.

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