

Short Communication

Monitoring the effluents of the trichloroacetic acid process by high-performance liquid chromatography[☆]

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ABSTRACT

A simple and rapid high-performance liquid chromatographic method for the simultaneous determination of small amounts of nitric acid and trichloroacetic acid in process effluents was developed. Acidic components of the effluents were separated on a reversed-phase C₁₈ column using 0.15 M ammonium sulphate as mobile phase and determined quantitatively by UV absorption at 210 nm. The detection limits for nitric acid and trichloroacetic acid were 1.4 and 10 µg/l, respectively.

INTRODUCTION

Trichloroacetic acid is an important intermediate in the chemical industry and is also used as a herbicide against couch grass and wild oats [1]. It is manufactured [2–4] in large amounts either by oxidation of chloral or by chlorination of acetic acid. Our laboratory has studied the production of trichloroacetic acid by the oxidation of chloral using nitric acid. Effluents obtained during this process contain nitric acid and trichloroacetic acid in considerable amounts. Their recovery would be helpful in improving the yield of trichloroacetic acid and for recycling the nitric acid through the process. Rapid and reliable analytical methods are needed not only for monitoring the reactions but also for disposing of the effluents safely.

Titrimetric, potentiometric and polarographic techniques [5,6] have been employed extensively to determine trichloroacetic acid in water, but these

methods are tedious and time consuming. Spectrophotometric methods [7–9] have been found to be unattractive owing to a lack of specificity. Gas-liquid chromatographic methods [10–12] have limitations because carboxylic acids dimerize through hydrogen bonding in the vapour state. Ion-exchange chromatography [13], size-exclusion chromatography [14] and high-performance liquid chromatography (HPLC) [15] have been attempted but were unsuccessful.

In this paper, we describe a simple and rapid HPLC method for the separation and determination of small amounts of nitric, acetic and trichloroacetic acids in process effluents using a ChromSphere C₁₈ column and an eluent containing 0.15 M ammonium sulphate at ambient temperature.

EXPERIMENTAL

Materials and reagents

All reagents were of analytical-reagent grade unless stated otherwise and glass-distilled water was

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used throughout. Nitric acid, acetic acid, chloral and trichloroacetic acid were obtained from Spectrochem (Bombay, India) and ammonium sulphate from BDH (Poole, UK).

Apparatus

A high-performance liquid chromatograph (Shimadzu, Kyoto, Japan) with a 20- μ l loop injector having a high-pressure six-way valve was used. A Model SPD-6AV variable-wavelength UV-VIS spectrophotometric detector (Shimadzu) was connected after the column. A ChromSphere C₁₈ (10 μ m) column (250 mm \times 4.6 mm I.D.) (Chrompak, Middelburg, Netherlands) was used for separation. The chromatograms and the integrated data were recorded with a Chromatopac-CR3A processing system.

Chromatographic conditions

The mobile phase used was 0.15 M aqueous ammonium sulphate. Samples were dissolved in the mobile phase. Analyses were carried out under isocratic conditions at a flow-rate of 1 ml/min and a chart speed of 5 mm/min at room temperature (27°C). Chromatograms were recorded at a wavelength of 210 nm.

Analytical procedure

Standard mixtures containing known amounts (10–20 mg) of nitric acid and trichloroacetic acid were prepared by dissolution in 25 ml of the mobile phase. A 10- μ l volume of each mixture was injected and chromatographed under the above conditions and the response factors were calculated. Process effluents were analysed under identical conditions.

TABLE I
RETENTION DATA

Compound	Retention time (min)	Relative retention time	λ_{\max} (nm)
Nitric acid	2.78	1.00	210
Acetic acid	3.20	1.15	207
Dichloroacetic acid	4.15	1.49	205
Trichloroacetic acid	9.78	3.52	205
Chloral	16.90	6.08	208

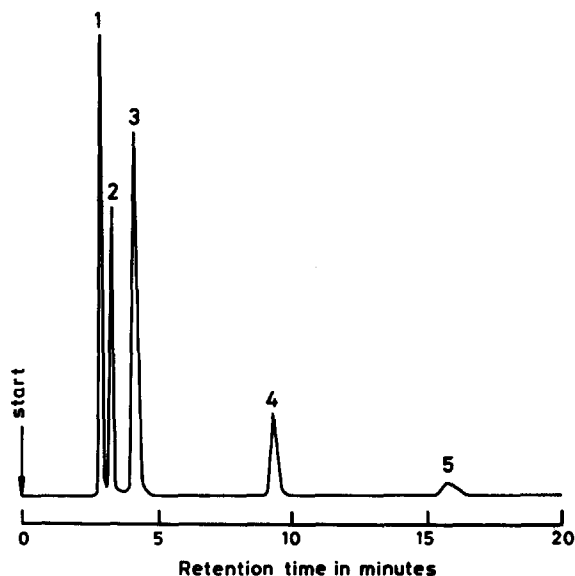


Fig. 1. HPLC profile of a synthetic mixture (10 μ g) containing 1 = nitric acid, 2 = acetic acid, 3 = dichloroacetic acid, 4 = trichloroacetic acid and 5 = chloral. Chromatographic conditions: column, ChromSphere, 10 μ m (250 mm \times 4.6 mm I.D.); mobile phase, 0.15 M aqueous ammonium sulphate; flow-rate, 1 ml/min; UV detection at 210 nm.

The amounts of nitric and trichloroacetic acid were calculated from the peak areas.

RESULTS AND DISCUSSION

HPLC separation of nitric, acetic and trichloroacetic acids is shown in Fig. 1. The peaks were identified by injecting the individual compounds. The retention data and the λ_{\max} values are given in Table I. It can be seen that trichloroacetic acid is well

TABLE II
RESPONSE FACTORS OF NITRIC ACID AND TRICHLOROACETIC ACID

Sample	Area under the peak ^a	R.S.D. ^b (%) (n = 5)
Nitric acid	8353	1.72
Trichloroacetic acid	1074	2.58

^a For 1 ml of sample.

^b Relative standard deviation.

TABLE III
ANALYTICAL DATA FOR STANDARD MIXTURES

Sample No.	Nitric acid (%)				Trichloroacetic acid (%)			
	Taken	Found ^a	Error	S.D.	Taken	Found ^a	Error	S.D.
1	0.63	0.62	-1.59	3.22	0.55	0.56	+1.82	3.57
2	0.97	0.99	+2.06	2.50	1.08	1.11	+2.77	1.80
3	1.54	1.52	-1.30	1.97	1.92	1.89	-1.04	2.12
4	2.76	2.81	+1.81	2.76	2.50	2.45	-1.99	2.04

^a Average of three determinations.

separated not only from nitric acid but also from acetic acid. Further, nitric acid elutes at 2.78 min, which is close to the void volume of the column. Therefore, inorganic impurities such as hydrochloric acid and sodium nitrate may interfere in the

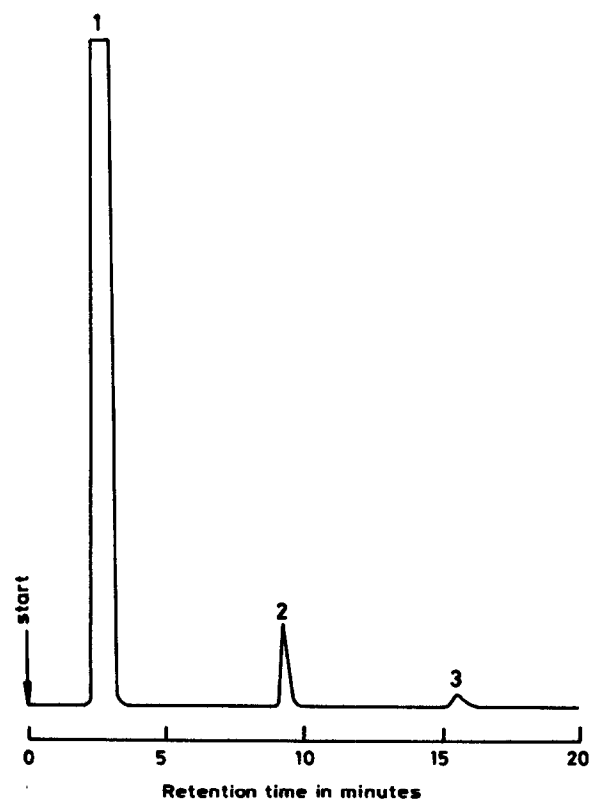


Fig. 2. Typical chromatogram of effluent of trichloroacetic acid process. Peaks: 1 = nitric acid; 2 = trichloroacetic acid; 3 = chloral. Chromatographic conditions as in Fig. 1.

analysis as they also elute in the same region. However, their interference can be avoided by adjusting the concentration of the mobile phase and increasing the elution time of nitric acid. The response factors for all the compounds were determined and are given in Table II. When the UV detector was set at 0.001 a.u.f.s. the limits of detection for nitric acid and trichloroacetic acid were 1.4 and 10 $\mu\text{g/l}$, respectively, with a signal-to-noise ratio of 4.0.

Standard mixtures containing different amounts of nitric acid and trichloroacetic acid were prepared and analysed by HPLC. The results are given in Table III. The measured amounts of nitric acid and trichloroacetic acid agreed with the actual values to within 0.06% and 2.77%, respectively.

Process effluents were collected during the course of oxidation of chloral with nitric acid and analysed by the proposed method. A typical chromatogram of an effluent is shown in Fig. 2. The unreacted chloral does not interfere, as it elutes at 16.90 min. The results are given in Table IV and show that the method is simple, rapid and convenient for monitoring effluents of the trichloroacetic acid process.

TABLE IV
ANALYTICAL DATA FOR PROCESS EFFLUENTS

Sample No.	Nitric acid (%) ^a	Trichloroacetic acid (%) ^a
1	1.60	3.52
2	1.45	1.49
3	2.10	4.50
4	1.19	0.41

^a Average of three determinations.

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