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Note

Gas chromatographic determination of nitrilotriacetic acid using a nitrogen-selective detector

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In preparation for a survey to determine levels of nitrilotriacetic acid (NTA) in drinking water, previously published methods of analysis for NTA[1–7] were evaluated. The method of Aue *et al.*[1] was considered to be the most appropriate but quantitation of NTA was difficult at the very low levels (*ca.* 1 ppb*), expected in drinking water. We now report the use of a nitrogen-selective detector which allows gas chromatographic (GC) quantitation of NTA as its tri-*n*-butyl ester, at sub-ppb levels in raw water and drinking water.

EXPERIMENTAL

General procedure

The method of Aue *et al.*[1] was followed. The formic acid was re-distilled in glass before use and the ion-exchange resin was washed well with this formic acid before use. All glassware was soaked for at least 24 h in concentrated hydrochloric acid, rinsed with distilled water and dried before use.

Gas chromatographic analysis

A Perkin-Elmer Model 910 gas chromatograph, equipped with a single column, a two-way effluent splitter, a flame ionization detector and a nitrogen–phosphorus detector operating in the nitrogen mode was used for this study. The column was 6 ft. × 1/4 in. O.D. glass, packed with either 5% OV-101 or 3% OV-210 on 80–100 mesh Chromosorb W HP. The carrier gas was helium at a flow-rate of 60 ml/min and the effluent splitter diverted 60% to the flame ionization detector and 40% to the nitrogen detector. Hydrogen and air flows were optimized for each detector. The injector and detector temperatures were 240° and 280°, respectively, and the column temperature as indicated in the text.

Gas chromatographic–mass spectrometric analysis

Qualitative and quantitative analysis were performed on a Finnigan Model 4000 GC–mass spectrometry (MS)–data system operating in the electron-impact mode.

* Throughout this article, the American billion (10^9) is meant.

The GC conditions were: injector temperature, 220°; column temperature, 200°; interface temperature, 250°. The column was glass, 6 ft. × 2 mm I.D., packed with 3% OV-1 on 80–100 mesh Chromosorb W HP and the carrier gas helium at a flow-rate of 40 ml/min.

The MS conditions were: source temperature, 270°; electron energy, 70 eV; resolution $M/\Delta M = 1200$ (10% valley).

RESULTS AND DISCUSSION

Evaluation of methods of analysis for NTA indicated that the method of Aue *et al.*[1] was the most suitable for low levels of NTA and was applicable to the wide variety of waters likely to be sampled during a survey to determine levels of NTA in drinking water. Essentially this procedure[1] consists of passing the water sample through an ion-exchange column, washing off interferences and then eluting the NTA. The NTA is then converted to its tri-*n*-butyl ester which is analysed by GC using a flame ionization detector. Aue *et al.*[1] claimed a limit of detection of 1 ppb NTA for a 50-ml water sample, but our preliminary investigations with standard solu-

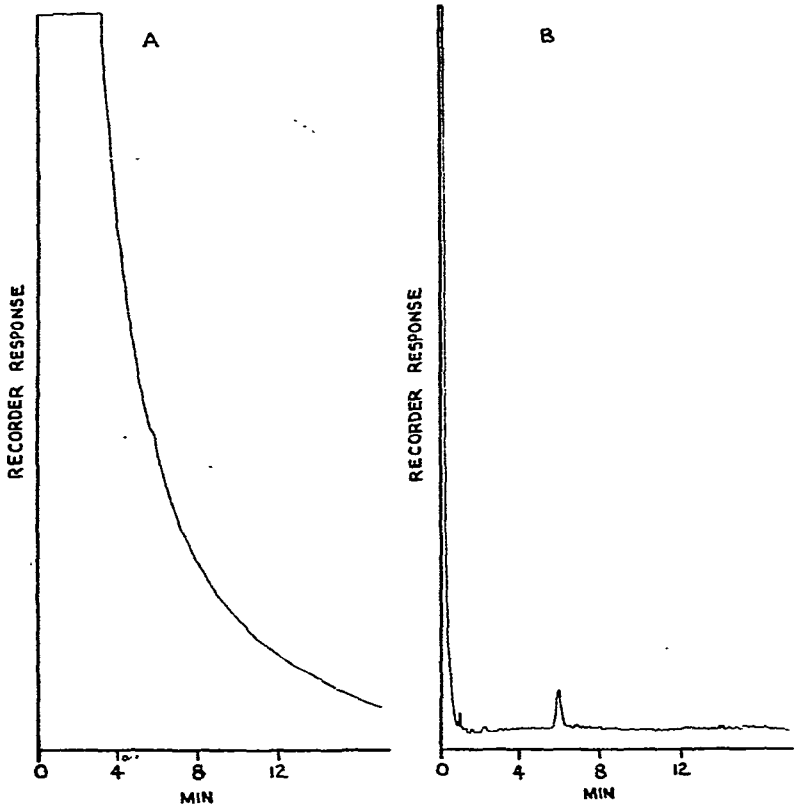

Fig. 1. Gas chromatograms of tri-*n*-butyl ester of NTA, retention time 6 min. Column, 5% OV-101 at 220°; 2.6 ng injected. (A) Flame ionization detector, 60% of effluent, attenuation 10 × 4; (B) nitrogen-selective detector, 40% of effluent, attenuation 10 × 1.

tions of the tri-*n*-butyl ester showed that quantitation at this level was difficult due to interference from the solvent peak (Fig. 1A) when using acetone as the injection solvent as specified by Aue *et al.*[1]. The use of alternate injection solvents gave some improvement but quantitation was still difficult.

Somewhat surprisingly no one has previously reported the use of a nitrogen-selective detector for GC detection of esters of NTA. Analysis of standard solutions of the tri-*n*-butyl ester, equivalent to 1 ppb NTA in a 50-ml water sample, showed that the sensitivity of this detector was adequate, quantitation was straight forward and there was minimal interference from the injection solvent, acetone (Fig. 1B). The nitrogen-selective detector gave a linear response over the range 1–1000 ng injected of the tri-*n*-butyl ester of NTA.

The isolation procedure of Aue *et al.*[1] gave a satisfactory chromatogram (Fig. 2A) for a control blank water sample provided that all solvents were re-distilled in glass and the ion-exchange resin and glassware were thoroughly washed before use. The

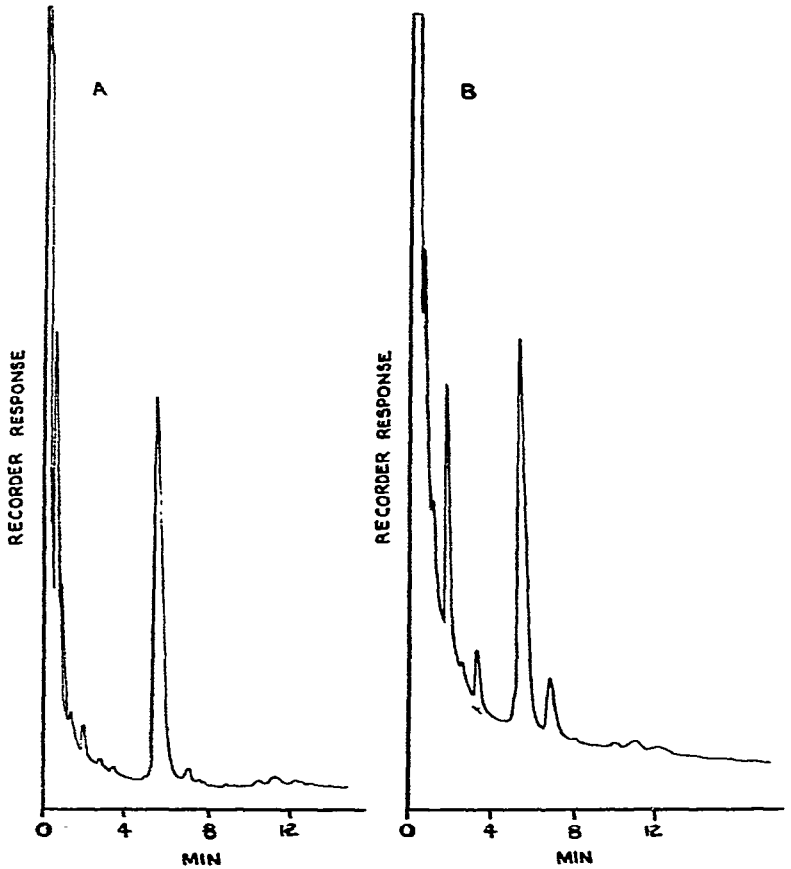

Fig. 2. Gas chromatograms on 5% OV-101 column at 235°, nitrogen-selective detector, attenuation 10 × 1. (A) Control water blank, butylated residue dissolved in 100 μl acetone and 4.8 μl injected; (B) raw water sample containing 0.4 ppb NTA butylated residue dissolved in 100 μl acetone, 4.9 μl injected, retention time 3.4 min.

lower detection limit was considered to be four times the level of the blank which would give a detection limit of *ca.* 0.2 ppb NTA for a 50-ml water sample. A typical chromatogram obtained from a 50-ml raw water sample analysed as containing 0.4 ppb NTA is shown in Fig. 2B. Recoveries of NTA from water samples spiked with 1–1000 ppb NTA were greater than 90%.

Confirmation of the *n*-butyl ester at the ppb level by GC–MS was possible using multiple ion monitoring of the major fragments, *m/e* 88, 158, 258, (Fig. 3) obtained in the electron impact mass spectrum of the tri-*n*-butyl ester of NTA (Fig. 4).

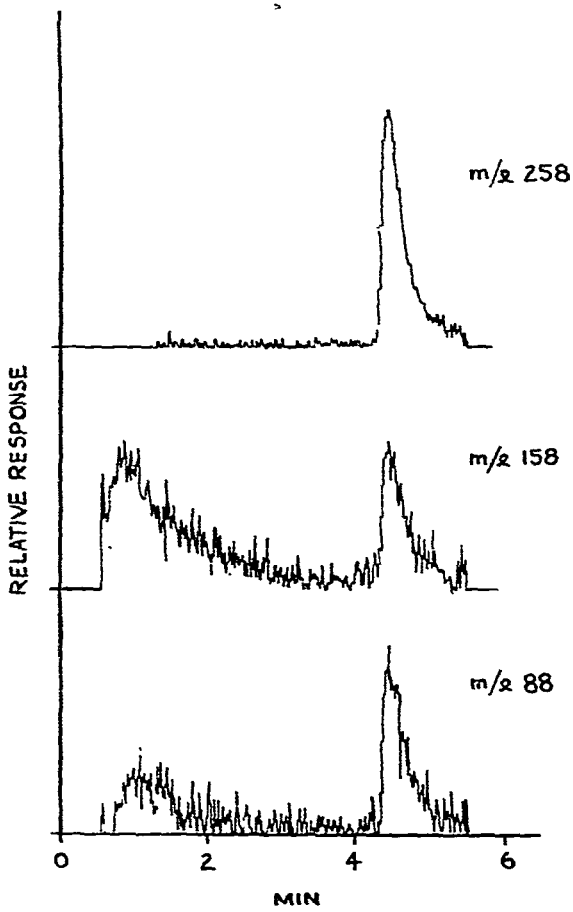

Fig. 3. Gas chromatography–mass fragmentography of tri-*n*-butyl ester of NTA, 3% OV-1 column at 200°, 15 ng injected, retention time 4.4 min.

Analysis of some typical water samples for NTA using the nitrogen-selective detector (Table I) showed that the method was applicable to both raw water and drinking water and that using this method NTA could be detected and quantitated at the sub-ppb level.

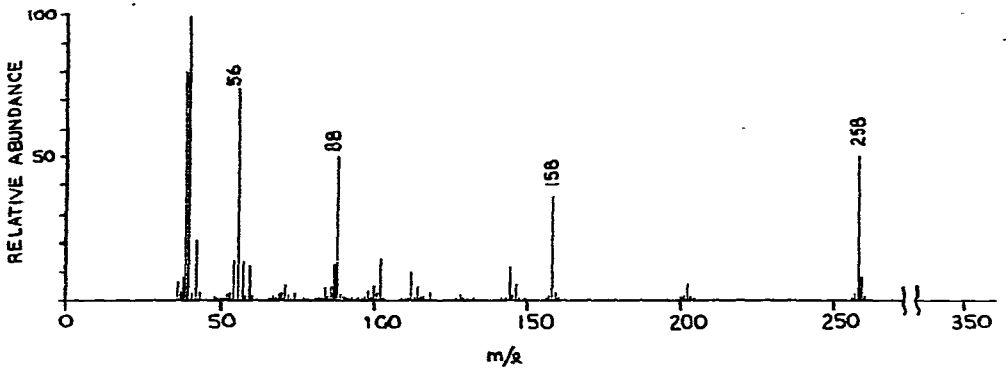

Fig. 4. Electron impact mass spectrum of tri-*n*-butyl ester of NTA. The molecular ion, *m/e* 359, can be detected if the spectrum is magnified *ca.* 10×.

TABLE I

LEVELS OF NTA IN RAW WATERS AND DRINKING WATERS

The letters A–H refer to local municipalities from where the samples were obtained.

Sample	*Concentration of NTA (ppb)*
Raw water A	1.03
Drinking water A	0.84
Raw water B	Trace*
Drinking water B	Trace*
Raw water C	1.75
Drinking water C	1.37
Raw water D	0.42
Drinking water E	Trace*
Drinking water F	0.87
Drinking water G	1.60
Drinking water H	0.84

* Indicates detectable levels <0.2 ppb.

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