Short Communication

Gas chromatography of chloride and bromide as phenylboronic acid/mercuric nitrate derivatives with microwave induced plasma atomic emission detection

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ABSTRACT

Capillary column gas chromatography (GC) with flame ionization detection (FID) or microwave induced plasma atomic emission detection (MIP-AED) were examined for the determination of chloride, using phenylboronic acid as derivatizing reagent. Phenylboronic acid and mercuric nitrate were used in a 1:1 molar ratio to produce phenylmercuric chloride (PMC).

The limit of detection for chloride as PMC using FID was $3.3 \cdot 10^{-10}$ g and using AED, measuring the mercury response at 185 nm, it was $6.25 \cdot 10^{-11}$ g. Under the conditions used, chloride and bromide (as PMC and PMB) failed to separate adequately, but they could be determined by GC–AED using the wavelengths 478 nm and 479 nm for bromide and chloride, respectively. The specific detection limits for bromide and chloride obtained from bromine and chlorine responses were $2.9 \cdot 10^{-9}$ g and $1.8 \cdot 10^{-9}$ g per injection.

INTRODUCTION

Packed column gas chromatographic (GC) determination of chloride following reaction with phenylmercuric nitrate (PMN) and trifluoromethylmercuric nitrate (TMN) was reported on glass columns with diethylene glycol adipate stationary flame ionization detection (FID) and electron-capture detection (ECD) [1–3].

Microwave induced plasmas (MIPs) have been employed as element-selective atomic emission detectors for GC since 1965 [4] and their analytical utility has been extensively reviewed [5–8]. They may monitor a single element or, with appropriate multi-channel spectrometers, a number of elements simultaneously. GC–atomic emission detection (AED) has been used for example for the determination of organomercuric compounds at low levels [9–14].

Phenylboronic acid (PBA) and various substituted phenylboronic acids have been used, in the presence of mercuric nitrate, as derivatizing reagents for GC determination of halides, but those studies involved packed columns and FID or ECD [3]. The present study examines capillary column GC for the determination of chloride using PBA in the presence of mercuric nitrate, and also the separation of derivatized chloride, bromide and iodide with simultaneous atomic emission detection for chlorine and bromine.

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EXPERIMENTAL

A Model 3700 gas chromatograph with FID (Varian, Walnut Creek, CA, USA) and a Model 5890 II gas chromatograph [Hewlett-Packard (HP), Avondale, PA, USA] with an HP 7673A automatic injector and split/splitless capillary injection port, operated in split mode, were used. The latter instrument was coupled with an HP 5921A atomic emission detector, controlled by an HP 330 computer with HP 35920A GC–AED software. Helium was used as carrier and make-up gas, and hydrogen and oxygen were employed as reagent gases. An HP 5890A gas chromatograph equipped with an HP 5970 mass-selective detector was also used.

A DB 5 methyl-phenyl silicone fused-silica column (30 m × 0.25 mm I.D., with film thickness of 0.25 μm) and a DB-Wax polyethylene column (6 m × 0.25 mm I.D. with 0.31 μm film thickness) were used (J and W Scientific, Rancho Cordova, CA, USA).
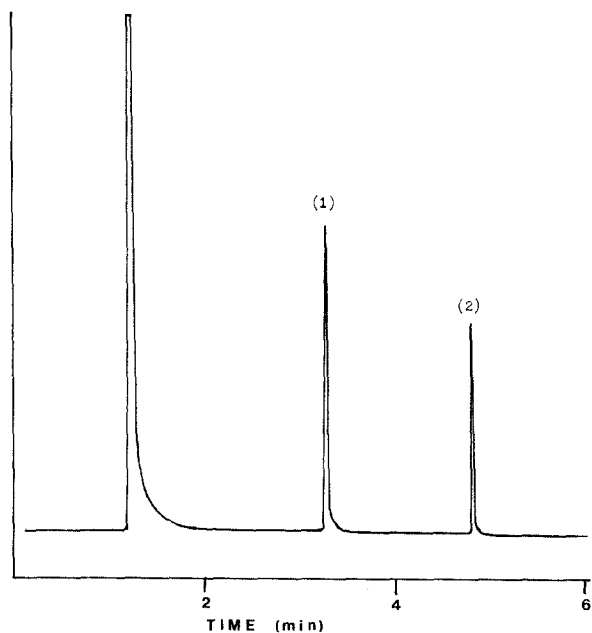

Fig. 1. Chromatographic separation of (1) phenylmercuric chloride and (2) diphenylmercury on a DB-5 (30 m × 0.25 mm, I.D.) fused-silica open tubular column, with temperature programming (150–200°C, at 10°C/min), injection port and detector temperatures 220°C, carrier gas (helium) flow-rate 1.2 ml/min and inlet split ratio 1:20.

Preparation of phenylmercuric compounds

PBA (0.01 M, 10 ml), mercuric nitrate (0.01 M, 10 ml), nitric acid (1 M, 2–3 ml) and an appropriate amount of chloride (2 · 10^{-3} M) were mixed in a separating funnel to bring the pH of the solution to 1–2. The white precipitate of PMC that was formed was extracted into chloroform, the organic layer separated and evaporated on a water bath. The residue was purified by sublimation at 0.1 Torr. The same procedure was used for the preparation of phenylmercuric bromide (PMB) and phenylmercuric iodide (PMI), using bromide and iodide reactants.

Diphenylmercury (DPM) was prepared by mixing 0.01 M PBA (20 ml), 0.01 M mercuric nitrate (10 ml) and a suitable amount of pH 10 buffer solution to keep the pH of the solution at that value, to give quantitative precipitation of DPM. The remaining procedure was as for PMC.

Standard 1000 ppm solutions of PMC and PMB were prepared from the pure compounds in benzene or methyl isobutyl ketone (MIBK). Further solutions were prepared by serial dilution in the same solvent.

RESULTS AND DISCUSSION

Capillary GC–FID

The elution and possible separation of PMC from PMB and PMI was examined on DB-5 and DB-Wax columns with FID. PMC was readily eluted on DB 5 at a column temperature of 190°C, injection port and detector temperatures of 220°C, and a helium carrier gas flow-rate of 1.2 ml/min, giving fairly symmetrical peaks, but no separation between PMC, PMB and PMI. However, DPM was well separated from PMC, as shown in Fig. 1. When the DB-Wax column was evaluated, some separation between PMC, PMB and PMI was obtained (Fig. 2), but on-column adsorption of PMC and its subsequent displacement by PMB was observed (some PMC was observed to be eluted upon injection of pure PMB). Also under similar conditions, no separation between PMC and DPM was obtained. Some adsorption of PMC was also observed on the DB-5 column, but after four repeated injections, reproducible response was obtained and this column was thus chosen for further study. The identity of the prepared PMC and DPM was also
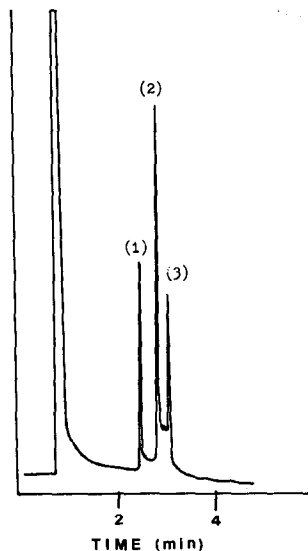
Fig. 2. Chromatographic separation of (1) phenylmercuric chloride, (2) phenylmercuric bromide and (3) phenylmercuric iodide on a DB-Wax (6 m × 0.25 mm) column with column, injection and detector temperatures 190°C, 220°C and 220°C, respectively, helium flow-rate 1.2 ml/min and inlet split ratio 1:20.

checked by GC–MS using the DB-5 column. Molecular ions for both PMC and DPM were obtained, corresponding to m/z 314 and 356, respectively (for ^{202}Hg).

Quantitative response for PMC on the DB-5 column was checked by injecting different amounts of PMC in triplicate and measuring average peak areas; linear calibration was obtained up to 100 mg/ml chloride ($R^2 = 0.998$). The detection limit measured at twice the signal-to-noise ratio was $3.3 \cdot 10^{-10}$ g, a value about an order of magnitude lower than that reported on a packed column using an FID detector [1,2].

GC–AED

In order to obtain better sensitivity for the determination of chloride, GC–AED was performed using the same DB-5 column and monitoring the mercury response at 185 nm. A low flow-rate of make-up gas (*ca.* 30 ml/min of helium) and hydrogen and oxygen plasma reagent gases as recommended by the manufacturer for mercury were used, but an asymmetrical peak with extensive tailing was observed (Fig. 3A). Other plasma discharge tubes, silica and alumina (sapphire), were tried with little improvement. However, some improvement in peak shape was obtained upon using a high flow-rate of helium make-up gas (*ca.* 150 ml/min) (Fig. 3B). The column temperature was 190°C, and the injection port and transfer line were at 200°C. With these conditions a linear calibration curve was obtained up to 100 mg/ml chloride ($R^2 = 0.996$). An approximate limit of detection was observed at $6.25 \cdot 10^{-11}$ g chloride showing MIP-AED to be *ca.* 5 times more sensitive than FID.
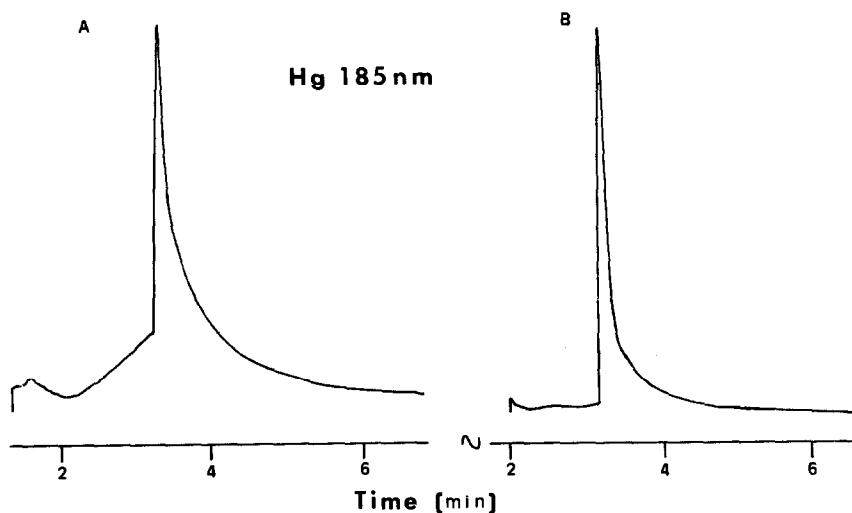

Fig. 3. GC–AED response of mercury as phenylmercuric chloride (at 185 nm) with GC conditions as Fig. 1, but using (A) O_2, H_2, low make-up flow and (B) O_2, H_2, high make-up flow.

Under the foregoing conditions, chloride and bromide co-eluted, thus only their total content should be determined by monitoring mercury emission. In order to determine chloride and bromide in a mixture, individual GC–AED monitoring of chlorine and bromine is necessary. To examine the quantitation of this response, AED responses were measured at 479 nm and 478 nm for chlorine and bromine, respectively, for an injected mixture of PMC and PMB. An optimal response for these elements was obtained by use of a high flow-rate of helium make-up gas, and oxygen as reagent gas (Fig. 4). It was noted that chlorine and bromine responses indicate similar tailing to that observed for mercury emission. However, examination of chlorobenzene under similar GC–AED flow conditions, or under those using a low flow-rate of plasma helium make-up gas, showed no appreciable peak tailing. The fact that very much less tailing was noted for PMC etc. with FID, using the same column, and also that minimal tailing occurs with many other GC peaks using the same GC–AED configuration [15], suggests that peak tailing is a function of elemental behavior in the MIP discharge tube, and that the chlorine and bromine responses are affected by the presence of the mercury in the eluent peak.

The selectivities of chlorine and bromine against carbon were measured using n-dodecane as a source

of carbon and were found to be about $20 \cdot 10^3$ and $11 \cdot 10^3$, respectively. Despite the proximity of the emission lines used for chlorine (479 nm) and bromine (478 nm) determination, there is a reasonable selectivity of ca. 350 between them; the photodiode array enables the maximum emission for the two elements to be collected on diodes separated 3–4 units from each other. The detection limits for chloride and bromide as PMC and PMB were 1.8 ng (100 pg/s), and 2.98 ng (200 pg/s) respectively, as compared to the limits of ca. 62.5 pg (1.5 pg/s) for the undifferentiated halides obtained by measuring the mercury response. It seems probable that if some sacrifice in elemental sensitivity is acceptable for chlorine and bromine, other pairs of emission wavelengths could be chosen to afford greater selectivity between these elements.

CONCLUSIONS

The study indicates that a sensitive GC procedure for the determination of halides using FID and AED may be feasible. The method using FID is about ten times more sensitive than with a packed column; detection limits can be further improved approximately five-fold with AED. Also, in the absence of complete GC separation of the halides as PMC and PMB, chloride and bromide may be measured simultaneously using different AED wavelengths for Cl and Br detection.
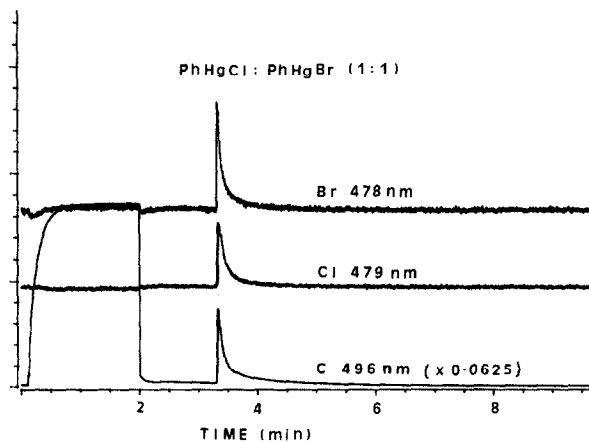
Fig. 4. Simultaneous GC–AED responses of Br, Cl and C as phenylmercuric chloride and phenylmercuric bromide at the chromatographic conditions of Fig. 1, but using O_2 and high make-up gas flow.

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