Gas Chromatographic Determination of Chloride using 2,4-Dichlorophenylboroic acid as a Derivatizing Reagent

[1] A. SARAFRAZ-YAZDI AND [2] W.I. STEPHEN

[1]Department of Chemistry, Faculty of Science, University of Mashhad, Mashhad, Iran
[2]Chemistry Department, Birmingham University, Birmingham, B15, U.K.

Summary: 2,4-Dichlorophenylboronic acid (CPBA) was examined as analytical reagent for the gas chromatographic determination of chloride, bromide and iodide. Flame Ionization Detector (FID) and glass column (90 cm x 4 mm) packed with SE-52 (2.5% w/w) on Universal B (65-85 mesh) were used to evaluate their GC behaviors.

2,4-Dichlorphenylboronic acid in the presence of excess of mercuric salt in the acidic solution (pH 0-2) reacts quantitatively with chloride, bromide and iodide to form dichlorophenylmercuric halides. The halides derivatives are easily extracted in chloroform with transfer of halide from aqueous to organic phase within 92-95%. Linear calibration ranges for GC determination of chloride, bromide and iodide were evaluated and extraction method has been developed for the determination of chloride at trace levels with detection limit of 0.06 μg/ml Cl⁻ in original solution. Method has been used for the determination of chloride in tap water.

Introduction

Halides (in particular chloride) are widely distributed over the earth as a variety of salts. They also exist in biological materials, food, beverages, natural waters and air. The determination of chloride at trace levels continues to be of analytical interest. Belcher et al. have reported GC determination of chloride using phenylmercuric nitrate (PMN) as derivatizing reagent [1,2]. Later on PMN and Trifluoromethylmercuric nitrate (TFMN) were used as reagent for determination and partial separation of chloride, bromide and iodide [3,4].

Phenylboronic acid has been used for the preparation of arylmercuric compounds and the reactions are reported to be in quantitative yield [5-7]. It is therefore CPBA, in the presence of excess of mercuric ions as nitrate has been examined for the determination of halides in the present work.

Results and Discussion

The preparation of dichlorophenylmercuric derivatives using CPBA is quite satisfactory. The CPBA is sparingly soluble in water, thus was dissolved by adding sufficient amount of alkali for the preparation of dichlorophenylmercuric derivatives. However for quantitative determination of halides, the boronic acid was dissolved in 25% ethanol in water producing ester $Cl_2C_6H_3B(OC_2H_5)_2$. Whenever this solution is used, the ester is hydrolyzed very easily in aqueous solution.

TG of CPMC, CPMB and CPMI indicate (Fig. 1) that arylmercuric derivatives are volatile and there is no sign of decomposition. It is therefore predicted that dichlorophenylmercuric halides are quite suitable for GC, but higher column temperature would be required.

Because of the need to use higher temperatures for the volatilization of dichlorophenylmercuric halides short column (90 cm x 4 mm) were used to reduce the retention times. A number of stationary phase, i.e., SE-52, OV-1, OV-17, OV-210, OF-1, DEGA and Carbowax 20M at the same loading (2.5%) on Universal B were investigated. The stationary phases SE-52, OV-1 and OV-3 gave symmetrical peaks, without any sign of decomposition, but OV-17, OV-210, QF-1, DEGA and Carbowax 20M indicated asymmetrical and broad peaks with long retention times. Thus SE-52 as stationary phase was selected. The optimal elution was obtained at column 200°C, injection port 210°C and carrier gas flow rate of 60 ml/min.

TG of CPMC, CPMB and CPMI indicate only a slight difference in their volatilities, which resulted in little difference in the retention time. The volatilities
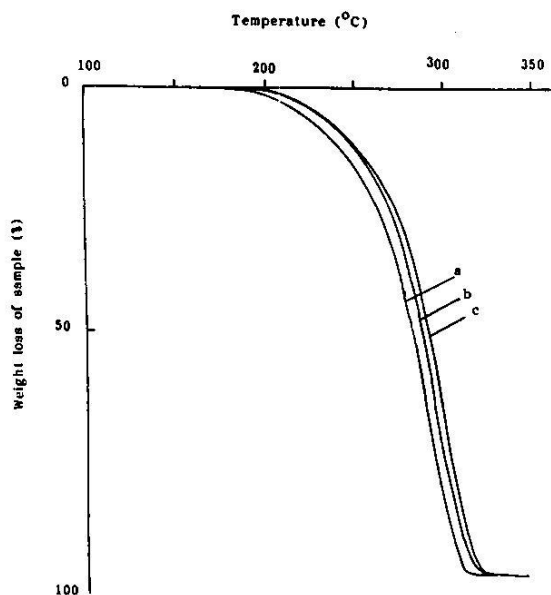
Fig. 1: Thermogravimetric curves of (a) CPMC, (b) CPMB, (c) CPMI.

and retention times follow the order CPMC >CPMB >CPMI. The retention times increase as the molecular weights increase. This is different than reported for phenylmercuric halides, where their retention times decrease as the molecular weights increased [1,2].

When CPMI was injected on GC column, two peaks were observed which possibly correspond to CPMI and DCPM. The latter was not obtained in the case of CPMC and CPMB. The reason for this most likely is due to breakage of Hg-I bond producing diaryl derivative. Dessy and Panlik [8] have studied rate constant reactions of halomercuric derivatives in different solvents and have suggested that rate constant increases on going from chloride through bromide to iodide. Thus HG-X bond weaken in sequence ArHgCl, ArHgBr and ArHgI.

In order to examine the response of FID detector with the amount of chloride, bromide and iodide injected as dichlorophenylmercuric halides linear calibration curves were obtained in the range of 20-250 mg/ml, 40-300 mg/ml, 50-500 mg/ml of chloride, bromide and iodide respectively with relative standard deviation of ± 1.6%. The limits of detection for chloride, bromide and iodide as CPMC, CPMB and CPMI measured as twice the signal to noise ratio were 5×10^{-9} g, 6.3×10^{-9} g and 1.9×10^{-8} g respectively.

Analytical procedures require suitable methods for quantitative converting the halide samples to volatile organomercuric halde before injecting into the gas chromatograph. Direct reaction of mercuric salts, in acidic media (pH 1), followed by solvent extraction have been used for this purpose. It was observed that the reagent is not extracted in organic phase and only arylmercuric halides are extracted.

Effect of variation of pH, equilibration time, reagent and mercuric salt concentration were investigated on the recovery of the halides from aqueous solutions. It was observed that maximum recovery was obtained within pH 0-2 (Fig. 2), equilibrium time of 2 min. being sufficient for the extraction (Fig 3) and two fold excess of the reagent and mercuric salt with respect to halides are sufficient for the quantitative analysis with respect to halide at maximum percentage of recovery within 92-96%.
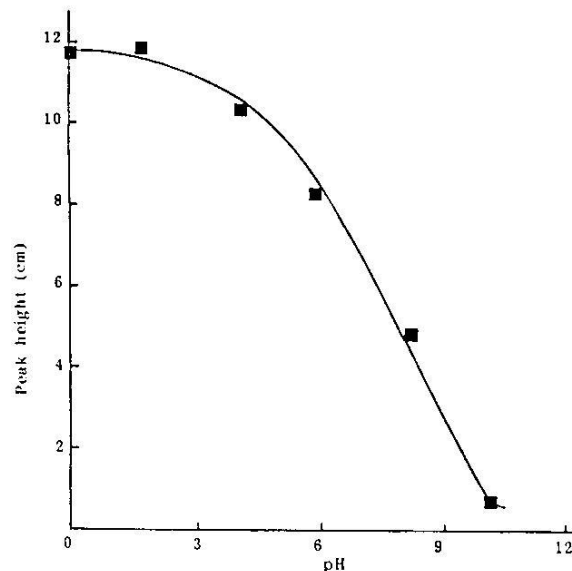

Fig. 2: Effect of pH on extracting of 2,4-dichloro phenylmercuric halides.

Linear calibration ranges for chloride, bromide and iodide were determined using solvent extraction procedure by taking different amounts of halides. Calibration graphs indicated linear ranges for chloride (0-177 μg/ml), bromide (0-400 μg/ml, and iodide (0-635 μg/ml). The relative standard deviations for seven injections were in the range of 1.2-1.8%. All the calibration graphs passed through origin. When recommended for dilute chloride solution was used, the limit of detection was found to be 0.06 mg/ml chloride in original solution.
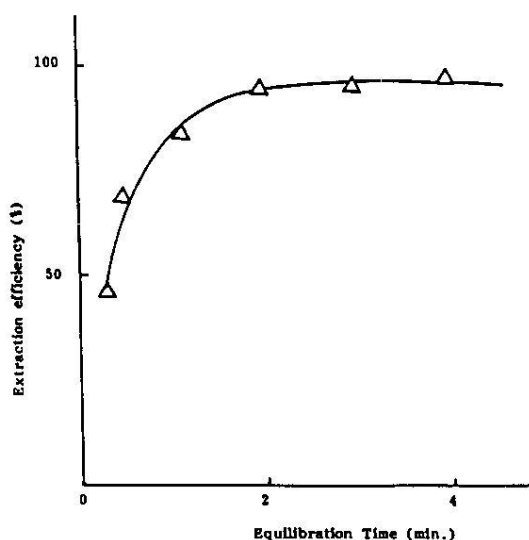
Fig. 3: The effect of equilibration time (shaking time) on the extraction of chloride as CPMC.

The effect of interfering ions were investigated for the determination of halides ion. The effect of anions were considered more important in comparison with metal ions. Diverse ions were introduce to the halide solutions in the form of soluble salt at a concentration factor of ten greater than the analyte. Recovery of the chloride in the presence of various ions were compared with the recoveries from control extraction, which contained no diverse ion and was analysed simultaneously. It was observed that Na^+, Mg^{2+}, Cr^{+3}, Mn^{+2}, Fe^{+2}, Ni^{+2}, Cu^{+2}, Cd^{+2}, Al^{+3}, Pd^{+3}, NO_3^-, SO_4^{-2}, NO_2^-, PO_4^{-3} and ClO_4^- did not interfere. However a considerable interference was noticed in the presence of $Hg(1)$, $Ag(I)$, CN^-, SCN- and S-2.

In the case of silver and mercury (1) the GC of the extract showed no peak for CPMC. This is caused by the reaction of the halide with silver and mercury (1), producing a white precipitate. These interferences can be eliminated by two methods, (a) passing hydrogen sulphide through the solution for 5 min. and the filtering Ag_2S and Hg_2S from the solution and then the excess of hydrogen sulphide is removed by heating (b) sodium hydroxide solution is added to both the solutions and the precipitates of silver and mercuro-oxides are filtered off and the filtrate is acidified with dilute nitric acid for the following experiments. After removing these interferences the recovery was 90-95%.

Similarly in the case of thiocynate and sulphide two methods can be used, (a) dilute nitric acid is added to both the solutions and heated and nitrogen is passed through the solution to remove HCN, NO and H_2S formed during the reaction, (b) thiocynide and sulphide can be precipitated by adding of copper sulphate solution. The precipitates are filtered off and the filtrate is used for further analysis. After removing these interferences 92- 96% recoveries were obtained. In the case of cyanide interference ratio of 10:1 (CN^- Cl^-) no GC response was obtained in respect to CPMC, due to the formation of a complex of mercuric ions with cyanide, preventing the reaction of CPBC. To eliminate this interference hydrogen peroxide was added in alkaline solution to destroy the cyanide. The solution was then boiled to remove hydrogen peroxide. After that the solution was used for the analysis and 92-96% recovery was obtained.

Finally the method was applied for chloride determination in tap water and standard chlorobenzoic acid as real samples, and also for bromide in standard bromobenzoic acid. Table 1 and 2 show the data which are in good agreements with standard methods.

Tble 1: Determination of chloride in tap water

Method	chloride found ($\mu g/ml$)	standard deviation	Rel.std. Devn. (%)
Gas liquid chromatography Mercuric-thiocyanate	8.06	±0.0547	120
	8.10	±0.0040	0.98

standard deviation of seven analytical results.

Table 2: Determination of chlorine and bromine in organic compounds

Sample	Chlorine found (%)	Chlorine Expected(%)	Bromine found(%)	Bromine expected(%)
p-bromo-benzoic acid			38.20 38.40	39.80
p-chloro-benzoic acid	21.88 21.92	22.68		

standard deviation and relative standard deviation for seven measurements were ± 0.07 1.25% respectively.

Experimental

Preparation of 2,4-Dichlorophenylmercuric chloride (CPMC)

In a 25 ml beaker CPBA (5 ml, 0.1 M prepared in slightly alkaline medium), mercuric nitrate (5 ml,

0.1 M) chloride solution (5 ml, 0.1M) and water 15 ml were added. The mixture was acidified to pH 1 with nitric acid. The precipitate was filtered after 10 min. and purified by sublimation, m.p. = 197-8°C, CPMC requires %, C=18.84, H=0.78; found %, C=191.1, H=0.80. Mass spectrum shows M+ at m/e relative intensity 382 (100%) and m/e 347 (80%), 202 (50%), 146 (100%).

Preparation of di(2,4-pichlorophenyl) mercuric (DCPM)

In a 25 ml beaker mercuric nitrate (5 ml, 0.1 M) and CPBA (10 ml, 0.1 M) were diluted to 25 ml. The pH of the solution was adjusted to 1 with nitric acid. The mixture was mixed well and filtered after 5 min. and recrystallized from ethanol, m.p. = 184-6°C DCPM requires %C=29.23, H=1.22; found %C= 30. 23, H=1.22. Mass spectrum showed M$^+$ at m/e 494 (60%), 347 (70%), 202 (50%) and 146 (100%).

CPBA was obtained from Lancaster synthesis Ltd. Mass spectra were recorded on A. E. I. MS-9 double focusing mass spectrometer operating at an ionization voltage of 70 ev at an accelerating potential of 8 KV. The samples were evaporated into the source with direct insertion probe. Thermogravimetry (TG) of the compounds (1-2 mg) were recorded in platinum sample pan on Perkin Elmer Model TGS-1 thermobalance at a heating rate of 20°C/min and nitrogen flow rate of 20 ml/min in temperature range 25-450°C.

A Pye Series 104, gas chromatograph equipped with FID and Philips PM 8220 chart recorder was used. Glass column (90 cm x 4 mm, 1D) packed with SE-52, OV-1, OV-3, OV-17, OV-210, QF-1, DEGA and Carbowax 20M (2.5% w/w) on Universal B (60-85 mesh) AW, DMCS were used.

Quantitative Analysis

A stock solution (1000 ppm, with respect to halides) of CPMC (0.441 g), dichlorophenylmercuric bromide (CPMB) (0.223g) and dichlorophenylmercuric iodide (CPMI) (0.0159 g) in 50 ml were prepared. Appropriate dilution of stock solution with chloroform to give 20-400 mg/ml of chloride, bromide and iodide were prepared. Samples were introduced in GC on glass column (90 cm x 4 mm) packed with 2.5% SE-52 coated on Universal B at a column, injection port and detector temperatures of 200, 210 and 250°C respectively. Carrier gas flow

was 60 ml/min. Average peak height and area were measured.

The Formation and Solvent Extraction of dichlorophenylmercuric halides from Aqueous solutions:

Standard solution of CPBA (8 ml, 0.01 M) and mercuric nitrate (6 ml, 0.01 M) were placed in 50 ml separating funnels. The solution containing halides (0-5 ml) was added and volume of aqueous phase was adjusted to 30 ml with water. The pH of the solution was adjusted at 1 by using nitric acid. Each funnel was then shaken for 1-2 min. Dichlorophenylmercuric halides were extracted with 7 ml and 3 ml portion of chloroform. The extracts were collected in 10 ml volumetric flask. The volume was adjusted to mark. Extract (2 µl) were injected at optimized conditions.

Recommended procedure for the determination of chloride in dilute solutions

To a 500 ml separating funnel, sample 250 ml solution was transferred and enough nitric acid was added to make a final pH 1. Mercuric nitrate (2.5 ml, 0.001 M) and, CPBA (2.5 ml, 0.001 M) were added Chloroform (10 ml) was added and contents were shaken for 2 min. and layers were allowed to separate. The extract was collected and extraction was repeated with 5 ml of chloroform. Extract was concentrated to 2 ml by distillation and was poured into 5 ml graduated flask. Distillation flask was washed twice with solvent and was diluted to the mark with chloroform. The extract (10 µl) injected onto the gas chromatograph.

Determination of chloride in Tap water

Tap water (70 ml) was substituted for the halides solution in the analytical procedure for the extraction chloride as CPMC and volume of all the standards and sample solutions were adjusted to 90 ml with water. Seven injections (2 µl) of the extracts were made onto the GC and the concentration of the chloride in the tap water was determined from the calibration graph. The chloride in tap water were also determined using mercuric-thiocyanate method [4].

Determination of Chloride and Bromide in Organic Compounds

Chlorobenzoic acid and bromobenzoic acid are used as standard compounds in elemental analysis.

These compounds were used as samples. Chloride and bromide were determined after the decomposition of these compounds using the oxygen flask method and followed by the same recommended procedure using CPMC as reagent.

Acknowledgements

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