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QUANTITATIVE GAS CHROMATOGRAPHIC ANALYSIS OF BORON TRICHLORIDE, BORON AND BORON NITRIDE[*]

ALDO DI LORENZO

Laboratorio Ricerche sulla Combustione, C.N.R.-Napoli, Istituto di Chimica Industriale e Impianti Chimici, Università Piazzale V. Tecchio, Naples (Italy)

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SUMMARY

The quantitative on-line analysis of the gaseous products of a nitrogen plasma jet, containing trace amounts of chlorine and boron trichloride, has been carried out. The quantitative analysis of the solid products, boron and boron nitride, has also been carried out by *in situ* reaction with chlorine followed by gas chromatography. The chlorine attacks the boron and the boron nitride in a specially designed reaction–injection system of the gas chromatograph at 500° for a 1-min period. Then, the reaction products are immediately swept into the column through the gas sampling valve. Both of the analyses are carried out with a 2-m Teflon column containing 10% Kel-F 3 on Teflon 6 at 40°. About 1% (v/v) of boron trichloride vapour is incorporated in the carrier gas so as to prevent irreversible adsorption of the small amount of boron trichloride that is to be detected.

INTRODUCTION

During work on the decomposition of boron trichloride in a nitrogen plasma jet[1], there arose the problem of the quantitative gas chromatographic analysis of the gaseous products from the reactor that contained trace amounts of chlorine and boron trichloride in admixture with nitrogen. The quantitative analysis was also required of boron and boron nitride, formed by decomposition of the boron trichloride and reaction with the nitrogen plasma.

The principal difficulty in analysing gas mixtures containing chlorine and boron trichloride arose from their high reactivity and from their corrosive action on the metal parts of commercial instruments.

It has been reported that trace amounts of chlorine in air can be detected by gas chromatography (GC) by using a glass column containing DC 200 methyl-silicone oil on Chromosorb W (ref. 2). Mixtures of boron compounds, including boron trichloride, were separated by GC on squalane on Celite, and on tricresyl phosphate on porous glass or Celite[3]. MYERS AND PUTNAM[4] determined mixtures containing hydrogen chloride and boron trichloride by using a copper column containing mineral oil on Chromosorb or Fluorolube on Teflon. Prior to use, the columns were dried

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thoroughly by passing several 5-ml samples of boron trichloride gas through them at 25°. Also, by using Chromosorb T (Teflon 6) as the support in the quantitative analysis of the volatile metal fluorides, JUVET AND FISHER[5] found that it was necessary to saturate the column with the fluoride being analyzed before consistent and reproducible results could be obtained. Saturation of the column with one fluoride does not result in saturation of the column with respect to other fluorides. Therefore, before a mixture can be analyzed quantitatively, the column must be saturated with respect to all of the components being determined.

No information has been found in the literature concerning the GC analysis of boron and boron nitride.

EXPERIMENTAL

Analysis of gas mixtures

All of the analyses were carried out on a Carlo Erba gas chromatograph, Model GT, with a thermal conductivity detector. The carrier gas was helium. Samples were injected with a gas sampling valve.

In preliminary analyses of synthetic mixtures of nitrogen, chlorine and boron trichloride, various columns, including those described for the determination of chlorine in air and for the separation of boron compounds, were tested in order to select the most suitable operating conditions for separating the products obtained from the reactor.

TABLE I

GAS CHROMATOGRAPHIC COLUMNS TESTED

| No. | Solid support | Liquid phase | Loading (%) | Column | | |
				Material	Dimensions	Temperature (°C)
1	Chromosorb W	DC 200 methyl-silicone oil	20	Glass	2 m × 2 mm	60
2	Celite	Squalane	20	Glass	2 m × 2 mm	60
3	Porous glass	Tricresyl phosphate	0.5	Glass	2 m × 2 mm	50
4	Celite	Tricresyl phosphate	20	Glass	2 m × 2 mm	50
5	Celite	Arochlor	10	Glass	2 m × 2 mm	40
6	Celite	Arochlor	10	Glass	5 m × 2 mm	40
7	Celite	Arochlor	20	Glass	5 m × 2 mm	40
8	Porapak Q	Arochlor	10	Glass	2 m × 2 mm	100
9	Teflon	Arochlor	10	Glass	2 m × 4 mm	40
10	Teflon	Kel-F3	10	Glass	2 m × 4 mm	40
11	Teflon	Kel-F3	10	Teflon	2 m × 5 mm	40

The columns tested are listed in Table I. The first group (1–4) gave good results for the separation of nitrogen and chlorine, but the boron trichloride was partially decomposed. The presence of various peaks, one of which was eluted between nitrogen and chlorine, was noted.

With the second group of columns (5–8), it was noted that injections of boron trichloride at 5–10-min intervals produced a gradual increase in the heights of the

peaks until they became asymptotic. When the injections were stopped and then resumed after 2 or 3 h, the increase in the heights of the peaks to the same asymptotic value was repeated. However, this was not so evident when Teflon was used as the solid support (columns 9–11), especially with the last column.

When the last column was used for the quantitative determination, the calibration curve for boron trichloride was not linear and did not pass through the origin. Samples with a boron trichloride concentration of less than 1 % were not eluted. This anomalous result could be ascribed either to the presence of trace amounts of water in the carrier gas or to the absorption of boron trichloride by the connection lines and by the gas sampling valve. Therefore, helium was dried in two condensers containing molecular sieves, the first of which was cooled with acetone and dry ice and the second with liquid nitrogen. The commercial gas sampling valve of the gas chromatograph was modified so as to ensure that surfaces in contact with the samples were made of Teflon. Connections between the gas sampling valve and the column and between the latter and the thermal conductivity detector block were made with 1/16-in. O.D. Teflon tubing and Swagelock connectors and reducers. The small diameter of this tubing resulted in only a slight increase in the instrumental dead-volume.

With these modifications, it was possible to elute samples with a boron trichloride concentration of about 0.3 %. The tailing of the boron trichloride peak and the elution of gradually higher peaks were again evident but to a lesser extent than under the previous conditions. This showed that the absorption of the small amounts of boron trichloride had not been completely prevented. Therefore, to prevent even this small absorption, about 1 % (v/v) of boron trichloride vapour was added to the carrier gas.

Fig. 1 shows the final arrangement of the apparatus, including the feeds of gases from the cylinders and of the products from the reactor in lines to the gas chromatograph, the feed of boron trichloride in the carrier gas and the GC apparatus. With this arrangement, the boron trichloride always gave a symmetrical peak and there was no difficulty in achieving steady-state conditions. A linear response was
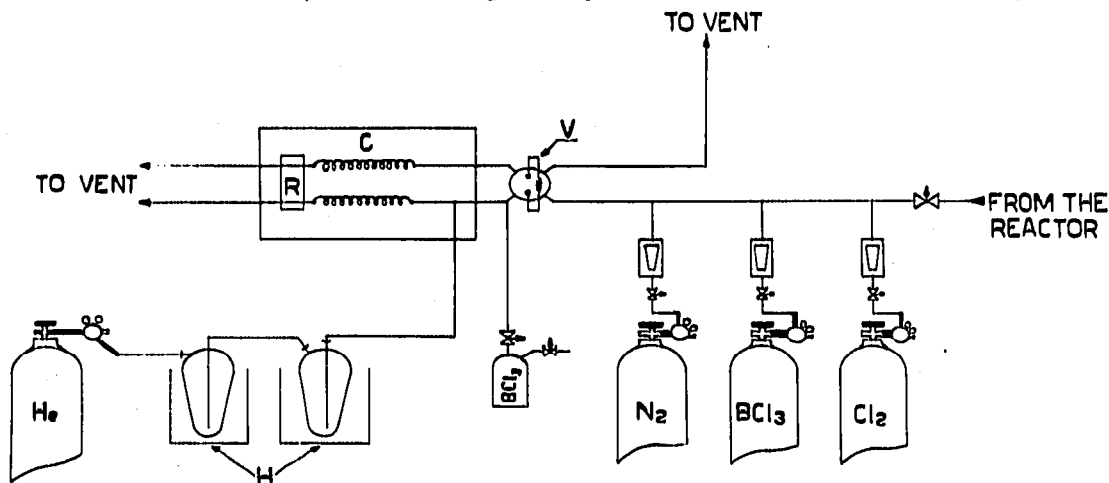

Fig. 1. Final arrangement of the apparatus. R, Thermal conductivity detector; C, columns; V, gas sampling valve; H, condensers.

found with both chlorine and boron trichloride even in the range 0–2 %, with calibration curves passing through the origin. A typical separation is shown in Fig. 2.

Fig. 3 gives, as an example, the calibration curve for boron trichloride in the range 0–2 %. Because of very low concentrations of boron trichloride and chlorine, the analytical conditions for the maximum detector signal were tested as a function of the carrier gas flow-rate and of the filament current, bearing in mind the need for rapid analysis as well as the avoidance of filament corrosion. The final analytical conditions adopted are given in Table II.
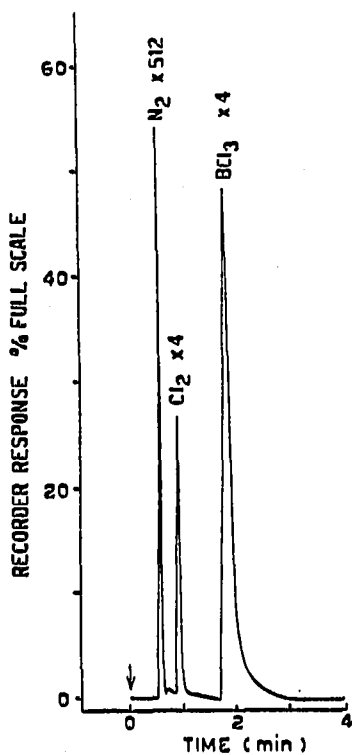
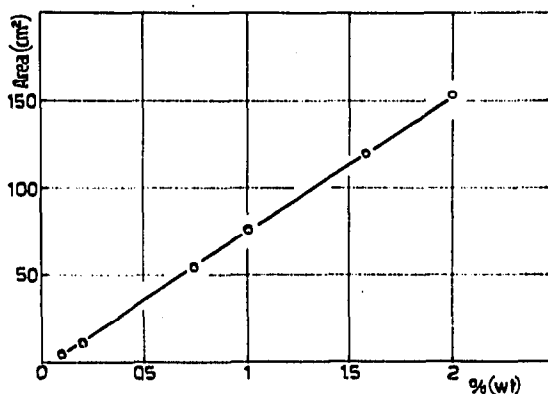Fig. 2. GC separation of nitrogen, chlorine and boron trichloride.

Fig. 3. Calibration curve for boron trichloride.

TABLE II

OPERATING CONDITIONS

Instrument	Carlo Erba gas chromatograph, Model GT
Column	2 m × 5 mm Teflon column; 10% Kel-F3 on Teflon
Column oven temperature	40°
Detector	Thermal conductivity detector
Current	250 mA
Detector block temperature	100°
Helium flow-rate	40 ml/min
Sample volume	2 ml
Time for single analysis	3 min

After about 500 analyses had been carried out, it was found that the corrosion of the thermal conductivity cell filaments by the reactive gases was not as severe as had been expected.

Determination of boron and of boron nitride

It is well known that boron reacts with chlorine to form boron trichloride. The chlorination is effected rapidly at temperatures in excess of 500° (ref. 6). Moreover, boron nitride reacts with chlorine at 600° according to the following equation (ref. 7):

$$2\,BN + 3\,Cl_2 \xrightarrow{\,600°\,} 2\,BCl_3 + N_2$$
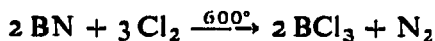
Therefore, by reaction of chlorine with mixtures of boron and boron nitride, formed by decomposition of the boron trichloride and reaction with the nitrogen plasma, it was possible to obtain gaseous mixtures of the same components present in the gaseous phase produced in the reactor nitrogen, boron trichloride and chlorine, although in this case the concentrations of the single components were very different. Hence the GC technique described previously for the gaseous mixtures could be used under the same analytical conditions.

The main problem was to design a reaction chamber for the chlorination of boron and boron nitride that could then be used to analyze directly the gaseous products and the excess of chlorine. The idea of building a specially designed reactor–injection system, which was used by JUVET AND FISHER[5] for the *in situ* reaction of metals and alloys with fluorine, was excluded because the operating temperatures were too high. The reactor was therefore placed before the gas sampling valve.

Fig. 4 shows the reactor and the gas sampling valve. The reactor was made of nickel, as was the tubing that connected the chlorine cylinder to the reactor and the reactor to the sampling valve. The needle valve (Whitly 21 RS G) was made of Type 316 stainless steel. The total volume of the reactor was about 100 ml.
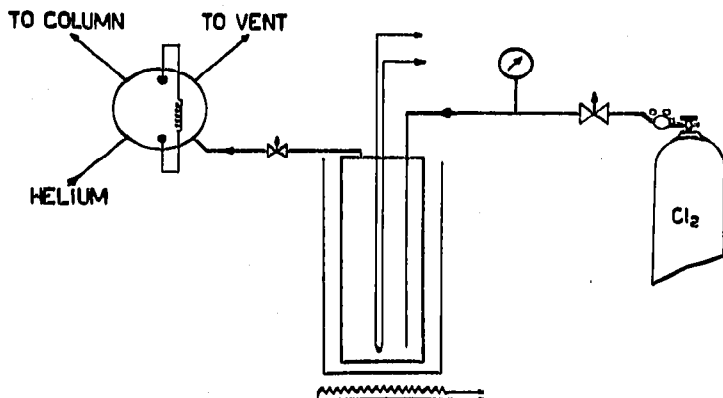

Fig. 4. Reactor and gas sampling valve.

Solid, comprising boron and boron nitride, produced from the plasma jet was weighed on a Model H20T Mettler electrobalance and introduced into the reactor. The reactor was then evacuated to a pressure of less than 1 mm Hg and chlorine gas was admitted at a pressure of 3 atm.

The reactor was heated to 600° and the temperature measured with a thermo-couple. The reaction time was about 2 min. The gaseous compounds produced and the excess of chlorine were then analyzed by means of the gas sampling valve.

The ratios of peak areas of nitrogen to boron trichloride were measured so as to obtain quantitative values for the boron and boron nitride present in the solid substances, by using calibration curves constructed with mixtures with known proportions of boron and boron nitride.

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