Notes

CHROM. 5556

Gas chromatography of some reactive gases on graphitized carbon black

The gas chromatographic (GC) analysis of reactive gases is of interest for several processes in the nuclear energy industry and several reports[1-3] have been published on this subject. All these processes involve the use of very inert supports, such as fluorine-containing polymers (Kel-F, Fluoropak, Teflon). These materials have the advantage of high chemical stability, but unfortunately there are serious limitations to their extensive use, which can be summarized as follows: poor wettability, which hinders the formation of a uniform layer of the liquid phase; and the presence of electric charges on the surfaces of these perfluorocarbon polymers, which make regular column packing impossible. For these reasons, Teflon columns are not very convenient for practical GC.

We have recently investigated the GC properties of graphitized carbon blacks as solid adsorbents and found that by treating them with hydrogen at 1000°, very polar compounds could be eluted[4], peak tailing and "ghosting" phenomena being avoided. In this paper we report the first results obtained in attempts to use these materials as supports for gas-liquid chromatography of highly reactive gases, such as halogen hydrides, chlorine and boron trifluoride.

Apparatus and material

A Carlo Erba (Milan, Italy) gas chromatograph, equipped with a thermal conductivity detector with gold filaments and conveniently modified has been used. Every contact of the reactive gases with metals has been avoided by inserting Teflon tubes into the gas lines connecting the samples with the column and the latter with the detector block. A special home-made gas sampler of a common design, but made entirely of Teflon, has been used. Tests were carried out with the column in the apparatus substituted with a Teflon capillary (10 cm long × 0.1 cm I.D.). Peaks from HF, HCl, Cl_2 and BF_3 were sharp and there was almost no tailing showing that practically no adsorption took place in the various parts of the apparatus. Teflon columns have therefore been used.

Graphon, a well known example of graphitized carbon black with a surface area of about 100 m^2/g, was treated with hydrogen at 1000° according to a procedure previously described[4]. This procedure has the purpose of eliminating the active centres constituted by surface oxygen complexes which are always present on an adsorbent surface. In this way, carbon black becomes a very inert support and it can be used even for the elution of reactive gases.

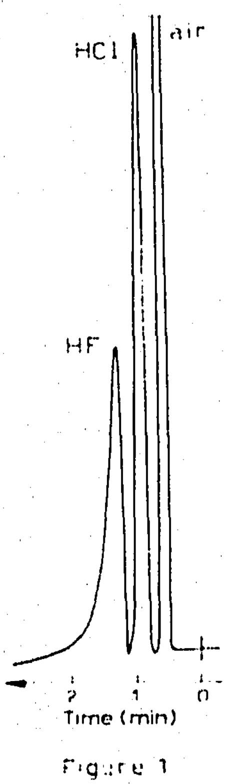
Results and discussion

Hydrogen halides. A good application of hydrogen-treated Graphon has been the elution and separation of HCl and HF from air. For this purpose, a mixture of

50 % of polyfluoroether (y/25 Montecatini Edison, Milan) and 50 % of benzophenone was used as the stationary phase and the Graphon was coated with 40 % w/w of this mixture. Benzophenone, which is a weak Lewis base, acts as the adsorbate and enhances the separation between HCl and HF, while the fluorinated liquid is used to disperse the benzophenone homogeneously on the support surface.

In Fig. 1 the separation of HCl and HF from air is shown. Tailing of the HF peak is unavoidable and is most likely due to the self-dimerization of the acid. Preconditioning of the column has been obtained by injecting small amounts of the two reactive gases into the column before its use. After this, reproducibility of successive injections was satisfactory, showing that no irreversible adsorption was taking place.

Chlorine. This halogen has been eluted by PHILLIPS AND OWENS using Kel-F on very long capillary columns[2]. Cl_2 was not retained but the interest of the paper is in the elution of ClF_3, even though the latter compound is quite markedly adsorbed. Similar behaviour of Cl_2 was observed by LYSYJ AND NEWTON[3] and by HAMLIN *et al.*[5]. In the latter paper the separation of Cl_2 from UF_6 and ClF_3 is reported.



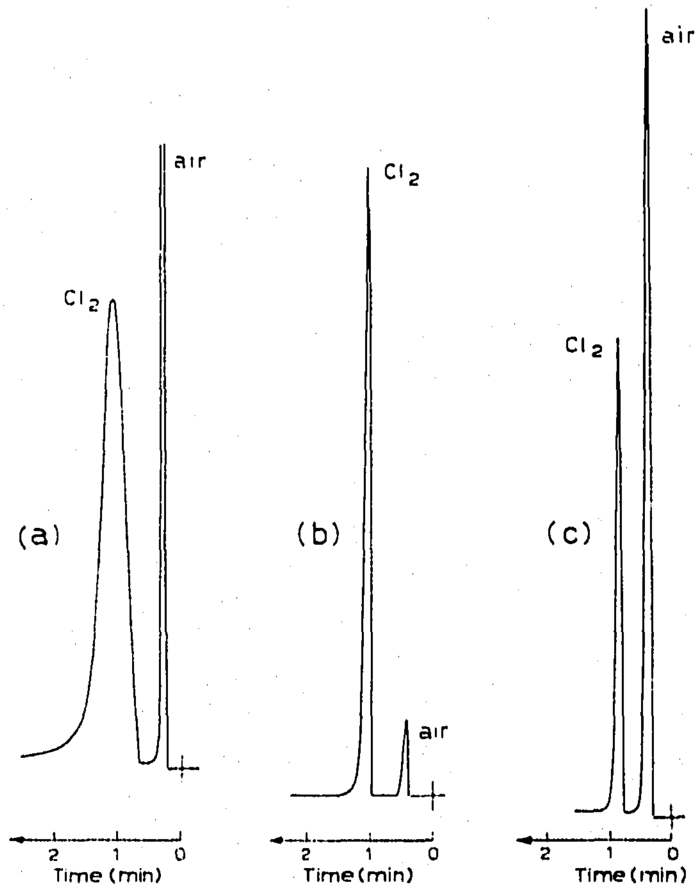


Fig. 1. Elution of HCl and HF. Column, 2 m × 3 mm; packing material, hydrogen-treated Graphon + 20% polyfluoroether + 20% benzophenone; temperature, 70°; carrier gas, helium; flow rate, 40 ml/min.

Fig. 2. Elution of Cl_2. Column, 2 m × 3 mm; packing material: (a) Graphon + 1% H_3PO_4; (b) Graphon + 5% H_3PO_4; (c) Graphon + 10% H_3PO_4; temperature, 60°; carrier gas, helium; flow rate, 50 ml/min.

In the present work, we used a column made of Graphon coated which phosphoric acid at various percentages, as shown in Fig. 2. In this case no hydrogen-treatment of the Graphon was necessary. The interesting point is that once the monolayer of H_3PO_4 is formed a sharp peak with no tailing is obtained. In any case we had to destroy the reducing impurities present in the column before a sharp peak could be obtained. The first injections yielded two peaks, one due to Cl_2, the other to HCl. After three or four injections the HCl peak disappeared and after that no further conditioning of the column was needed, even when leaving the column under a flow of helium overnight.

Boron trifluoride. To our knowledge this highly reactive and corrosive compound has never been eluted in GC. The first problem to be solved was to find a suitable substance capable of establishing weak interactions with BF_3 so that this compound could be retained by the column. As is well known, BF_3 is a very strong Lewis acid and forms very stable complexes with molecules containing atoms which can be electron donors (O, N, S). We found that most of the complexes commonly known were too stable for chromatographic needs, while in the case of benzophenone, the complex strength is strongly decreased by the presence of two aromatic rings close to

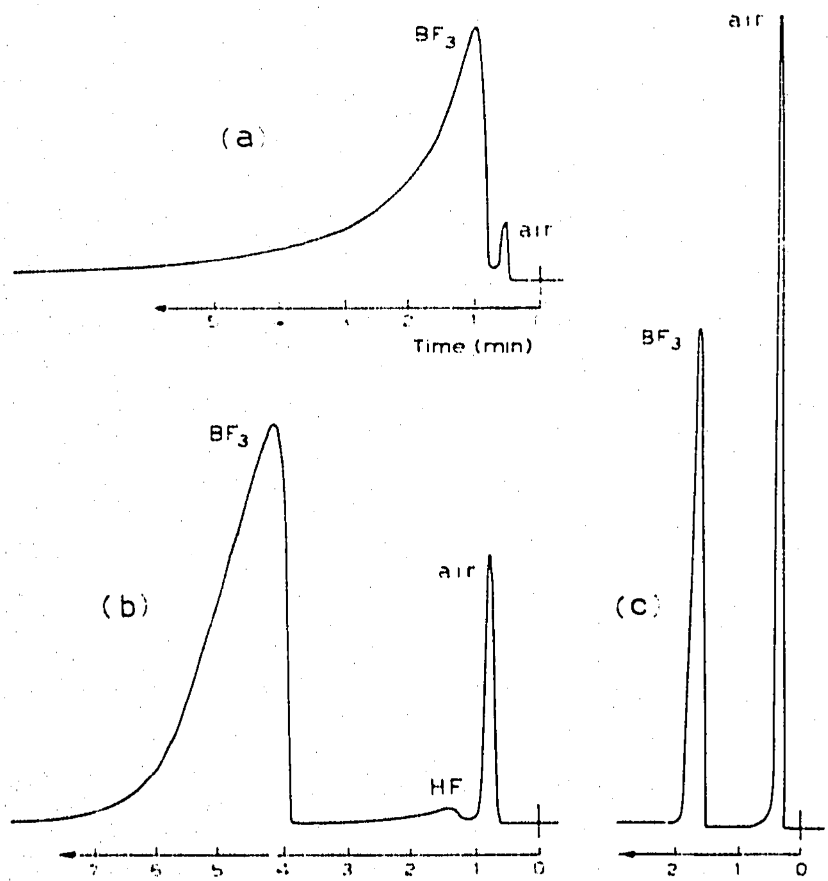


Fig. 3. Elution of BF_3. Column: 2 m × 3 mm; packing material: (a) Graphon + 20% Kel-F3, temperature: 30°; (b) Graphon + 10% benzophenone, temperature: 96°; (c) Graphon + 15% polyfluoroether + 5% benzophenone, temperature: 96°; carrier gas: helium.

the =CO group. Nevertheless, the heat of adsorption measured by the GC method was 10.3 kcal/mole, and this value is higher than the usual heat of solution or adsorption but lower than that usually observed in the formation of stable complexes.

In Fig. 3 the progress in obtaining satisfactory elution of this compound is shown. In (a) untreated Graphon is coated with 20% Kel-F3. The BF_3 peak is badly skewed and scarcely separated from air. Tailing is due to strong interactions occurring at the active sites of the carbon black surface and, furthermore, BF_3 is scarcely retained by the Kel-F3 at the working temperature. In (b) an improvement is observed and the peak is completely separated from air, the presence of the benzophenone also permitting the separation of the HF peak from air (this compound is always present in commercial BF_3). Tailing is still present but to a lesser extent than in the previous chromatogram. In (c), where Graphon treated with hydrogen at 1000° has been used, the best peak is obtained. The hydrogen-treatment eliminates peak tailing completely, and the retention time is decreased because of the lower amount of benzophenone used. Although in this case column preconditioning was again needed, after two or three BF_3 injections the reproducibility of peak areas was completely satisfactory.

The results of this work show that carbon black, especially after hydrogen-treatment can be used successfully for the GC of highly reactive substances. The interest of a satisfactory elution of BF_3 is particularly important because it can be employed, making use of suitably efficient columns, for the enrichment of boron isotopes.

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