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THE PURIFICATION OF GERMANIUM TETRAIODIDE BY
PREPARATIVE GAS CHROMATOGRAPHY

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SUMMARY

The use of adsorbents for the preparative separation of several high-boiling compounds is of practical interest. The choice of sufficiently pure adsorbents, which are capable of retaining the components being separated, is of great importance.

This paper deals with the purification of germanium tetraiodide by preparative gas-adsorption chromatography on carbon black.

INTRODUCTION

Preparative chromatography is being used increasingly in the preparation of highly pure compounds¹⁻³.

Preparative gas-liquid chromatography is used mainly for the preparation of low-boiling halides^{4,5}. However, preparative gas-liquid chromatography, although it has advantages, has one serious drawback that hinders the preparation of highly pure compounds; this is connected with the possibility of contamination by impurities caused by vaporization of the stationary phase, especially at high separation temperatures.

The use of absorption chromatography for preparing pure halides has been little investigated⁶⁻⁸.

As an example of preparative chromatographic purification, a study was made of the purification of germanium tetraiodide, the impurity content of which was determined by spectral analysis. Known amounts of impurities were previously added to the sample⁹. The purity requirements of such materials are very stringent¹⁰; in order to prepare material with a correctly oriented structure, it must contain less than 10^{-5} – 10^{-7} % of impurities^{10,11}.

EXPERIMENTAL

Absorbents

The following adsorbents were used for the investigation: modified silica gel with a specific surface area of 16 and 50 m²/g; activated carbon (BAU); granulated calcium fluoride; molecular sieves; and graphitised carbon black¹².

The evaluation of adsorbents for the separation of high-boiling inorganic compounds was carried out on a simple apparatus consisting of a short quartz tube,

5–6 mm in diameter, filled with an adsorbent layer 5–7 cm long. The tube containing the adsorbent was placed in a cylindrical furnace heated to the temperature at which the analysis would be carried out. After vaporization of the sample by heating the tube, a coloured or colourless (depending on the compound) ring appeared on the cold outlet end of the quartz tube.

On the basis of preliminary investigation graphitized carbon black was chosen as the best adsorbent for the separation of pure high-boiling compounds at about 250°. An especially pure carbon black powder, which was graphitized at 3000°, was placed in a special polyethylene vessel, which was rotated on the rolls of a ball-mill for 12 h. In this way, granules were obtained that were sieved to give carbon black spheres of diameter 0.25–0.6 mm and 0.5–1 mm.

The adsorbent prepared from graphitised carbon black was very soft and was readily compressed by slight pressure, especially in preparative columns. The most suitable fraction of graphitised carbon black had a diameter of 0.5–1 mm. It should be noted that in vertical columns of large diameter (> 20 mm), even the fraction of carbon black with diameter 0.5–1 mm becomes compressed. The resistance of a preparative column containing graphitized carbon was considerably greater than a column containing other adsorbents. This caused the carbon granules to break down, so that in order to increase the mechanical strength of the graphitized carbon adsorbent, it was supported on a Teflon support of the Polychrom type¹³, in a proportion of about 5 % by weight of the support. In this case, the retention times of the investigated compounds were considerably decreased, and the separation efficiency was not appreciably changed. However, it was necessary to increase the length of the chromatographic separating column in order to obtain similar results. The use of a Teflon support is possible only up to a temperature of about 250°.

Apparatus and method

During the assembly of the equipment, it is necessary to remove all possible sources of product contamination. One of the main sources of impurities is the carrier gas. The cylinder helium that was used as the carrier gas contains 10^{-2} % of water and 10^{-3} % of organic impurities. The carrier gas was dried and purified on silica gel activated carbon and molecular sieves, using a fine fibre filter before the inlet of the gas into the column. The filter was submerged in liquid nitrogen for the purification on the carrier gas, removing the aerosols which were formed.

The polyethylene tubes used for the transfer of gas were carefully washed and dried in a stream of purified gas. The preparation of the graphitized carbon black support was carried out under sterile conditions. However, the sieving of the finished adsorbent was carried out on copper sieves (this may explain an increased copper content in the purified product). After filling the column and sealing the glass equipment, the apparatus was conditioned for several days at 250° by flushing it with purified carrier gas.

The apparatus is shown in Fig. 1. The glass chromatographic equipment was sealed to the upper removable lid (12) of the air thermostat (13).

The three main parts of the equipment are the system for the introduction of solid samples, the column and detector, and the equipment for the collection of the product.

The introduction of solid samples is carried out with the aid of the special

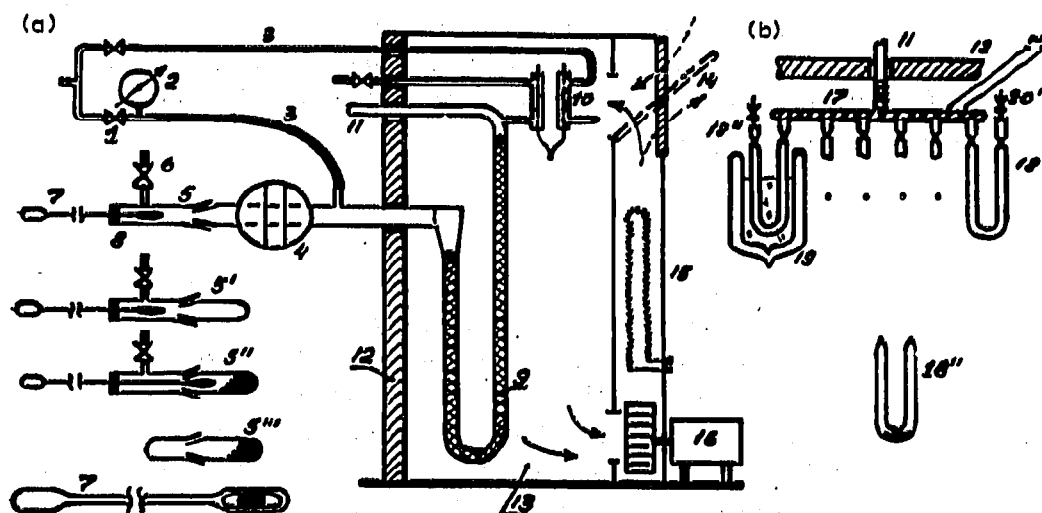


Fig. 1. Apparatus for preparative chromatography. (a) Introduction of the sample and separation scheme. 1 = Valve for the introduction of gas; 2 = manometers; 3 = inlet for the carrier gas; 4 = valve; 5 = equipment for the introduction of the solid sample; 6 = valve for flushing the equipment; 7 = spoon containing solid sample; 8 = silicone stopper; 9 = preparative chromatographic column; 10 = detector (katharometer); 11 = gas column outlet; 12 = thermostat lid; 13 = thermostat; 14 = partition; 15 = thermostat heater; 16 = turbine motor ventilator. (b) Scheme for fraction collection. 17 = Heated fraction collector; 18, 18' = traps with clamps on the outlets; 19 = trap containing sample; 20 = trap containing sample after sealing.

equipment shown in Fig. 1a. The equipment (5-8) consists of a tube with a ground-glass joint, a valve on the polyethylene tube (6) and a glass spoon (7), inserted through a silicone rubber gasket separated from the system and placed in a dry-box. A test-tube containing the sample is fitted on the glass joint (5); a known amount of solid sample is collected on the spoon from this tube.

The test-tube containing the sample is then removed, and an empty test-tube is fitted in its place (5') in which the sample is transferred from the dry-box to the apparatus. The amount of sample is determined by the decrease in weight of the test-tube containing the sample (5''). After flushing the space containing the sample, the spoon is inserted through an opening in the valve to the lid of the thermostat. The introduction of sample is carried out by inserting the spoon fully into the thermostat and rotating it, whereby the sample falls into the column directly on to the adsorbent layer. Glass cells with tungsten filaments are used as the detector. In this connection, the working cell is sealed to the preparative column through a capillary resistance and an additional stream of carrier gas is passed through the comparative cell. The collection of product in the trap is carried out periodically in the following way (Fig. 1b).

Leaving the column (11) through the lid of the thermostat (12), the stream of carrier gas and sample enters the receiver (15) where it is divided into six traps. The receiver is wound with wire and heated. On the outlets U-shaped traps are fitted with sealed polyethylene tubes provided with clamps.

When the clamp of trap 16' is open, the carrier gas leaves the chromatograph. At the moment when the peak of the main component appears, trap 16'' is opened and 16' is closed. After the peak has passed, the component being condensed out in trap 16'' with liquid nitrogen, trap 16' is again opened. In trap 16'' there is passed

a small back-flow of gas opposing the main flow, to prevent any further entry of carrier gas from the column into the receiver containing the product. The trap is sealed off in a stream of helium, first at the receiver, and then at the clamp, after which the trap is sealed off from the system.

RESULTS AND DISCUSSION

The chromatogram of the separated products is shown in Fig. 2. The absence of a large number of peaks is explained by the insufficient sensitivity of the katharometer to micro-impurities. It was considered that the choice of graphitized carbon black made it unlikely that germanium diiodide would be formed in the reducing medium on the carbon adsorbent, since it was itself a strong reducing agent. The small magnitude of the thermal decomposition constant of germanium tetraiodide (of the order of 8×10^{-9} at a temperature of 240°) and the departure of iodine from the column in the form of a peak rather than stepwise, may be taken as evidence that the decomposition does not take place on the column during the separation but as a result of the thermal decomposition of the sample during vaporization at the initial part of the column. This may explain the increased amount of iodine leaving the column (Fig. 2) compared with the initial sample.

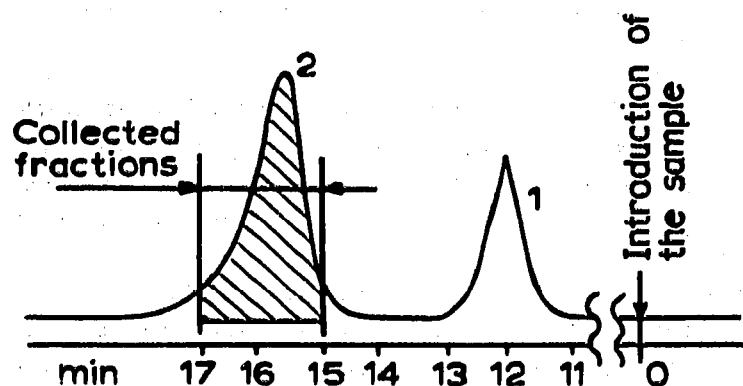


Fig. 2. Chromatogram of product separation on graphitized carbon black of granule size 0.5–1 mm ($1 = \text{I}_2$; $2 = \text{GeI}_4$). Glass column, length 0.85 m, I.D. 14 mm; temperature, 240° . Carrier gas (helium) flow rate, 4.30 l/min; bridge current, 380 mA; attenuation, 1:6; sample size, 1 g.

We were able to obtain about 1 g of pure product in one cycle of 20 min by using the above equipment on a column of I.D. 14 mm, the yield being about 80%. In spite of the relatively low efficiency of the preparative separation (about 70% based on continuous operation for 24 h), the proposed method may be used successfully for the preparation of oriented films, as only a relatively small amount of pure compound is required to make a sufficiently thick film for electrical measurements.

After carrying out the preparative separation, the contents of metallic impurities were determined by chemical and spectrochemical analyses. From the results (Table I) it can be seen that the contents of several impurities decreased by about a factor of two during purification.

The impurities present in concentrations of about $10^{-6}\%$ remained at this level. It should be noted that in chemical-spectroscopic analyses the determination of impurities in concentrations of less than $10^{-6}\%$ is difficult.

TABLE I

CHEMICAL AND SPECTROSCOPIC DETERMINATIONS OF IMPURITY CONTENTS

Element	Impurity content, % (w/w)	
	Initial sample	Purified sample
I	1.40	<0.01
Cu	$2 \cdot 10^{-6}$	$3 \cdot 10^{-6}$
Ag	$4 \cdot 10^{-6}$	$4 \cdot 10^{-6}$
Mg	$5 \cdot 10^{-4}$	$<3 \cdot 10^{-6}$
Al	$5 \cdot 10^{-4}$	$<4 \cdot 10^{-6}$
Sn	$5 \cdot 10^{-5}$	$<4 \cdot 10^{-6}$
Pb	$2 \cdot 10^{-5}$	$<4 \cdot 10^{-6}$
Bi	$4 \cdot 10^{-6}$	$4 \cdot 10^{-6}$
Cr	$6 \cdot 10^{-5}$	$<4 \cdot 10^{-6}$
Mn	$5 \cdot 10^{-6}$	$5 \cdot 10^{-6}$
Fe	$3 \cdot 10^{-6}$	$4 \cdot 10^{-6}$
Ni	$8 \cdot 10^{-6}$	$5 \cdot 10^{-6}$
B, P, As, Sb	$>10^{-6}$	$<10^{-6}$

The specific resistance of the oriented films prepared from the purified material was about one order of magnitude greater than that of films made from unpurified product.

It is probable that the present example is not the best one for showing the possibilities of the preparative separation of high-boiling halides.

In the present case, it was important to determine the possibility of using gas chromatography generally for obtaining such a separation of impurities and the preparation of products with a sufficient degree of purity.

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