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The determination of the boiling point of some isoalkyl astatides by use of a glass column gas chromatograph

The synthesis and identification of the organic compounds of radioactive elements in trace quantities is a difficult task in chemical practice. For this reason, the determination of physical constants is of some interest. Recently, some papers have appeared concerning the synthesis of phenyl and tolyl derivatives of astatine¹, perastatate² and some *n*-alkyl astatides³. The compounds thus obtained have been identified by electrophoresis, thin-layer and paper chromatography, coprecipitation and gas chromatography. SAMSON AND ATEN³, using gas chromatography, succeeded in determining the boiling points of ethyl, *n*-propyl, *n*-butyl, *n*-pentyl and *n*-hexyl astatides. The boiling point of astatobenzene has been determined in a similar way^{4,5}.

In recent years, gas chromatography has been used extensively for the analysis of organic and inorganic mixtures⁶ and for studying the chemical products that resulted from nuclear transformations and radiolysis^{7,8}. However, a number of organic compounds, especially halogen derivatives, show a significant tendency to decompose when stainless-steel columns are used. This fact should be considered when one is dealing with trace quantities of labelled compounds, because this decomposition may make the results rather uncertain. In this case it seems preferable to use columns made of inert materials.

The purpose of the present work was the separation of the constituents of a mixture of alkyl astatides and their identification by estimation of their boiling points. For this investigation we constructed a specially designed gas chromatograph which was used to determine the boiling point of some isoalkyl astatides. Calculations were performed using the linear relationship between the logarithm of the retention times of the alkyl astatides and their boiling points.

Experimental

The gas chromatographic column and the detection cell are shown in Fig. 1. The column (I) is a spiral-shaped molybdenum glass tube, 2 m long \times 4 mm I.D. The diameter of the spiral (90 mm) was chosen according to the recommended ratio $d_{sp}/d_{col} > 20$ (ref. 8). In this case, the separation efficiency is independent of the column convexity.

The stationary phase was 10% dinonyl phthalate supported on Chromosorb G (J. Manville, 30-60 mesh). The column was placed in a glass cylinder (II), connected to a thermostat containing silicone oil. Helium was used as carrier gas and was introduced into the inlet of the column after passing it through a glass tube (III) placed in the middle of the cylinder, where it was heated to the required temperature. The sample was injected (IV) directly into the column in the stationary phase, since it is well known that such a method of injection ensures good resolution of the peaks. After being separated in the column, the fractions of the injected sample flow through capillary tubing (V) of ca. 0.8 mm I.D. to a counting glass cell (VI) of volume 7 cm³ placed on a scintillation counter VA-S-963 (Vacutronik, G.D.R.). The flow rate of the carrier gas was adjusted to 30 cm³/min. It has been established that under those

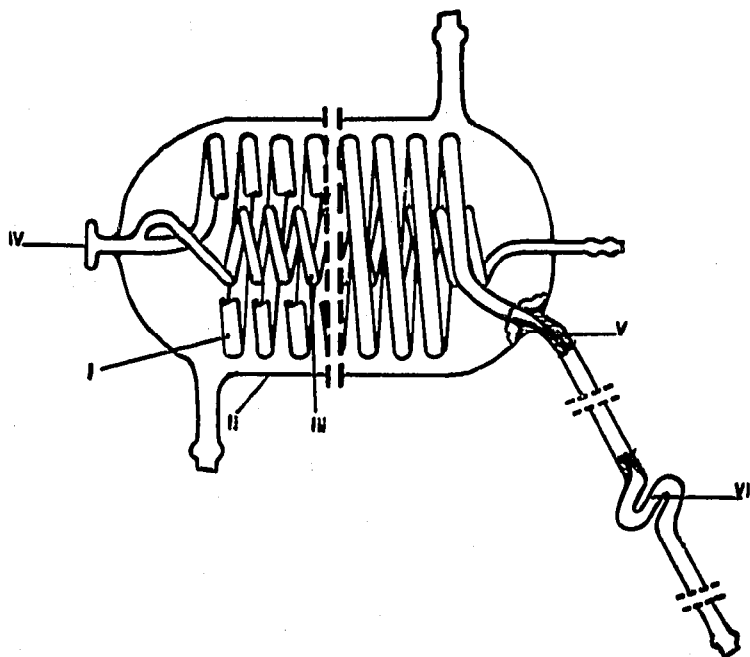


Fig. 1. Glass column gas radiochromatograph. I = working column; II = thermostating jacket; III = carrier gas tube; IV = vacuum resin gasket; V = capillary; VI = detector cell.

conditions good recording of the radioactivity and separation of neighbouring fractions is achieved⁸. To prevent condensation of the separated fractions on the outlet, the temperature of the capillary and the cell was kept 30–50° higher than that of the column by coiling a nichrome wire (0.1 mm diameter) around them, insulated with asbestos tape. The scintillation counter was fed to a linear pulse recorder VA-D-53.1 (Vacutronik, G.D.R.).

The alkyl iodides, labelled with ¹³¹I, were synthesized according to a known procedure⁹. Their chemical purity was checked with an LChM-7.A gas chromatograph. These alkyl iodides were used for the calibration of the gas radiochromatograph and the recording cell.

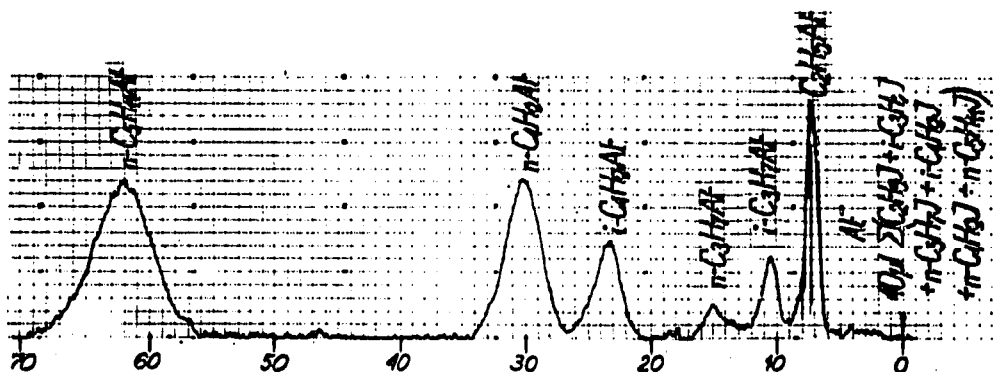


Fig. 2. Separation chromatogram of alkyl astatides produced as a result of exchanging astatine, adsorbed at the column inlet in the form of astatines, with iodine in alkyl iodides. Column: 2 m long \times 4 mm I.D.; stationary phase: Chromosorb G with 10% dinonyl phthalate; column temperature: 95°; He carrier gas, flow rate: 30 cm³/min.

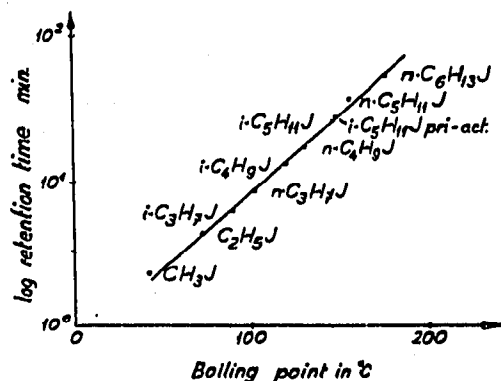


Fig. 3. Dependence of the logarithm of retention time of alkyl iodides on the column upon the boiling points of the compounds.

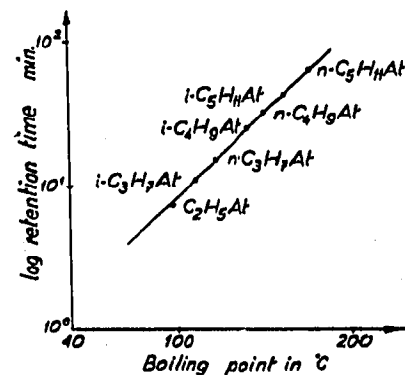


Fig. 4. Dependence of the logarithm of retention time of alkyl astatides on the column upon the boiling points of the compounds.

The monoastatide derivatives (*n*- and *iso*-) were synthesized by making use of Rn decay in the corresponding hydrocarbons and by isotope exchange of astatine with alkyl iodides, according to SAMSON AND ATEN's method³.

Results

Fig. 2 shows the effective separation of labelled halogen compounds achieved with the gas chromatograph described. In Fig. 3 the logarithm of the retention time (t_R) of some monoalkyl iodides is plotted as a function of their boiling points. It can be seen from Fig. 3 that at the selected conditions of the experiment this relationship is strictly linear. A similar relation was also obtained with the following alkyl astatides: C_2H_5At , $n-C_3H_7At$, $n-C_4H_9At$ and $n-C_5H_{11}At$ (Fig. 4). The values of the boiling points of the *n*-alkyl astatides have been taken from ref. 3. Table I presents the data for the retention times of the alkyl derivatives of astatine. Each value of t_R is a result of five independent measurements and the error is estimated as a mean square deviation of these values.

TABLE I

RETENTION TIMES OF ALKYL ASTATIDES

Alkyl astatides	Retention time ^a , t_R (min)	Boiling point (° C)
C_2H_5At	7.1 ± 0.1	98 ± 2^b
<i>iso</i> - C_3H_7At	10.7 ± 0.1	112 ± 2
<i>n</i> - C_3H_7At	15.5 ± 0.1	123 ± 2^b
<i>iso</i> - C_4H_9At	24.1 ± 0.5	142 ± 3
<i>n</i> - C_4H_9At	31.3 ± 0.4	152 ± 3^b
<i>iso</i> - $C_5H_{11}At$	41.1 ± 1.0	163 ± 3
<i>pri-act.</i> - $C_5H_{11}At^c$	43.2 ± 1.0	165 ± 3
<i>n</i> - $C_5H_{11}At$	60.5 ± 2.5	176 ± 3^b

^a GC column: length 2 m \times 4 mm I.D.; stationary phase: 10% dinonyl phthalate supported on Chromosorb G (30 mesh); He carrier gas, flow rate 30 ml/min; temperature 95°.

^b See ref. 3.

^c *pri-act.*- $C_5H_{11}At(I)$ = 1-iodo-2-methylbutane.

As the relation between $\log t_R$ and the boiling points of the monoalkyl halogenides is linear, the boiling points of the isoalkyl astatides could be estimated by interpolation of the straight-line graph. These temperatures were estimated to be: *iso*-C₃H₇At, $112 \pm 2^\circ$; *iso*-C₄H₉At, $142 \pm 3^\circ$; *iso*-C₅H₁₁At, $163 \pm 3^\circ$; and *pri*-act. C₅H₁₁At, $165 \pm 3^\circ$.

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