*iso*Thiocyanates XXIX* Separation of Volatile *iso*Thiocyanates by Gas Chromatography

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The frequent occurrence in crucifers and certain other higher plants of mixtures of mustard oil glucosides (*cf. e. g.* Ref.[1]), enzymically hydrolyzed to corresponding mixtures of *iso*thiocyanates, renders the analytical separation of the latter a matter of considerable interest. Although liquid partition chromatography, on paper as well as columns, has served this purpose extensively, alternative methods of separation have occasionally been felt desirable. The present communication records preliminary results of an investigation, undertaken in order to study the applicability of gas chromatography for the separation of volatile *iso*thiocyanates.

All separations were performed in a 2 m column at various, but closely controlled and constant temperatures. Dixon helices served as support for the stationary phase, consisting of silicon grease, and nitrogen was used throughout as a carrier gas at a rate of 10 mg per min. The output pressure was 20 mm, and the total pressure drop through the entire column about 4 mm.

A typical separation of a five-component system, with a total weight of 6.7 mg, is reproduced in Fig. 1, A. The mixture had the composition:

Methyl *iso*thiocyanate	14	%
Ethyl *iso*thiocyanate	18	»
*iso*Propyl *iso*thiocyanate	17	»
n-Butyl *iso*thiocyanate	18.5	»
*iso*Pentyl *iso*thiocyanate	32.5	»

and a temperature of 68.5° was selected. Under these conditions the components emerged from the column in the above order, yet with the ethyl and *iso*propyl bands unresolved. However, some separation of these was achieved at 50°, and in an experiment conducted at 30.5° the two *iso*thiocyanates were recognizable as distinct bands (Fig. 1, B). Separate runs on the individual compounds indicated that the small peaks appearing briefly after the start, and the slight inflexion just ahead of the butyl derivative (Fig. 1, A), could be attributed to unknown impurities in the specimens of *iso*pentyl and *iso*propyl *iso*thiocyanates employed, respectively. Preliminary runs at fixed temperatures in the range 40° – 50° have further provided satisfactory separations of 3-butenyl and allyl *iso*thiocyanate, as well as of the latter and *iso*propyl *iso*thiocyanate.

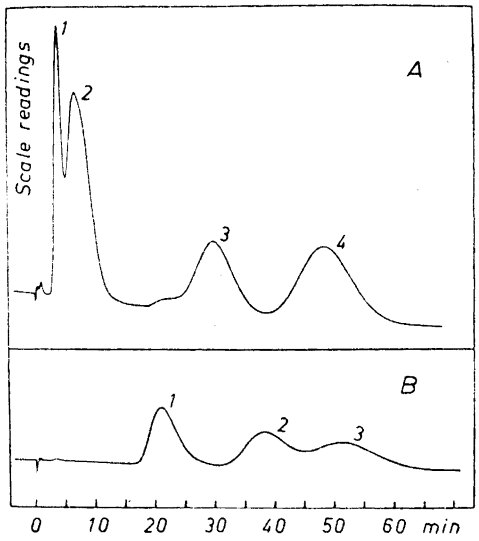

Fig. 1. A: Separation by gas chromatography of: 1. methyl, 2. ethyl and *iso*propyl, 3. *n*-butyl, and 4. *iso*pentyl *iso*thiocyanates. Total weight: 6.7 mg. Column temperature: 68.5°. *B:* Separation of: 1. methyl, 2. ethyl, and 3. *iso*propyl *iso*thiocyanate. Total weight: 4.4 mg. Column temperature: 30.5°.

Gas chromatography thus appears to be a method of great promise for the separation, analysis and identification of volatile *iso*thiocyanates, including those of natural provenance. Further work along this line is in progress and a more detailed account will appear at a later date.

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