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Gas chromatographic analysis of waste gases from a formaldehyde plant

Knowledge of the composition of the waste gases released from a formaldehyde plant, the process being based on methanol oxidation, is important from the viewpoint of plant control and corrosion prevention. These waste gases may contain components of air, CO, CO₂, H₂O, CH₃OH, HCHO and HCOOH. Gas chromatography seems to be the most suitable method for the analysis of this mixture, nevertheless this has not yet been reported, as far as we know.

Adsorbents or stationary phases proposed for mixtures containing some of these components can cause problems in the analysis of the others. For example a mixture of O₂, N₂, CO, CO₂ (containing H₂, C₂H₆ and C₂H₄ as well) could be analysed¹ by means of a two column system with molecular sieve and silica gel columns, with SF₆ as carrier gas but the analysis of the rest of the components of the mixture in question seems to be hopeless with such a system. On the other hand the majority of the numerous stationary phases proposed for the analysis of mixtures of H₂O, CH₃OH, HCHO and HCOOH are not suitable for the analysis of the permanent gas components.

In recent years the use of cross-linked porous polymers has been reported²⁻⁷ as being particularly suitable for the analysis of mixtures of highly polar compounds. It has also been found that some of these adsorbents could be adapted to rather similar problems^{2,8-14}. On the basis of these observations the application of Porapak Q and Chromosorb 102 columns has been investigated with respect to the present problem.

The separation of air, CO, CO₂, CH₃OH and HCHO could be achieved on a 2 m × 0.4 cm Porapak Q 60-80 mesh column in a Fractovap GT (Carlo Erba) chromatograph with thermal conductance detection. HCOOH was absorbed in the column. Using a Chromosorb 102 60-80 mesh column of the same size (it is preferable to use glass tube to reduce tailing*) mixtures of air, CO, CO₂, H₂O, CH₃OH, HCHO and HCOOH could be successfully analysed at 83°. If one needs to know the proportion of O₂ and N₂, a two column system can be used consisting of a Chromosorb 102 column (as described above) and a second column containing molecular sieves (5 Å, 60-80 mesh, 2 m × 0.4 cm size) maintained at 50°, using H₂ as carrier gas for both columns. In this case it is useful to determine O₂, N₂ and the CO as well, by means of the molecular sieve column to have a double check for the quantitative evaluation of the chromatogram obtained with the Chromosorb 102 column. The analysis takes 24 min if the separation of the air components is wanted and about 12 min if it is sufficient to know only the sum of the O₂ and N₂.

The relative retention times obtained by the method described above are listed in Table I. These values could be reproduced under conditions of serial analyses within an average relative standard deviation of ± 3.4%.

The relative simplicity of the operations and rapidity of the determination is advantageous in a serial industrial analyser, therefore attempts to solve the problem

* It should be noted that retention times measured with an Al tube of the same size were practically the same as with a glass tube in the case of air, CO₂, CO and HCOOH but considerably longer for H₂O, HCHO and CH₃OH.

TABLE I

RETENTION DATA FOR THE COLUMNS USED

Substance	Molecular sieves 5 Å ^a	Porapak Q	Chromosorb 102 ^b
O ₂	0.53	—	—
N ₂	1.00	—	—
air(O ₂ + N ₂)	—	1.00	1.00
CO	3.21	1.47	2.12
CO ₂	—	2.00	1.69
H ₂ O	—	5.65	5.35
HCHO	—	11.41	7.59
CH ₃ OH	—	11.67	13.0
HCOOH	—	—	53.6

^a Since plant samples do not always contain O₂, the relative retention data would be better if referred to N₂.

^b Data obtained using the glass column.

by means of preparing derivatives of some "problematic" components of the mixture (e.g. by silylation, esterification, etc.) were abandoned.

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- 1 C. L. GUILLEMIN AND F. AURICOURT, *J. Gas Chromatogr.*, 2 (1964) 156.
- 2 O. L. HOLLIS, *Anal. Chem.*, 38 (1966) 309 and 1860.
- 3 J. TRANCHANT, *Z. Anal. Chem.*, 236 (1968) 168.
- 4 W. P. WHITE AND O. L. HOLLIS, *J. Gas Chromatogr.*, 6 (1968) 84.
- 5 O. L. HOLLIS AND W. V. HAYES, in A. B. LITTLEWOOD (Editor), *Gas Chromatography 1966*, Institute of Petroleum, London, 1967, p. 57.
- 6 J. F. JOHNSON AND E. M. BARRAL, *J. Chromatogr.*, 31 (1967) 547.
- 7 L. I. MOSEVA AND K. I. SAKODINSKII, *Gazov. Khrom.*, No. 9 (1969) 86.
- 8 J. D. BURGER, *J. Gas Chromatogr.*, 6 (1968) 177.
- 9 L. ÉEK AND T. GALCERÁN, *Chromatographia*, 2 (1969) 541.
- 10 E. L. OBERMILLER AND G. O. CHARLIER, *J. Gas Chromatogr.*, 7 (1969) 580.
- 11 F. ONUŠKA, J. JANÁK, Š. ĐURAŠ AND M. KRČMÁROVÁ, *J. Chromatogr.*, 40 (1969) 209.
- 12 H. L. GRUBER AND H. PLAINER, *Chromatographia*, 3 (1970) 490.
- 13 R. N. BAKER, A. L. ALENTY AND J. F. ZACK, *J. Chromatogr. Sci.*, 7 (1969) 312.
- 14 V. PALO AND H. ILKOVÁ, *J. Chromatogr.*, 53 (1970) 363.
- 15 G. C. CARLE, *J. Chromatogr. Sci.*, 8 (1970) 550.

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