

Gas-liquid chromatographic analysis of trace amounts of acetonitrile in acrylonitrile

In the catalytic process of propene ammoxidation¹, acrylonitrile is contaminated by acetonitrile which must be eliminated by an extractive distillation with water. In order to obtain "pure grade" monomer (containing less than 500 p.p.m. of acetonitrile), it is necessary to optimise distillation parameters by checking the acetonitrile content by a rapid and sensitive method.

It seemed to us that gas-liquid chromatography could elegantly resolve this problem.

Choice of the stationary phase

The efficiency of separation of acrylonitrile and acetonitrile on polyethylene glycol is insufficient for quantitative analysis of trace amounts of acetonitrile^{2,3} because of the broadening of the acrylonitrile peak due to the high concentration of this compound (see Fig. 1).

Another phase, β, β' -thiodipropionitrile, suggested by Russian authors⁴ shows the same pattern. On paraffin wax suggested by TARAMASSO *et al.*⁵, acetonitrile is eluted before acrylonitrile but water interferes seriously.

It thus became necessary to increase column efficiency by using a new stationary phase. It is well known that the organoclay, Bentone 34, has selectivity properties such that isomer separation becomes possible on short columns, the best example being the separation of *o*-, *m*-, and *p*-xylenes⁶⁻¹⁰.

With this in view, the influence of increasing amounts of Bentone 34 on acrylonitrile-acetonitrile-water separation was studied with PEG 200 as the primary phase.

Experimental

Chromatograph: Perkin Elmer II6 with a thermistor detector.

Column: length 1.5 m, inner diam. 4 mm copper tube.

Solid support: Chromosorb P 60-80 mesh.

Temperature: $70^\circ \pm 0.2^\circ$.

Carrier gas: hydrogen; flow rate: 40 ml/min.

Recorder: Philips PR 1040; 2 mV full scale.

Injected volume: 10 μ l.

Five mixed stationary phases were tested:

B 20: 20 % of Bentone 34

BK 15-5: 15 % of Bentone 34 + 5 % of PEG 200

BK 10-10: 10 % of Bentone 34 + 10 % of PEG 200

BK 5-15: 5 % of Bentone 34 + 15 % of PEG 200

K 20: 20 % of PEG 200

Results

Retention volumes, corrected for dead volume, were measured and compared with acrylonitrile as reference (see Table I).

The behaviour of *n*-alkanes was also tested on the various columns: the plot of

TABLE I

RELATIVE RETENTION VOLUMES OF NITRILES ON BENTONE 34-PEG STATIONARY PHASES

	<i>B</i> ₂₀	<i>BK</i> 15/5	<i>BK</i> 10/10	<i>BK</i> 5/15	<i>K</i> 20
Acrylonitrile	1.00	1.00	1.00	1.00	1.00
Acetonitrile	3.09	2.42	1.93	1.37	1.28
Propionitrile	2.30	1.76	1.50	1.61	1.59
Butyronitrile	2.06	2.60	2.40	2.50	2.49
Water	0.33	2.60	2.69	3.84	4.36

logarithm of retention volume *versus* carbon number was found to be linear, with the same slope for each column.

Moreover, Bentone 34 retains acetonitrile more efficiently than other saturated nitriles. On Bentone 34 alone, nitrile peaks are very diffuse while the water peak is a symmetrical one.

The composition of the mixed stationary phase which gives the best separation of acrylonitrile-acetonitrile-water can be calculated from column efficiency formulae¹¹. By using the *BK* 10/10 column, separation of acrylonitrile-acetonitrile is complete, with a separation factor of 1.17; moreover, water is completely eluted after 30 min (see Fig. 2).

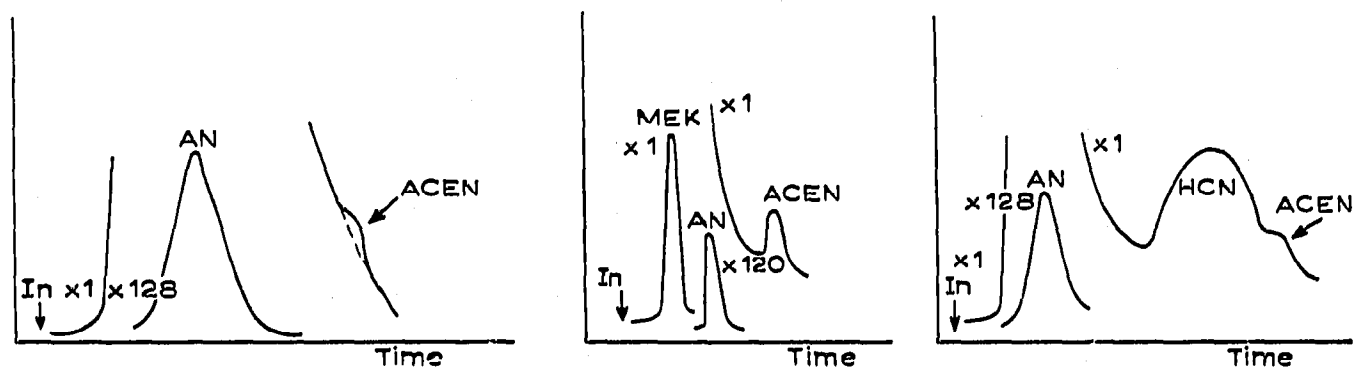


Fig. 1. Separation of acetonitrile (ACEN) and acrylonitrile (AN) on PEG 200.

Fig. 2. Separation of acetonitrile (ACEN) and acrylonitrile (AN) on PEG 200-Bentone 34. MEK = methyl ethyl ketone.

Fig. 3. Interference of hydrocyanic acid in the separation of acrylonitrile (AN) and acetonitrile (ACEN).

From HEPT values, optimum flow rate and temperature were checked and, under the experimental conditions described above, relative retention volumes (compared with acrylonitrile) of some compounds were measured as well as Kovats indices of nitriles (see Table II).

TABLE II

RETENTION VOLUMES AND KOVATS INDICES ON BK 10/10 COLUMN

	<i>Relative retention volumes</i>	<i>Kovats indices</i>
Acrolein	0.206	
Acrylonitrile	1.000	845
Acetonitrile	2.09	930
Water	2.36	
Propionitrile	1.45	890
Acetone	0.226	
<i>n</i> -Propanol	1.435	
Methyl ethyl ketone	0.504	

Quantitative analysis

The external standard addition method was chosen, with methyl ethyl ketone as the reference compound (Fig. 2). Standardisation was carried out with artificial mixtures containing from 0.01 to 0.4% (by weight) of acetonitrile. Statistical analysis gives a reproducibility of 5% (relative value) for values higher than 0.1% and of 10% for lower values.

Interference of hydrocyanic acid

High contents of hydrocyanic acid disturb the chromatogram as this compound is slowly eluted (see Fig. 3). To avoid this phenomenon, reaction chromatography was used involving irreversible absorption of hydrocyanic acid on a preliminary column. The best results were obtained with a 0.5 metre pre-column of tetra-(hydroxyethyl)-ethylenediamine (THEED, 30% on Chromosorb P): there was complete absorption of the hydrocyanic acid with no observed influence on the acrylonitrile-acetonitrile separation. Thirty injections of acrylonitrile with a high content of hydrocyanic acid (about 10%) were made without any disturbance being noticed in the chromatograms.

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Laboratoire Central des Recherches, S.A. Union Chimique-Chemische
Bedrijven N.V., Drogenbos (Belgium)

J. DANDOY

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