## Notes

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# Gas chromatography of acetonitrile and its chlorinated derivatives

In the course of investigations carried out in another section of this laboratory, a method was required for the analysis of mixtures containing acetonitrile and its chlorinated derivatives, *i.e.* monochloro-, dichloro- and trichloroacetonitrile.

Although some work has been reported on the gas chromatography of acetonitrile[1] and some other unsubstituted aliphatic nitriles[2], there does not appear to be any reference to the analysis by gas chromatography of mixtures of acetonitrile and its chlorinated derivatives. In this paper the retention times of these compounds relative to chloroform are reported for four different liquid phases. Area correction factors for conversion of peak areas into weight per cent results are also given.

An attempt has been made to explain the order of elution of these compounds on the various liquid phases.

*Experimental*

*Apparatus.* The gas chromatograph used was a Perkin Elmer Vapor Fractometer model 154-D equipped with a thermistor thermal detector. The columns used were 5/32 in. I.D. and 6 ft. in length.

Helium was used as the carrier gas and its flow rate was adjusted so that the chloroform peak was eluted approximately 7 min after the air peak. This corresponded to flow rates of about 50 ml/min.

The columns contained 20 % by weight of liquid phase. The solid support was "Gas Chrom Z" for the Apiezon L and "Embaphase" Silicone Oil; and "Gas Chrom P" for the QF-1 and XF-1150 liquid phases. Particle size range was 80–100 mesh. Elution times were determined at 40° except for Apiezon L. In this case an oven temperature of 70° was used to avoid the peak broadening found at lower temperatures with this phase.

*Reagents.* Acetonitrile: Spectro grade Eastman Organic Chemicals D.P.I., Rochester, N.Y.

Monochloroacetonitrile: Benzol Products Company, Newark, N.J.

Dichloroacetonitrile: K. & K. Laboratories, Inc., Plainview, N.Y.

Trichloroacetonitrile was prepared in these laboratories by the dehydration of trichloroacetamide[4].

All reagents used gave one peak when examined by gas chromatography.

*Area correction factors.* Area correction factors for conversion of peak areas to weight percentages were determined at 40° using either the Embaphase silicone or QF-1 columns. These factors were determined relative to trichloroacetonitrile as this was the major component in the samples submitted for analysis

Peak areas were determined by triangulation, the area being calculated as the product of the peak height and the peak base[3].

TABLE I

AREA CORRECTION FACTORS AND RELATIVE RETENTION TIMES OF CHLOROACETONITRILES

| *Compound* | *B.p.* (°C) | *A.C.F.* (40°) | *Relative retention time* ($CHCl_3$ = *1.00*) | | | |
|---|---|---|---|---|---|---|
| | | | *Apiezon L* (70°) | *Embaphase silicone* (40°) | *QF-1* (40°) | *XF-1150* (40°) |
| $CH_3CN$ | 82 | 0.56 | 0.20 | 0.27 | 2.88 | 1.63 |
| $ClCH_2CN$ | 124* | 0.74 | 1.12 | 1.50 | 7.72 | 15.0 |
| $Cl_2CHCN$ | 112* | 0.90 | 2.10 | 2.14 | 5.77 | 11.2 |
| $Cl_3CCN$ | 83* | 1.00 | 1.46 | 1.74 | 2.62 | 0.86 |
| $CHCl_3$ | 61 | 0.85 | 1.00 | 1.00 | 1.00 | 1.00 |
| $n$-$C_6H_{14}$ | 68 | 0.89 | 0.82 | 1.00 | 1.04 | 0.085 |

* See ref. 4.

## *Results*

Boiling points, area correction factors, and retention times relative to chloroform are shown in Table I. Chloroform was present as a minor impurity in most mixtures of chlorinated acetonitriles and hence made a useful reference point. The retention data are also given in terms of the Kovats Retention Index in Table II.

The most useful stationary phase for the analysis of the acetonitrile mixtures appears to be the non-polar Embaphase Silicone Oil. Retention times on the cyanoethyl silicone XF-1150, were very long and the acetonitrile peaks were well separated but chloroform and trichloroacetonitrile overlap. A short column of this phase would be ideal for the analysis of acetonitrile mixtures if chloroform is known to be absent.

TABLE II

KOVATS RETENTION INDICES OF CHLOROACETONITRILES

| *Compound* | *Retention index* | | | |
|---|---|---|---|---|
| | *Apiezon L* (70°) | *Embaphase silicone* (40°) | *QF-1* (40°) | *XF-1150* (40°) |
| $CH_3CN$ | 457 | 460 | 828 | 959 |
| $ClCH_2CN$ | 675 | 643 | 948 | 1434 |
| $Cl_2CHCN$ | 717 | 681 | 911 | 1200 |
| $Cl_3CCN$ | 630 | 659 | 817 | 877 |
| $CHCl_3$ | 621 | 600 | 696 | 896 |

## *Discussion*

The boiling points of the chloroacetonitriles decrease as their molecular weights increase. Trichloroacetonitrile with the highest molecular weight in the series has a boiling point close to that of acetonitrile. Monochloroacetonitrile with the lowest molecular weight has the highest boiling point.

The presence of the electron attracting nitrile group and chlorine atoms in the molecule tends to deplete the $\alpha$-carbon position of electrons causing hydrogen atoms attached to that site to become protonic. These hydrogen atoms can then bond with electron rich positions in other molecules. It is suggested that this hydrogen bonding is a controlling factor in determining the boiling points of these compounds. Trichloroacetonitrile with no hydrogen atoms in the molecule is presumably the least associated of these compounds in the liquid state and therefore has a low boiling point. Monochloroacetonitrile with two hydrogen atoms has the highest boiling point.

The number of hydrogen atoms in the acetonitrile molecules is also of importance in determining their elution volumes (and hence elution times) during gas chromatography. The factors influencing the magnitude of solute retention on a stationary phase have been discussed by BROWN[5].

The relation of the retention volume $V$ to the activity coefficient $\gamma_1$, of the solute in solution in the stationary phase and the vapour pressure $p^\circ_1$, of the pure solute is:

$$V \propto \frac{1}{\gamma_1 p^\circ_1}$$

$\gamma_1$ is controlled by the balance of intermolecular forces between solute 1 and stationary phase 2. The number of hydrogen atoms in the acetonitrile molecule is important in controlling $p^\circ_1$ as shown above and also the (1,2) interaction between solute and polar stationary phases such as QF-1 and XF-1150. On these phases the acetonitriles (including acetonitrile itself) tend to elute in boiling point order. Retention times are large due to a large (1,2) interaction (hydrogen bonding or dipole–dipole interaction) causing $\gamma_1$ to be small and hence $V$ large. The retention times of trichloroacetonitrile on these phases appears to be smaller than expected. In this case the strong association of the stationary phase with itself [(2,2) interaction] would tend to "squeeze" out the solute resulting in a high value of $\gamma_1$ and hence a low retention volume.

In the non-polar stationary liquids the retentions are still mainly controlled by $p^\circ_1$. However retention volumes are small as the associated solutes give large values of $\gamma_1$ [(1,1) interaction predominates]. The highly associated monochloroacetonitrile has a lower retention time than expected from its boiling point as the effect of the high value of $\gamma_1$ apparently overshadows the effect of the low value of $p^\circ_1$.

Further evidence of these interactions has been obtained by BROWN[6] using phases of higher polarity than those investigated in this report.

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