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Abstract

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CHEMISTRY

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A GAS-CHROMATOGRAPHIC STANDARDLESS METHOD FOR THE IDENTIFICATION OF *n*-ALIPHATIC AMINES

(Presented by Academician A. N. Nesmeyanov on January 6, 1965)

In gas-chromatographic analyses, standard substances are usually used for identification; in the case of complex mixtures these sometimes have to be specially synthesized. In this connection, the development of analytical methods that do not require the use of standards becomes important.

We have proposed a gas-chromatographic standardless method for identifying primary, secondary, and tertiary *n*-aliphatic amines. The method is based on the ability of amines to form hydrogen bonds with polar liquid phases. The difference in the strength of this interaction made it possible to develop a method for identifying amines. To characterize the substances leaving the column, Kovats indices ([1,2]) were chosen, in which a series of *n*-hydrocarbons is taken for comparison.

It is known that gas-chromatographic analysis of *n*-aliphatic amines presents a certain difficulty because of their adsorption on the support. To reduce adsorption of amines, the wetting preparation "Novator" ([3]) was chosen as the support; Vaseline oil, tristearin, PEG-1000, and Tween-80 were used as liquid phases. Primary amines from methylamine to heptylamine, secondary amines from dimethylamine to diamylamine, and tertiary amines from trimethylamine to triamylamine inclusive were investigated.

The analysis was carried out on a "Panchromatograph" from the firm "Pye," simultaneously on two columns with flame-ionization and β-ionization detectors. The retention indices of the amines studied were determined by the Kovats formula:

$$I = 100\frac{\lg V_{Ax} - \lg V_n}{\lg V_{n+1} - \lg V_n} + 100n,$$

where $n+1 > x > n$, I is the retention index of an amine with x carbon atoms, V_{Ax} is the corrected retained volume of the amine under study, V_n is the corrected retained volume of a hydrocarbon with n carbon atoms, and V_{n+1} is the corrected retained volume of an n-hydrocarbon with $(n+1)$ carbon atoms.

For calculating the retention index of amines with short retention times, the accuracy of determining the position of the air peak is of great importance. Since the detectors used in the work are insensitive to air, the position of the air peak was determined by an analytical method according to the modified Evans and Smith procedure ([4]).

The corrected retained volumes of n-hydrocarbons were calculated using a calibration line computed by the method of least squares from data on the chromatographic analysis of n-hydrocarbons from pentane to dodecane inclusive.

The resulting equation $\lg V_n = a + bn$ makes it possible to determine the corrected retained volumes of any n-hydrocarbon needed for calculating the index. In practice, if the gas-flow rate po-

Table 1

Retention indices of *n*-aliphatic amines

Substance	TC	VM	TV	PEG	Substance	TC	VM	TV	PEG
Methylamine	465	460	560	777	Diethylamine	595	609	714	780
Ethylamine	470	565	668	764	Dipropylamine	777	780	873	934
Propylamine	583	687	759	866	Dibutylamine	977	973	1064	1126
Butylamine	682	785	863	965	Diamylamine	1174	1172	1264	1330
Amylamine	786	888	960	1071	Trimethylamine	467	445	530	558
Hexylamine	887	987	1060	1170	Triethylamine	691	684	745	778
Heptylamine	985	1087	1164	1271	Tripropylamine	927	924	952	965
Dimethylamine	467	450	604	684	Tributylamine	1184	1179	1201	1203
					Triamylamine	1438	1439	1456	1480

Columns (150 cm, 4 mm): 10% tristearin (TC), 109 Tween-80 (TV), 10% PEG-1000 and 2% NaOH + 5% vaseline oil (VM) on "Novator" ; temperature 100°, carrier-gas flow rate 10–200 ml/min depending on the boiling point of the amine; CHTT 800–1000 for tripropylamine.

constant in the analysis of the substances studied and of the n-hydrocarbons taken for comparison, then the reduced retention times are substituted into the formula. The calculated retention indices no longer depend on the carrier-gas flow rate.

Table 1 gives the retention indices we found for 17 n-aliphatic amines.

The accuracy of determining the indices is $±$6 units for the first two members of each series, and $±$2 units for the remaining amines. Complete separation of amines was observed when the indices differed by 20 units.

As is evident from the data in Table 1, for all amines the retention indices increase on passing from a nonpolar to a polar phase. The maximum increase is observed in the series of primary amines on PEG-1000, and the minimum increase in indices is found for tertiary amines. The difference between the retention indices on polar and nonpolar phases makes it possible to assess the degree of interaction of primary and secondary amines with the phase.

For each of the liquid phases studied, the index values found for primary amines can be described, within the accuracy of index determination, by the equation of a straight line:

$$I_{\mathrm{TC}} = 100n + 285; \qquad I_{\mathrm{VM}} = 100n + 385;$$

$$I_{\mathrm{TV}} = 100n + 460; \qquad I_{\mathrm{PEG}} = 100n + 570.$$

The equations obtained reflect the homologous dependence of the retention indices of primary n-aliphatic amines on the increase in the number of carbon atoms.

In the case of tertiary amines, the minimal difference in indices on passing from nonpolar to polar phases is associated with the weak interaction of the free electron pair of the amino group with the mobile hydrogen of the liquid phase. For them, a dependence of the retention indices on the number of carbon atoms in the amine is observed, which is expressed by the equation

$$I_{\mathrm{VM}} = 86n + 146.$$

Of considerable interest is the relationship we found between the retention indices and the boiling temperature for primary n-aliphatic amines. For tertiary and secondary amines such a relationship is observed only on columns with vaseline oil. The equations obtained, given in Table 2, can be used to calculate indices from the boiling temperature of amines.

Table 2

Dependence of retention indices on the boiling temperature of amines

Equations	Amine	I_{VM}	I_{TS}	I_{TV}	I_{PEG}	Boiling temp. according to literature data, °C
$I_{TS} = 4.0\,(\text{b.p.} + 94)$ $I_{VM} = 4.0\,(\text{b.p.} + 116)$ $I_{TV} = 4.0\,(\text{b.p.} + 135)$ $I_{PEG} = 4.0\,(\text{b.p.} + 164)$	Propylamine	55	54	54	52	49—50
$I_{TS} = 4.0\,(\text{b.p.} + 94)$ $I_{VM} = 4.0\,(\text{b.p.} + 116)$ $I_{TV} = 4.0\,(\text{b.p.} + 135)$ $I_{PEG} = 4.0\,(\text{b.p.} + 164)$	Butylamine	80	80	78	75	78—79
$I_{TS} = 4.0\,(\text{b.p.} + 94)$ $I_{VM} = 4.0\,(\text{b.p.} + 116)$ $I_{TV} = 4.0\,(\text{b.p.} + 135)$ $I_{PEG} = 4.0\,(\text{b.p.} + 164)$	Amylamine	106	105	105	102	104
$I_{TS} = 4.0\,(\text{b.p.} + 94)$ $I_{VM} = 4.0\,(\text{b.p.} + 116)$ $I_{TV} = 4.0\,(\text{b.p.} + 135)$ $I_{PEG} = 4.0\,(\text{b.p.} + 164)$	Hexylamine	130	130	129	128	130

Equations	Amine	I_{VM}	I_{TS}	I_{TV}	I_{PEG}	Boiling temp. according to literature data, °C
$I_{TS} = 4.0\,(\text{b.p.} + 94)$ $I_{VM} = 4.0\,(\text{b.p.} + 116)$ $I_{TV} = 4.0\,(\text{b.p.} + 135)$ $I_{PEG} = 4.0\,(\text{b.p.} + 164)$	Heptylamine	155	155	156	153	155
$I_{VM} = 4.0\,(\text{b.p.} + 79)$	Triethylamine	92				89
$I_{VM} = 4.0\,(\text{b.p.} + 79)$	Tripropylamine	152				156
$I_{VM} = 4.0\,(\text{b.p.} + 79)$	Tributylamine	215				216

$I_{VM}, I_{TS}, I_{TV}, I_{PEG}$ are the retention indices of amines on columns with vaseline oil, tristearin, Tween-80, and PEG-1000.

The easy reproducibility of the retention indices, as well as the constancy of the differences of the indices, were used for identifying mixtures of amines even in the absence of complete separation on each of the phases studied. As can be seen from the data in Table 3, the difference of the indices is characteristic for each series of amines. Thus, for example, for primary amines the difference of the retention indices on PEG-1000 and tristearin is maximal and is equal to $\simeq 285$, while on PEG-1000 and Tween-80 it is $\simeq 110$.

Thus, in analyzing a mixture of n-aliphatic amines it is sufficient to compare the chromatograms and to match the retention indices on three

Table 3

Differences of retention indices of n-aliphatic amines

Amine	ΔI_1	ΔI_2	Amine	ΔI_2
Methylamine	279	164	Diethylamine	65

Amine	ΔI_1	ΔI_2	Amine	ΔI_2
Ethylamine	294	96	Dipropylamine	60
Propylamine	283	108	Dibutylamine	62
Butylamine	283	102	Diamylamine	65
Amylamine	285	114	Trimethylamine	30
Hexylamine	283	110	Triethylamine	30
Heptylamine	286	110	Tripropylamine	13
Dimethylamine		80	Tributylamine	0
			Triamylamine	24

$$\Delta I_1 = I_{\mathrm{PEG}} - I_{\mathrm{TS}}$$

$$\Delta I_2 = I_{\mathrm{PEG}} - I_{\mathrm{TV}}$$

liquid phases: tristearin, Tween-80, and PEG-1000. From the difference of the indices, the primary, secondary, and tertiary amines are determined; these are then readily identified from the magnitude of the index.

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Note: Figure translations are in progress. See original paper for figures.