

strictly intercomparable and independent of apparatus and experimental conditions.

Fig. 1 shows some of the results of these calculations. Fig. 2, on the other hand, shows the retention times relative to *n*-pentane for the same data as were used in calculating the indices for Fig. 1.

Some experimental details used by the various authors are presented in Table 1.

Table 1

Ref.	Column temperature (°C)	Stationary phase	Length of column
2	25	3 per cent squalane	50 ft.
3	100	Squalane modified 'Pelletex'	20 ft.
4	78.5	<i>n</i> -Hexatriacontane	
5	Room temperature	3.1 per cent chloronaphthalene	26 ft.
6	100	Squalane Gelay column	100 ft.
7	22.5	Tetra iso-butene	6 m
8	100	'Convoll 20' (saturated hydrocarbon oil)	1 m

From these results it is clear that the Kovats index, at least for this class of compounds, is superior to the relative retention time commonly used in indicating eluted components.

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<sup>1</sup> Kovats, E., *Z. Anal. Chem.*, **181**, 351 (1961).

<sup>2</sup> Eggertsen, F. T., and Groennings, S., *Anal. Chem.*, **30**, 20 (1958).

<sup>3</sup> Simmons, M. C., and Snyder, L. R., *Anal. Chem.*, **30**, 32 (1958).

<sup>4</sup> Desty, D. H., and Whyman, B. H. F., *Anal. Chem.*, **29**, 320 (1957).

<sup>5</sup> Martin, R. L., and Winters, J. C., *Anal. Chem.*, **31**, 1954 (1959).

<sup>6</sup> Zlatkis, A., *Anal. Chem.*, **31**, 620 (1959).

<sup>7</sup> Schomburg, G., *Z. Anal. Chem.*, **104**, 147 (1958).

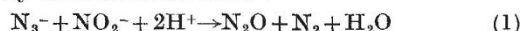
<sup>8</sup> Tenney, H. M., *Anal. Chem.*, **30**, 2 (1958).

<sup>9</sup> Wehrli, A., *Diss.*, Zurich (1961).

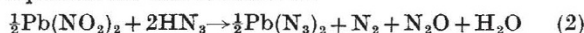
## A New Synthesis of Lead Azide

LEAD azide is still prepared by using, in principle, a method first described by Curtius<sup>1</sup>. This method involves reacting a soluble inorganic azide, preferably sodium azide, with a soluble lead salt, preferably lead nitrate or lead acetate, in aqueous solution whereby lead azide is formed as a precipitate. The precipitate is always contaminated with the cation coming from the azide and the anion coming from the lead salt. Purification by recrystallization is difficult for the following reasons: The solubility of lead azide in pure water is very small. Using an ammonium acetate solution in which the solubility is higher introduces new impurities. Furthermore, lead azide has a tendency to detonate spontaneously on recrystallization<sup>2</sup>. A direct synthesis of lead azide from lead oxide and hydrazoic acid yields inhomogeneous yellow products because the lead azide formed on the surface of the lead oxide grains is very insoluble and prevents further reaction.

We have therefore tried to use the reaction between the nitrite and azide ions in acid solution which was first described by Sommer and Pincas<sup>3</sup>:



In a system consisting of lead nitrite and an excess of hydrazoic acid the latter would have two functions: First to destroy the nitrite group to form nitrogen and nitrogen dioxide and second to react with the lead cation. The equation for this reaction is:



Gaseous hydrogen azide as obtained by reacting sodium azide with a mixture of 85 per cent phosphoric acid (750 c.c.) and phosphorus pentoxide (250 g) in a nitrogen stream was passed into 100 c.c. of ethanol at room temperature until the alcoholic hydrazoic acid solution had reached a concentration of 10 per cent. Higher concentrations were avoided to reduce the danger of an explosion.

50 g sodium nitrite were dissolved in 100 c.c. of water and placed in a flask provided with a dropping funnel containing about 150 c.c. of 25 per cent sulphuric acid, a nitrogen gas inlet, and an outlet tube. After the apparatus had been flushed with nitrogen, the sulphuric acid was added to the sodium nitrite solution and the outflowing gas consisting of nitrogen and an equimolar mixture of nitric oxide and nitrogen dioxide was passed through a tube filled with glass wool to retain droplets of the reaction mixture and then into another flask containing a suspension of lead oxide (2 g in 25 c.c. of water). After about 30 min a clear yellow solution of  $\text{Pb}(\text{NO}_2)_2$  was obtained. Nitrate could not be detected in this solution. The lead nitrite solution was then added dropwise to the alcoholic hydrazoic acid solution. With amounts given here the acid was present in a five-fold excess. The solution started to froth as soon as the lead nitrite solution was added, and a white precipitate of lead oxide was formed. This white precipitate was obtained only when spectroscopically pure lead monoxide (Jarrell Ash) was used. Reagent grade lead monoxide (Fisher) gave a slightly yellow product. The precipitate was filtered, washed with ethanol, and dried under vacuum at room temperature. Due to the sensitivity of the lead azide to light, the precipitation had to be carried out in darkness. The yield of lead azide was 2.4 g (91 per cent) based on the lead oxide used. The material obtained by this procedure was the  $\alpha$ -modification as demonstrated by X-ray analysis. The average analytical values for lead and nitrogen (5 determinations) were as follows:

	Pb (%)	70.76 ± 0.12	Theory
	N (%)	28.91 ± 0.09	71.14 28.86

The advantage of using an alcoholic hydrazoic acid solution over an aqueous solution lies in the fact that the solubility of the lead azide is less, giving a higher yield, and the danger of a surface hydrolysis (to form basic lead azides, and, by absorption of carbon dioxide, lead carbonate) is reduced.

It is planned to use this lead azide for thermal decomposition investigations and for growing single crystals.

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<sup>1</sup> Curtius, T., *Ber.*, **24**, 3345 (1891).

<sup>2</sup> Bowden, F. P., *Proc. Roy. Soc. A*, **246**, 150 (1958). Kaufman, J. V. R., *ibid.*, 153. Rogers, G. T., *ibid.*, 153.

<sup>3</sup> Sommer, F., and Pincas, H., *Ber.*, **48**, 1967 (1915).

## Acetonitrile as a Constituent of Cigarette Smoke

ACETONITRILE (methyl cyanide) has been identified in the body fluids of smokers while it is essentially absent in the body fluids of non-smokers<sup>1</sup>. This work indicated that urine acetonitrile content may provide a more accurate measure of the actual degree of exposure to tobacco smoke than the number of cigarettes smoked, or other similar measures commonly used. Therefore, it became desirable to determine the source of this compound; namely, whether it came from the cigarette smoke itself or was produced in the body as a derivative of some other smoke constituent. Tobacco smoke was then examined for acetonitrile specifically, rather than for its broad spectrum of components.

Gas chromatographic techniques were used for separation and the mass spectrometer was used for identification.