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- 1 B. DE VRIES, *Chem. Ind. (London)*, (1962) 1049.
- 2 B. DE VRIES, *J. Am. Oil Chemists' Soc.*, 40 (1963) 184.
- 3 B. DE VRIES, *J. Am. Oil Chemists' Soc.*, 41 (1964) 403.
- 4 C. B. BARRETT, M. S. DALLAS AND F. B. PADLEY, *Chem. Ind. (London)*, (1962) 1050.
- 5 B. DE VRIES AND G. JURRIENS, *Fette, Seifen, Anstrichmittel*, 65 (1963) 725.
- 6 K. DE JONG, K. MOSTERT AND D. SLOOT, *Rec. Trav. Chim.*, 82 (1963) 837.
- 7 P. HAVERKAMP BEGEMANN AND J. C. KOSTER, *Nature*, 202 (1964) 552.
- 8 G. URBACH, *J. Chromatog.*, 12 (1963) 196.
- 9 H. T. BADINGS AND J. G. WASSINK, *Neth. Milk Dairy J.*, 17 (1963) 132.
- 10 B. DE VRIES AND G. JURRIENS, *J. Chromatog.*, 14 (1964) 525.
- 11 J. G. KEPPLER, J. A. SCHOLS, W. H. FEENSTRA AND P. W. MEIJBOOM, *J. Am. Oil Chemists' Soc.*, 42 (1965) 246.

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### Thin-layer chromatography of long-chain tertiary amines and related compounds\*

Long-chain tertiary amines, *e.g.* trilaurylamine, tri-*n*-octylamine etc. are currently being examined as extraction agents in reprocessing systems for nuclear fuels. Certain commercially available amines sold as "tricaprylamine" are mixtures of straight-chain (normal) saturated tertiary amines where the alkyl groups comprise a C<sub>8</sub>-C<sub>10</sub> mixture with the C<sub>8</sub> chain predominating. Gas chromatographic analysis has established<sup>1</sup> that the main tertiary amines present are members of a homologous series: tridecyl-, didecyl-, dioctyl-, trioctyl-, and dioctylhexyl-amines. Secondary and primary amines with these alkyl groups are present as impurities, usually not amounting to more than 5 % by weight of the mixture. Many commercial samples of the higher *n*-alkyl tertiary amines containing only one alkyl group, *e.g.* tri-*n*-octylamine or tri-*n*-dodecylamine contain similar quantities of the corresponding secondary and primary amine impurities.

The extraction of uranium and plutonium by these long-chain amines varies according to the nature of the amino nitrogen present so that it is necessary in partition studies to be able to determine the relative amounts of primary, secondary and tertiary amine groups present in a particular sample of amine. Furthermore, if the amine has been exposed during use to conditions causing chemical degradation, *e.g.*, radiation in the presence of mineral acids, the type and amount of such degradation must be determined to define the limits of effective performance.

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Methods are available for the analysis of long-chain amine mixtures based on gas chromatography<sup>1</sup>, and on non-aqueous titrimetry<sup>2</sup>, but in view of the speed and simplicity of TLC techniques it was of interest to devise suitable separation processes for the determination of the main amine components of such mixtures. Whilst it is not possible to separate the homologous series of tertiary amines present in "tricaprylamine" or to separate tri-*n*-octylamine from tri-*n*-dodecylamine, a facile separation into primary, secondary and tertiary long-chain amines has been made.

### *Experimental*

Two sizes of glass plates were used: (i) 20 × 20 cm were coated with an aqueous slurry of Aluminium Oxide G using a Desaga type spreader and were dried by heating in an oven at 100° for 1 h; (ii) 3¼ × 3¼ in. lantern slide cover glasses were coated by the technique due to PEIFER<sup>3</sup> using a slurry of 60 g Aluminium Oxide G in 100 ml of a 70:30 mixture of chloroform and methanol. This type of plate was prepared immediately before use, dried in a stream of air for 5 min and used without further activation. Substrates prepared by these methods barely resolved the standard Desaga dye-mixture with the developing solvent (see below and Fig. 2) but were suitable for the separation of long-chain amines according to their functionality.

### *Spotting, development and detection*

0.25 µl of amine (or an equivalent amount of a diluted sample) was a suitable sample size and isobutyl acetate was the most satisfactory solvent for separating long-chain amines from the associated secondary and primary amine impurities at room temperature. With the larger size plate where the solvent front moved through 10 cm it was sometimes preferred to use a 98:2 mixture of isobutyl acetate and glacial acetic acid, which produced a much more coherent secondary amine spot although at the expense of a slightly more diffuse tertiary amine spot. After evaporation of the developing solvent the plates were sprayed with an aqueous solution of cobalt thiocyanate [NH<sub>4</sub>CNS, 10 g; Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O, 10 g; H<sub>2</sub>O, 100 ml]. Primary, secondary and tertiary amines give blue colorations with this reagent against a pink background of the substrate. The colour of the sprayed plate fades to a uniform blue after exposure to air for approx. 2 h but the contrast may be restored by respraying with water or by steaming. Long-chain quaternary salts and long-chain amine oxides (but not long-chain alcohols or hydrocarbons) also give blue colours with cobalt thiocyanate and in some cases the colour produced differs slightly from that of the parent tertiary amine. Permanent records were preserved by photography.

### *Results*

Fig. 1 is a typical chromatogram obtained by the above procedure using a 20 × 20 cm plate.  $R_F$  values are not quoted; the only significant value, the  $R_F$  value of secondary amine, varied widely with the activity of the substrate, which as stated above was low and difficult to reproduce from different plates. The tertiary amine spot was invariably found in or slightly below the solvent front whilst the primary amine spot only spread slowly from the point of application.

Fig. 2 shows the effect of omitting the acetic acid from the developing solvent. The secondary amine spots are more diffuse than in Fig. 1 but the tertiary and primary amine spots are more coherent.

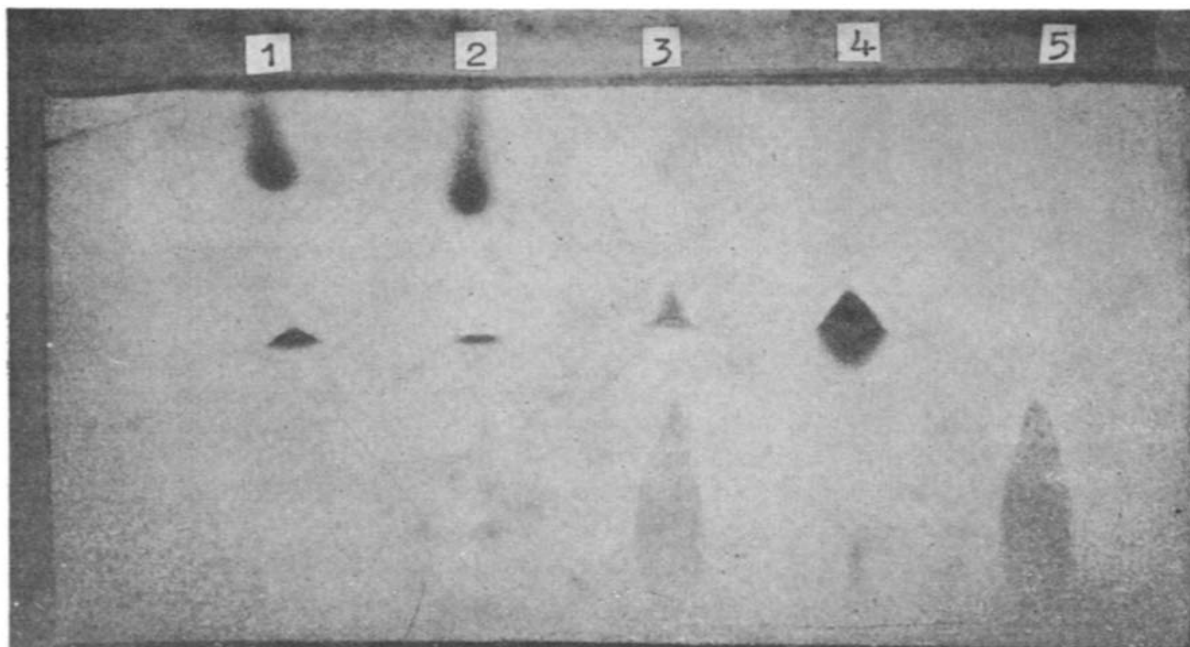


Fig. 1. Chromatograms (20 × 20 cm) on alumina, developed with isobutyl acetate-acetic acid (98:2). (1) Tri-*n*-octylamine containing 5% v/v di-*n*-octylamine. (2) Tri-*n*-octylamine containing 2% v/v di-*n*-octylamine. (3) Mono-*n*-octylamine showing di-*n*-octylamine as impurity. (4) Di-*n*-octylamine showing *n*-octylamine as impurity. (5) Mono-*n*-octylamine.

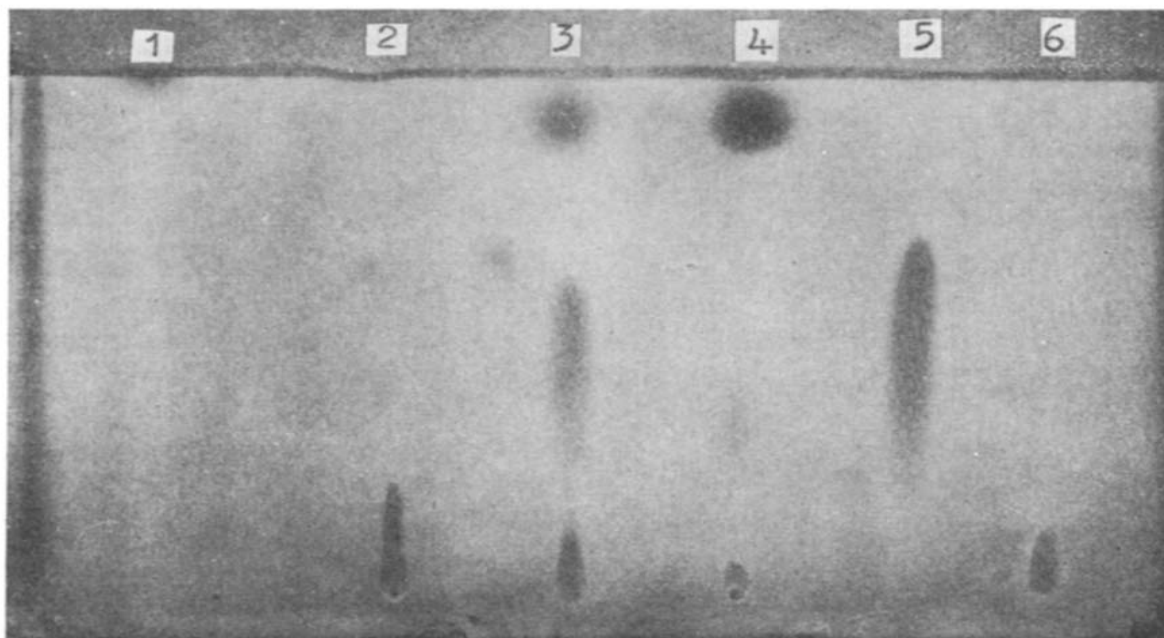


Fig. 2. Chromatograms (20 × 20 cm) on alumina, developed with isobutyl acetate. (1) Dyemarker. (2) "Tricaprylamine oxide". (3) Mixture of equal parts by vol. of mono-, di- and tri-*n*-octylamine. (4) Tri-*n*-octylamine. (5) Di-*n*-octylamine. (6) Mono-*n*-octylamine.

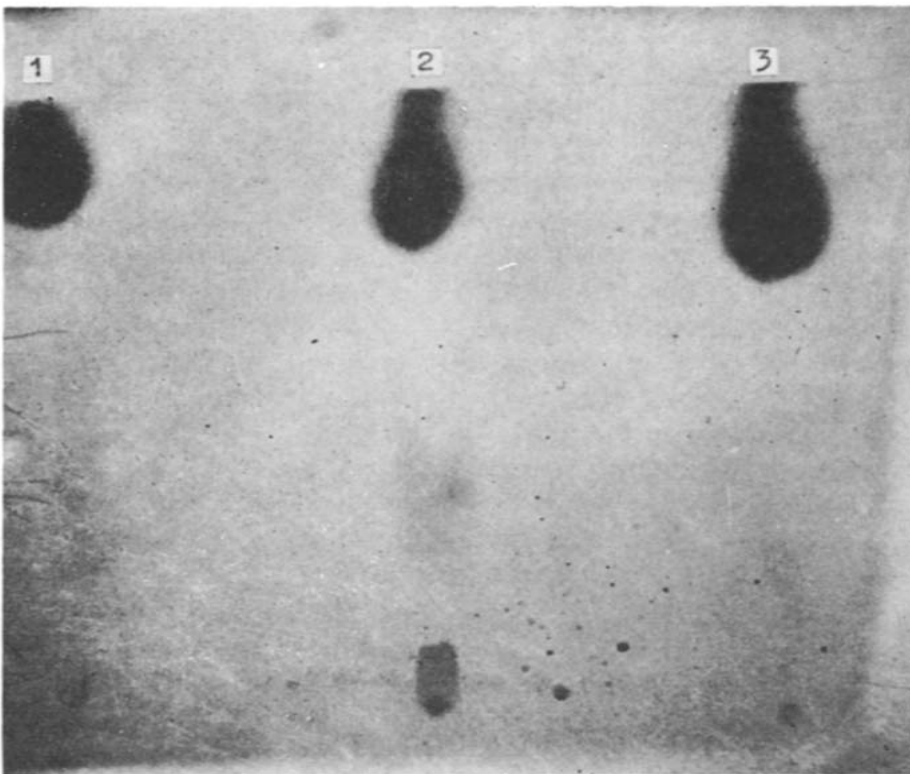


Fig. 3.  $3\frac{1}{4} \times 3\frac{1}{4}$  in. alumina coated chromatoplate developed with isobutyl acetate showing three different samples of "tricaprylamine".

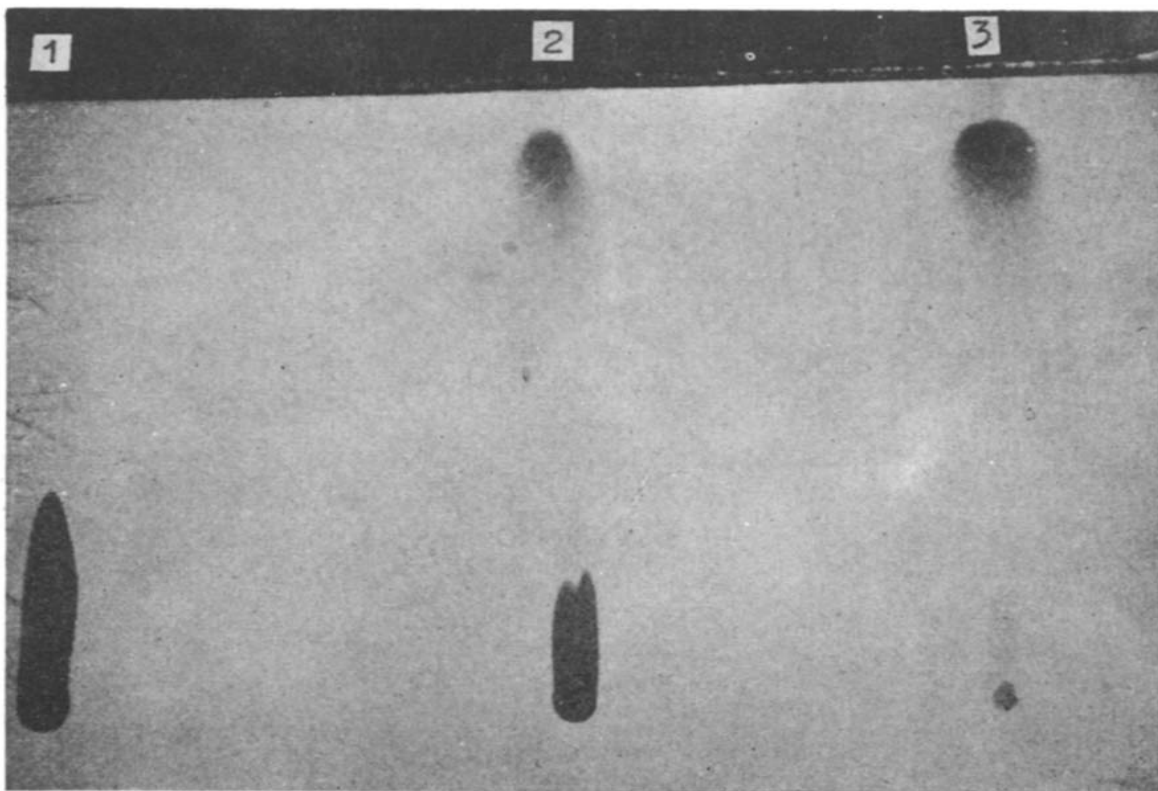


Fig. 4.  $3\frac{1}{4} \times 3\frac{1}{4}$  in. alumina coated chromatoplate developed with benzene. (1) "Tricaprylamine methosulphate." (2) "Tricaprylamine methosulphate" containing 25% unreacted "tricaprylamine". (3) "Tricaprylamine" with primary and secondary amine impurities.

The use of the smaller plate to compare the primary and secondary amine impurities in three commercial samples of "tricaprylamine" is shown in Fig. 3. The solvent front moves through 5 cm and the development requires only 30 min. Sample (2) clearly shows an increase in primary and secondary amine content over samples (1) and (3). Comparison with samples of known composition was preferred for quantitative work. Whilst lacking the precision of the gas chromatographic (GC) method the TLC method is faster and more convenient because the size of the primary and secondary amine spots is a measure of the total quantities of these components present whereas the GC method requires the measurement of the peaks of the individual components, which, in the case of "tricaprylamine" with its homologous series of amine components to identify and measure, becomes rather involved.

The conversion of long-chain tertiary amines to quaternary salts or to amine oxides by reaction with appropriate reagents (*e.g.* dimethyl sulphate or hydrogen peroxide, resp.) may also be followed by this TLC technique. Quaternary salts and amine oxides are more polar than the parent tertiary amine and are more strongly adsorbed on the substrate. Progress of a reaction where tertiary amine is being converted may be followed by spotting on to the smaller chromatoplate, developing with benzene and spraying with cobalt thiocyanate. Unreacted tertiary amine is carried in the solvent front whilst the reaction product moves only a short distance from the point of application (see Fig. 4). In this way, it is possible to detect as little as 0.2% amine oxide in "tricaprylamine" using a 1  $\mu$ l sample and 0.5% of "tricaprylamine" in a "tricaprylamine oxide" preparation using the same size sample.

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1 R. VECE (C.N.E.N., Rome), *Report LATC*, (62) 4 (1962).

2 G. D. GAL'PERN AND N. N. BEZINGER, *Zh. Analit. Khim.*, 13 (1958) 603.

3 J. J. PEIFER, *Mikrochim. Acta*, (1962) 529.

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