It should be possible to identify unknown particles by running at the same time as dusts of known composition or standard chemical mixtures. Halo or zone areas might then be taken as a measure of quantity, and the weight of completely dissolved particles calculated. The method might also be suitable for studying radioactive dusts in combination with autoradiography.

My thanks are due to Dr. J. Stern, of the Fountain Hospital, London, S.W.17, for advice, and to Mrs. A. Turner for assistance in preparing the manuscript.

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Chromatography by Liquid–Liquid Partition and Liquid–Liquid Interface Adsorption

FOR liquid–liquid partition chromatography with columns a linear relationship exists between the logarithms of corrected retention volumes (R_t) of terms of homologous series and the order n of these terms[1].

Thus :
$$\log R_t \sim \lim n \qquad (1)$$

where R_t is defined as the retention volume minus the volume of the mobile phase in the column itself. However, the experimental verification of equation (1) often encounters difficulties in which the carriers of the immobile phases seem to be involved.

An extensive investigation has been carried out in order to gain an insight into the nature of these deviations from ideality. Homologous series of coloured derivatives of aliphatic alcohols, aldehydes, ketones, acids, amines, mercaptans and alkyl halides were used. In these derivatives the occurrence of acid, basic, ionogenic or OH-groups was avoided. Light petroleum, alone or mixed with carbon tetrachloride or benzene, was used as the non-polar phase. A number of polar solvents, including nitromethane, NN'-dimethylformamide, formamide, acetonitrile, 'Methylcellosolve', methanol, propylene glycol, either alone or mixed with each other or with small percentages of water, were used as polar phases. Silica gels were prepared according to Gordon, Martin and Synge (G-gels) or to Nykamp (N-gels), and served as carriers of the immobile phases[2].

It was observed that the amount of loading of the gels with immobile phases relative to their maximum capacity was of the highest importance with respect to the nature of the phenomena. If the gels were loaded over a certain limit, equation (1) was invariably obeyed. Under these conditions all aliphatic series tested could be separated and the individual terms identified by a multitude of variants, each of which displayed its own merits with regard to sharpness of separation or the range of terms which could be separated efficiently. In this way many isomers could be unravelled too (for example, cis and *trans* azo-compounds, and syn- and anti-isomers of 2, 4-dinitrophenylhydrazones of *n* aliphatic aldehydes).

Loading the gels with quantities of immobile phases less than the limit indicated above resulted in the simultaneous operation of liquid–liquid partition and liquid–liquid interface adsorption. The participation of the latter is clearly demonstrated by experiments with the N-gels of high capacity (maximum capacity ± 3 ml./gm.). Loading these gels to less than ± 2 ml./gm. resulted in increased adsorption. This adsorption, occurring in a loading range where the immobile phase is still in excess of the weight of the carrier itself, should be interpreted as liquid–liquid interface adsorption, and its importance in this region is due to the great extension of these interfaces. This view could be confirmed by eliminating the liquid–liquid partition mechanism by using water as the immobile phase. Loading the N- and G-gels below the level of ideal behaviour invariably resulted in a certain retention of the coloured bands.

This liquid–liquid interface adsorption could be exploited as an independent tool for chromatographic separations. On the interface between light petroleum and water the azo-isomers, as well as the dinitrophenylhydrazone isomers, could be resolved.

This variant of chromatography, which is applicable in a reversed-phase form as well, can be carried out in a very simple way and seems particularly suitable for the separation of labile substances because of its mild conditions and uniformity of the adsorption surfaces.

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Group Localization Energy and Polarographic Half-Wave Potentials of Aromatic Nitro Compounds

IN a number of publications[1,2] it has been established that the reduction potential of aromatic compounds may be correlated with the π-electron energy change associated with the localization of electron or electrons at different positions of the molecule. Thus in the reduction of quinones the electron-localization took place at the two oxygen atoms, while in the case of aromatic hydrocarbons they were localized at the two p-carbon atoms. In the case of more complex compounds the localization may take place at certain groups of atoms undergoing reduction.

It is now fairly well established that aromatic nitro compounds undergo reduction at a dropping mercury electrode by a four-electron four-proton addition step and in the acid region one sharp polarographic wave is obtained. The process may be represented as :

$$C_6H_5NO_2 + 4e^- + 4H^+ \rightarrow C_6H_5NHOH + H_2O$$
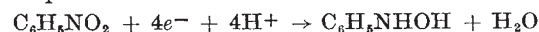
We suggest that the reduction potential should be proportional to the π-electron energy difference between the parent compound and the transition state with four electrons localized on the nitro group. This energy difference may be calculated by the linear combination of atomic orbitals method if we assume that the energy of four electrons localized