These measurements were carried out in the laboratory, so we had to apply the corresponding correction (30 cm. of concrete, equivalent to 5–6 cm. of lead) and we obtained a maximum at 18–19 cm. of lead. We did not correct the intensities for temperature and barometric pressure, and our minimum thickness of absorber material was only 20 cm.

We are at present carrying out further theoretical and experimental investigations, in order to be able to explain these anomalies.

ESTRELLA MAZZOLLI DE MATHOV
Instituto de Física,
Facultad de Ciencias Exactas,
Físicas y Naturales,
Universidad de Buenos Aires.

[1] Fenyves, E., and Haiman, O., *Nature*, 165, 244 (1950).
[2] Mazzolli de Mathov, E., *Rev. Unión Mat. Argentina*, 12, 167, 168 (1948). Trabajo de Tesis, presented to the Facultad de Ciencias Exactas, Físicas y Naturales, Buenos Aires, Rep. Argentina, July 31, 1948.
[3] Boethe and Kolhörster, *Z. Phys.*, 56, 751 (1929).
[4] Rossi, *Phys. Rev.*, 36, 606 (1930).
[5] Auger, Leprince-Ringuet and Ehrenfest, *J. de Phys.*, 7, 58 (1936).
[6] George and Appapillai, *Nature*, 155, 726 (1945).

Refractive Index Correction in Relative Raman Intensity Measurements

THE development of automatically recording Raman spectrometers has led to increased use of Raman intensities for the quantitative analysis of liquid mixtures. A method frequently adopted is to choose a Raman line characteristic of one component and to compare its intensity in the mixture with that in the pure component. This may be done either directly or (as with the so-called scattering coefficients of Rank and co-workers[1]) by means of an auxiliary reference substance. The basis of the analysis is the assumption that the Raman intensity is directly proportional to the volume concentration. The purpose of this communication is to direct attention to the fact, apparently not previously taken into account, that even if the assumption were completely valid with respect to the total Raman scattering, it would not be valid for the intensities as measured with a spectrometer. The reason is that, on account of the different refractive indices of the two liquids which are compared, there will be different amounts of refraction of the scattered light as it emerges from the Raman tube ; and in consequence the effective volumes of scattering liquid 'seen' by the spectrometer will be different.

The light flux passing through the collimator of a spectrometer from a spatially extended source of uniform luminosity has been considered by Nielsen[2]. By extending his treatment, which was restricted to a source of refractive index equal to that of air, we find that for a source of refractive index μ the light flux is less by the factor $1/\mu^2$. The same result is obtained whether or not a condensing lens is used between Raman tube and spectrometer. Hence in order to obtain the true ratio of the Raman intensity of a component in a mixture (refractive index μ) to its intensity in the pure component (refractive index μ_0), the observed ratio must be multiplied by the correction factor $(\mu/\mu_0)^2$.

With the experimental accuracy at present attainable, the omission of this correction causes no appreciable error in the analysis of mixtures (for example, of similar hydrocarbons) where the components have nearly equal refractive indices. For mixtures of hydrocarbons of different kinds (for example,

paraffinic and aromatic) the correction becomes significant ; and for other mixtures it can far exceed the limits of error. As experimental accuracy is improved, the correction will become correspondingly more important.

The value of the correction factor given above is for uniform luminosity of the liquid, a condition well realized when Raman tube and lamps are surrounded with reflectors, In applying the method for the quantitative analysis of liquids involving considerable differences of refractive index, the use of such an arrangement would seem to be important ; for with non-uniform irradiation it would be practically impossible to calculate the magnitude of the refractive index effect.

The full theoretical treatment will be published elsewhere. It is also intended to carry out experimental tests of the applicability of the correction, using suitably chosen liquids.

L. A. WOODWARD
J. H. B. GEORGE
Physical Chemistry Laboratory,
University, Oxford.
Sept. 26.

[1] Fenske, M. R., Braun, W. G., Wiegand, R. V., Quiggle, D., McKormick, R. H., and Rank, D. R., *Anal. Chem.*, 19, 700 (1947).
[2] Nielsen, J. R., *J. Opt. Soc. Amer.*, 20, 701 (1930).

Measurement of Contact Potentials at the Oil–Water Interface

ALTHOUGH the contact potential of the air–water interface is easily measured[1], this is not so for the oil–water interface. Many measurements have been made on the latter system ; but in all cases the change in contact potential, ΔV, caused by the spreading or adsorption of a monolayer, decreases with time[2-4], or is but "moderately reproducible"[5]. Indeed, ΔV often reaches zero after only a few minutes. These difficulties have been shown[6] to be due to the diffusion of traces of ions from the aqueous phase into the oil, until at the equilibrium concentrations these 'counterions' balance out the potential due to the film.

The only way to overcome this difficulty is by the use of an oil such as petrol-ether (specific resistance about 10^{16} ω) in which ions are too insoluble to build up a double layer on the oil side of the interface[3]. This means also that little direct current can pass through the oil phase, and recourse to a.c. measurement of the contact potential with a vibrating plate[7] is necessary.

In the present investigation, a gold disk, 2 cm. in diameter, is vibrated while immersed in the oil phase. To avoid disturbing the interface, it is necessary that the amplitude of vibration should be as small as possible (less than 0·01 cm.) and that the disk should not be closer than 0·5 mm. to the water surface. For these reasons the accuracy of measurement of ΔV at the oil–water interface is necessarily less than for the air–water system. Nevertheless, by using a specially designed tuned amplifier, it has now been found possible to measure ΔV for films spread at the petrol-ether–water interface with an accuracy of 1 mV. (about 0·3 per cent).

Using petrol-ether (boiling point above 120° C.), we have obtained *permanent* changes in V when a monolayer is spread. Just as in the familiar case of the air–water surface, the film can be compressed, and a plot of ΔV vs. A is easily obtained. Here A is the area occupied by each long-chain ion in the surface.