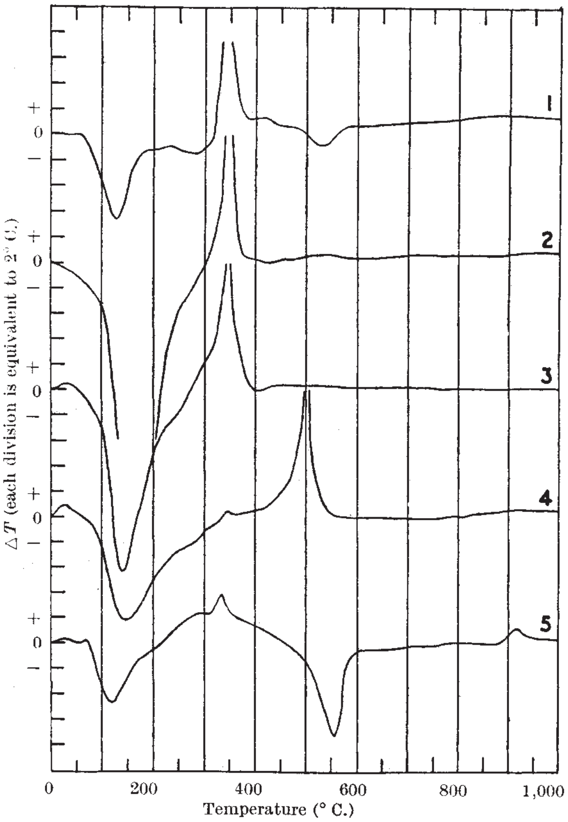
Nature of Free Iron Oxides in Soil Clays

A DIFFERENTIAL thermal analysis examination of soil clays at present in progress with the view of elucidating their mineral composition has provided some evidence regarding the nature of the iron oxide coatings on the clay micelles. One of the clays studied, which had a free iron oxide content of 31 per cent, had been separated from a *C*-horizon sample (depth 48–52 in.) of a soil developed on basic igneous till and had been treated several times with hydrogen peroxide on the steam-bath to remove organic matter. Its thermogram shows a strong exothermic peak at about 345° C. (curve 1 in the graph), which because of its sharp well-defined nature appears to be quite different from the broad, rather diffuse band usually associated with organic matter, but which bears a considerable resemblance to that quoted by Berg, Nikolaiev and Rode[1] for 'cold-precipitated' or 'glowing' hydrated ferric oxide[2].

The similarity of the curves may be readily observed in the graph, where curve 2 is that obtained for 'cold-precipitated' hydrated ferric oxide in this laboratory. The oxide was precipitated from a ferric chloride solution by addition of excess 1 : 1 ammonia at room temperature (about 18° C.), washed free from chloride and dried at 105° C. in the oven. Material dried over phosphorus pentoxide *in vacuo* gives an identical curve. Repeated treatment of the oxide with hydrogen peroxide on the steam-bath—the normal procedure for removing organic matter from soil clays—does not affect the curve appreciably (curve 3). In connexion with the formation of these ferric oxide gels, it is noteworthy that the temperature of precipitation affects the curve very appreciably; for example, precipitation at 100° C. displaces the exothermic peak to 503° C. (curve 4), whereas precipitation at temperatures between 18° and 100° C. causes the peak to appear at temperatures between 345° C. and 503° C. In view of these facts it would seem that the 'cold-precipitated' hydrated ferric oxide occurs as such in the soil and is not formed by any pretreatment, for example, by precipitation during the decomposition of organo-metallic complexes by hydrogen peroxide.



Differential thermal analysis curves.

1, Soil clay, No. 15260 ; 2, hydrated ferric oxide precipitated at 18° C. ; 3, 'cold-precipitated' hydrated ferric oxide treated six times with hydrogen peroxide ; 4, hydrated ferric oxide precipitated at 100° C. ; 5, soil clay No. 47343

Several other soil clays have since been found to contain this type of ferric oxide, but generally in smaller amounts (cf. curve 5). A survey of the literature reveals that somewhat similar small peaks have frequently been observed on thermograms of soil clays; but they apparently have been interpreted as organic matter incompletely removed. However, the sharpness of the peaks and the constancy of the peak temperature, as well as their occurrence on thermograms of clays from lower horizons of the profile which have been well peroxidized to remove organic matter, seem to exclude this possibility.

Goethite, which gives a strong endothermic effect at 380° C., has been observed in only a few of the soil clays examined.

These iron oxide coatings normally show up only as a diffuse background on X-ray photographs of soil clays, and an electron diffraction examination of four soil clays shows no sign of crystallinity in the coating. It would, therefore, appear that differential thermal analysis is at present the only method of investigating them.

The differential thermal analysis apparatus employed in these investigations is somewhat similar to that described by Grimshaw, Heaton and Roberts[3]: a ceramic specimen holder is used; exothermic peak temperatures are quoted as the temperature of the inert material at the peak; endothermic peak temperatures are corrected to the temperature of the sample at the peak; sample weights for soil clays are 0·2 gm., for iron oxides 0·35 gm.

Further work is in progress, especially with the view of elucidating the conditions of formation of these oxides in the soil, and a full report will be published elsewhere. I would like to thank Prof. G. I. Finch, of the Imperial College of Science and Technology, London, for supplying the electron diffraction data.

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Feb. 15.

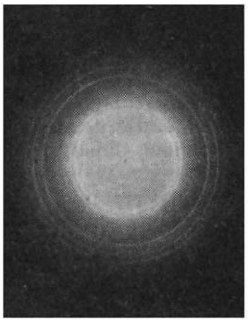
[1] "Thermographia", 85 (Acad. Sci. U.S.S.R., 1944).

[2] See, for example, Fricke and Huttig, "Hydroxyde und Oxyhydrate", 335 (Leipzig, 1937).

[3] *Trans. Brit. Ceram. Soc.*, **44**, 69 (1945).

Structure of Stearic Acid Films on Copper

IN a recent communication[1], Spink, using electron diffraction technique, postulates the presence of copper stearate after a copper surface covered with stearic acid has been heated. Two facts are quoted in support of this hypothesis. (1) When such a film is heated in the diffraction camera, the pattern finally fades at a temperature of 127–130° C., that is, close to the softening point of copper stearate. This observation confirms that of Brummage[2], and also corresponds well with friction measurements reported by Gregory and Spink[3]. It is generally accepted that both the electron diffraction and the friction evidence are circumstantial and do not offer a direct proof of the presence of the soap. (2) After the acid-covered surface has been heated, the film may be removed in benzene and then deposited on collodion. The resulting film gives an excellent diffraction pattern which is identical with that of copper stearate prepared in the laboratory.



In fact, the second observation does not conclusively prove the presence of the soap on the surface, as claimed, because the same pattern may also be obtained from stearic acid (see photograph), and also from other fatty acids, from esters[4], from normal paraffins[5] and from grease contamination in general[6]. Likewise, the arc patterns attributed by Spink to crystals of copper stearate have been observed in this laboratory in patterns from stearic acid deposited on stainless steel and subjected to rubbing on filter paper.

Thus, while Spink has been able to confirm previous indirect evidence of the presence of copper stearate on a copper surface after heating in the presence of stearic acid, he has not succeeded in producing definite electron diffraction evidence of its existence.

I wish to thank the Chairman of the Anglo-Iranian Oil Company for permission to publish this letter.

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[1] Spink, J. A., *Nature*, **163**, 441 (1949).
[2] Brummage, K. G., *Proc. Roy. Soc.*, A, **191**, 243 (1947).
[3] Gregory, J. N., and Spink, J. A., *Nature*, **159**, 403 (1947).
[4] Coumoulos, G. D., and Rideal, E. K., *Proc. Roy. Soc.*, A, **178**, 421 (1941).
[5] Brummage, K. G., *Proc. Roy. Soc.*, A, **188**, 414 (1947).
[6] Trillat, J. J., and Motz, H., *Trans. Farad. Soc.*. **31**, 1127 (1935).

The Uncertainty Principle

Mr. W. L. Cowley[1] raises a point of some importance to a popular presentation of quantum theory. The understanding of the Uncertainty Principle is confused by there being two quite distinct ideas associated with the one name. Mr. Cowley's discussion of Heisenberg's uncertainty principle relates to the form of it which could be derived from the old quantum theory of Planck, Einstein and Bohr (one may call it 'uncertainty I'). As he remarks, books intended for wide circulation usually introduce the principle in this form, by describing the 'microscope experiment', and often take it no further. However, the connexion between uncertainty I and uncertainty II (which depends on the new quantum theory) is slight. The old quantum theory only recognized the so-called 'wave-particle duality' of light, and not of matter; uncertainty I is a rather artificial statement about the precision of observation practicable with an optical microscope. In the new quantum theory of de Broglie and others, however, the 'duality' is formulated for matter also, and uncertainty II expresses a consequence of this.

In the wave mechanical representation of new quantum theory, a particle is represented by a region of waves, the position of the particle being defined only in so far as the region is limited; but if the wave is such that its amplitude is negligible outside a defined region, then the wave may be shown by Fourier analysis to be comprised of a group of waves with a range of wave-lengths. The smaller the region for which the wave is finite (the more precise the definition of the position where the particle is likely to appear), the more divergent from the mean are the significant components of wave-length, and this divergence defines the range of probable momenta of the particle. Uncertainty II states a relation between the probable ranges of position and momentum of the conceptual particle. It thus expresses an important limitation on the precision with which position and momentum may both be defined, and it is not to be compared with errors in macroscopic experiments to which there are no similar limits.

Mr. Cowley considers the observation of a single electron using a microscope. He raises two specific points: first, that the optical formula for the resolution of a microscope is derived from, as he calls it, the effect of bulk action while only a single photon is involved; secondly, that the optics formula merely expresses a convenient and not a fundamental limit. On fuller consideration, however, one finds that the first point contains the answer to the second. Only one photon is scattered by the electron, and only one point, therefore, of what would normally be an Airy disk is excited; hence there is no evidence as to where the rest of the photons would appear if many were scattered by the electron. To interpret this single observation one must first take the most probable position of the electron to be the point conjugate to the observed photon, and secondly take the probable error (the error as likely to be fallen short of as exceeded) of this to be $0{\cdot}535\,\lambda/A$ (λ is wave-length, A is numerical aperture). It is important to note that both the mean error and the standard deviation of the first assumption are infinite. Mr. Cowley, like most authors who discuss this hypothetical experiment, refers to the 'resolution' of a microscope: however, this is wrong, as only one electron and one photon are postulated, and there is nothing else from which these are to be 'resolved'. The uncertainty in the determination of position of the electron depends on the uncertain association of the 'particle' with the 'wave' in light. The uncertainty of momentum arises from the Compton effect. Nowhere does the 'microscope experiment' depend on any specific property of matter, and therefore it cannot demonstrate any new property of matter.

That the formula given in uncertainty I (after a rather artificial analysis) is similar to that given in uncertainty II (apart from a numerical factor) arises from the fact that a 'wave particle duality' may be formulated for both matter and light, and the fact that Planck's constant determines the relation