ROTHAMSTED RESEARCH

Report for 1969 - Part 1

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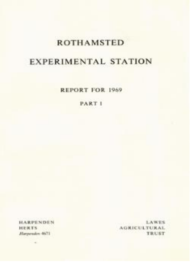

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PEDOLOGY DEPARTMENT

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The traditional concern of pedology is the development of the soil profile, that is the formation of more or less horizontal layers of different composition that result from inhomogeneity of the parent materials, and the influence of percolating water and the various chemical, biological and physical processes that occur in the soil.

Our research on the release of potassium from micas aims to establish the principles of the alteration reactions. Hitherto we have concentrated on mono-mineralic micas; now, in the light of the knowledge gained during this work, we are studying more complex potassium-bearing minerals separated from clays and silts of a wide range of British soils.

Because of their plate-like shape, clay particles readily become mutually oriented and pack more closely when subjected to stresses. The degree and distribution of clay orientation in a soil reflects its past treatment; these factors are important in determining many of the physical properties of the soil, and in understanding the mechanisms by which structures favourable for plant growth are created. We are developing methods to examine clay orientation and measure pore-size distribution in soils.

Toxic metals are concentrated in sewage sludge and town composts, and we are collaborating in a study of the hazards involved in using such materials as fertilisers. We are continuing our study of the mobilisation and immobilisation of trace elements under simulated soil conditions, in an attempt to increase understanding of the factors that govern the availability of trace elements to plants.

Work on the effects of partial sterilisation on the mineralisation of soil organic matter continues, and X-ray fluorescence spectrometry continues to find new applications.

In our report for 1965 we mentioned that montmorillonite is a major component of tuffaceous mudstones of Old Red Sandstone age from the Raglan district of Monmouthshire. As a result, the possibility of exploiting these deposits is being considered by the Institute of Geological Sciences.

Mineralogy

Irreversible exchange reactions of potassium in micas. Mica placed in a solution of a strongly-hydrated cation releases potassium very quickly at first, but as K accumulates in solution the rate of release decreases until the concentration of dissolved K reaches a terminal or stationary value. This terminal concentration is used as an empirical parameter to compare the release of K from different micas, and for a thermodynamic interpretation of its significance it is important to know whether it represents an equilibrium state. The condition for reversible equilibrium was tested by adding potassium to a solution of NaCl that contained the terminal concentration of K in quasi-equilibrium with partly-exchanged mica. The concentration of K had to be increased to 1·5 times the terminal concentration before reverse exchange occurred. Measurements of the rate of approach to the terminal concentration suggest that these results cannot be explained by failure to allow sufficient time for equilibrium; the differing terminal concentrations of K for forward and reverse exchange seem to be the result of hysteresis.

In addition to non-reversibility from hysteresis, micas also show 'absolute' irreversibility; because of a change in the structure, the original state cannot be regained by reversing the direction of exchange. Two micas differing greatly in their ability to release potassium (P1 : $R^{K}_{Na} = 1{\cdot}7 \times 10^{-5}$; P3 : $R^{K}_{Na} = 2{\cdot}4 \times 10^{-4}$. See *Rothamsted Report for 1968*, Part 1, 64) were depleted of K by extraction with Na-tetraphenylboron, saturated with Ca and treated with KCl solution until no further Ca was exchanged. Exchange parameters for these K-saturated alteration products (designated K-AP1, K-AP3), determined by exchange against NaCl, were $R^{K}_{Na} = 2{\cdot}9 \times 10^{-5}$ and $R^{K}_{Na} = 4{\cdot}8 \times 10^{-4}$ respectively, showing that K sorbed by altered micas was released more readily than from the original micas. X-ray examination showed that the structural details of K-AP1 and K-AP3 differed from those of the corresponding untreated micas; increases in the mean basal spacing of about 0·03 Å, and broader diffraction lines, indicate that there were structural irregularities in the alteration products. The irregularities may be associated with trapping of Ca and water, and deficit of K.

To gain insight into the sequence of chemical and structural changes that occur when K is reintroduced into depleted micas, the distribution of small amounts of added K between NaCl solution and depleted micas was determined, and the products examined by X-ray diffraction. A sample holder was made to permit oriented aggregates of altered micas to be examined on the diffractometer while remaining in contact with the reaction solution. The diffraction patterns, together with chemical analysis of the solutions and solids, showed that the solids were segregated mixtures of expanded mica with a regular repeat unit, coexisting with an irregular structure of interstratified collapsed and expanded layers, with a tendency for a collapsed K-containing layer to follow an expanded layer. This structure contrasts with the segregated mixture of regular expanded and collapsed structures that develops in mica when K is removed under high stress. It indicates that the mechanism of K sorption differs from K-desorption; the implications of this in exchange processes are being evaluated. (Brown and Newman)

Effect of pH on the rate of potassium exchange. In a flake of partly-exchanged mica, a core of unchanged mica is surrounded by a rim of expanded material in which potassium is replaced by a hydrated cation; the interface between the two regions is marked by an optical discontinuity visible under the microscope (*Rothamsted Report for 1964*, 78). The rate potassium is replaced can be determined by measuring the movement of this interface, and in a recent report of such measurements on micas exchanged in solutions of different acidities (Wells & Norrish (1968) *Trans., 9th int. Congr. Soil Sci.*, II, 683–694), the authors suggested that hydrogen ions have no specific role in accelerating the rate of replacement. This conclusion seemed to conflict with our observation that the exchange parameters for micas were greater in weakly acid solutions (*Rothamsted Report for 1967*, 66). To resolve this disagreement the rates of replacement of K at different acidities were measured by the optical method, using micas previously shown to exhibit an enhancement of replacement at acid pH. Comparison of the amounts of K replaced in the same time in a neutral salt solution, in a very dilute acid, and in a mixture of the two, showed that the effect of the combined solutions was greater than the sum of those of the acid and salt solutions alone. This synergism implies that hydrogen ions do have a specific action in accelerating the replacement of K in natural micas.

The synergetic effect of hydrogen ions ranges from a slight depression of replacement in a fluorphlogopite, to a three-fold increase of the rate between pH 9 and pH 4·5 for several biotites. The effect seems largest in micas that have a deficit of structural hydrogen, $(OH + F) < 4$ per unit formula. (Newman)

During these observations on the movement of optical discontinuities in mica flakes, the exchanged region sometimes developed unevenly, and occasionally failed to develop. Edges that were slightly roughened during cutting developed the usual alteration rim, but sharply fractured edges often failed to show an altered rim, or developed one only after some delay. Examination of selected areas of such flakes by X-ray diffraction confirmed the optical evidence that edges without visible boundaries were less than 1% altered, whereas edges with visible altered rims had altered to an expanded structure. Similar inhibition of alteration also occurred at a natural crystal edge. Diffusion of the replacing cation between the silicate layers has been widely thought to be the rate-limiting step when K is exchanged from micas, and a single diffusion coefficient has been used to describe the process. We have confirmed that the width of the exchanged region is often not proportional to the square root of the time, so processes other than diffusion may modify K exchange rates in mica.

The delayed exchange from edges of mica crystals that are not mechanically abraded suggests that one such process may be cleavage of mica crystals into units thin enough to allow interlayer expansion. At more perfect edges swelling will be delayed until incoming hydratable cations diffusing slowly through the unexpanded structure produce a swelling stress sufficient to initiate new cleavage cracks. (Brown and Newman)

Determination of the structure of a phlogopite mica by neutron diffraction. The position of the hydrogen atom in the unit cell of a layer silicate has not previously been determined directly. Probable positions are inferred from chemical analysis, crystal chemistry and infra-red spectra. The positions of the atoms other than hydrogen have been found by X-ray diffraction, but the hydrogen atom, with only one electron, scatters too weakly for its position to be found; it can be detected in talc, but not accurately placed. Crystal chemical considerations show that the hydrogen atoms should be bonded to those oxygen atoms in the octahedral layer that are not attached to silicon. Infra-red spectra show that in trioctahedral micas the O–H bonds are perpendicular to the mica layers, and in dioctahedral micas at a large angle (about 74° in muscovite) to this direction. Hydrogen atom positions have been inferred from this evidence, and from the expected length of an OH bond.

In micas where the OH bond is perpendicular to the sheets, the hydrogen atom is in the second co-ordination sphere of the inter layer cation, and influences the stability of the latter. It is important that explanations of effects that depend on this stability, such as the alteration and ion exchange properties of layer silicates, have a firm basis in accurately determined positions and occupancies of the hydrogen sites. Many trioctahedral micas differ from the ideal structure, in which there are perpendicular OH bonds in every unit cell, because some of the hydroxyl groups are replaced by fluorine atoms; other differences from ideal composition, such as occasional octahedral vacancies, may displace some of the H atoms.

In neutron diffraction the scattering power of the H atom is of the same order as that of the other atoms, so that it should be possible to determine its position with the same accuracy. Neutron diffraction measurements were made on a phlogopite mica (P5) previously examined by X-ray diffraction. The measurements were made at the Atomic Energy Research Establishment at Harwell using a crystal reflected beam of neutrons from the DIDO nuclear reactor and a Hilger–Ferranti four-circle diffractometer with paper tape control. The beam strength is much less than was used for the X-ray experiments and so a much larger crystal, and a longer time to measure each reflection, were needed. The best available crystal of this phlogopite was 5 × 5 × 0·4 mm and weighed 0·036 g. It was cut by an Airbrasive cutter to remove a corner bent out of the plane of the mica sheet. The crystal was still not quite flat and slightly split near the edges. These imperfections were shown in the two neutron diffraction rocking curves for the 060 reflection. The curve taken with the crystal rocked by rotation of the sheet about its normal, c^*, was much sharper than when the rotation axis was in the plane of the sheet. Because of this some reflections would be more likely than others to have intensity wrongly measured as background. The thickness of this crystal, the thickest available, was still less than a tenth of the other two dimensions, and so for some reflections the crystal intercepts a small part of the beam, and for others a large part. This introduces errors in the measurement of the reflections, unless the beam is very uniform and the crystal accurately centred.

Two sets of measurements of the $0kl$ and $0k\bar{l}$ reflections were made. The symmetry of the crystal requires corresponding $0kl$ and $0k\bar{l}$ reflections to have the same intensity. The second set, measured with a slightly larger beam and a more carefully set crystal, gave better agreement for corresponding pairs of reflections, but there were systematic differences much greater than the standard deviation calculated from the counting statistics of the peak and background measurements. Averages of $F(0kl)$ and $F(0k\bar{l})$ were taken to calculate the $\boldsymbol{a}$ axis projection. The least squares weights were based on the standard deviation of the individual structure factors, rather than dividing by $\sqrt{2}$, as a partial but incomplete allowance for the extra error. Measurements were also made of *h*0*l*, *hhl* and some 1*kl* reflections. These should suffice to establish all the atomic co-ordinates and were obtained in half a reactor cycle. A full three-dimensional set would have taken two or three times as long.

Calculations on the averaged 0*kl* results show an agreement of $R = 0{\cdot}16$ with the structure based on the X-ray positions and omitting the H atom. R falls to 0·12 when the H atom is included at the expected site, confirming the presence of an H atom at about that position. Refinement of the 0*kl* results gave y and z co-ordinates for the atoms all consistent with the positions determined by X-ray diffraction, and placed the H site so that the perpendicular O–H distance, i.e. the projection of the O–H bond on to c^*, would be 0·90 Å with a standard deviation based on the experimental (under-estimated) error of 0·02 Å. The occupancy of the H site is refined at present to 0·5 ± 0·1 (about two-thirds of the chemically estimated OH content) but there is interaction between this parameter and the vibration of the atom in the z direction, so this occupancy is less certain than the position. (Rayner)

Genesis of loess soils. We reported last year the radiocarbon date of organic matter from a buried soil developed in the loess of Pegwell Bay near Ramsgate, Kent (*Rothamsted Report for 1968*, Part 1, 68); we have now completed a detailed petrographic study of this profile, and can infer the soil-forming processes, which occurred mainly during the Post-glacial climatic optimum. Similar processes probably occurred in many loess-containing soils in south and east England, but their effects have been largely obscured by changes such as those resulting from more recent pedological processes, from modern agricultural practices, or from the admixture of other soil parent materials with the loess. Our study of this buried profile should therefore help to clarify the complex history of present loess soils.

Particle size distribution. Seven horizons were recognised in the buried profile. We first investigated the particle size distribution of these by separating their sand fractions ($> 50\ \mu$m) at quarter ϕ intervals with sieves ($\phi = -\log_2 d$, where d is the diameter of the particles in mm), and by taking two staggered sets of measurements at half ϕ intervals from 5 to 150 μm with the sedimentation apparatus described by Stairmand (*Instn Chem. Engrs & Soc. Chem. Ind. Symposium on Particle Size Analysis*, (1947), p. 128). Fractions finer than 8 μm were divided at 2ϕ intervals by centrifugation, giving three clay fractions. The mean particle size, standard deviation, skewness and kurtosis of the fractions coarser than $7{\cdot}0\phi$ (8 μm) in each horizon were calculated by moment summation; the ranges of these four moments are extremely small, indicating that there is no significant difference between the skeletal components of the horizons, and that the profile was developed in uniform loess. However, there are significant differences in the amounts of fine and medium clay, which suggest translocation of material in these size fractions from horizons above 45 cm depth to lower levels.

Micromorphology. Further evidence for clay movement is seen in thin sections, which show illuviation cutans in horizons below 45 cm. Strong brown mottles, which resulted from local movement of iron in reducing conditions caused by poor drainage, are common below 45 cm. In thin section these are expressed as fairly dense areas of iron concentration. They become more diffuse upwards, but can still be seen in thin sections of horizons above 45 cm, which are not visibly mottled. This provides evidence of poor drainage throughout the profile. However, the colluvial deposit, beneath which the profile is buried, has no mottles and in thin section shows an almost even distribution of iron compounds. The present site drainage is therefore good, and the effects of poor drainage in the buried profile probably date from the time of soil formation. This is probable because the stratigraphic position of the buried organic horizon suggests that the soil formed in a broad hollow cut into the loess, and because palaeobotanical evidence from many parts of N.W. Europe indicates that the post-glacial climatic optimum was warmer and probably wetter than the present time.

Mineralogy. The sand ($> 50\ \mu$m) and coarse silt (20–50 μm) fractions were analysed mineralogically with a petrological microscope. Comparison of the results with mineral analyses of the same size fractions from Palaeogene deposits of N.E. Kent (*Rothamsted Report for 1967*, 71–73) shows that in the buried profile most of the sand and approximately 10% of the coarse silt was derived from the Thanet Beds. The remaining material is of more distant origin, and is mineralogically similar to the loess in other soils of S.E. England, for example those of Rothamsted Farm (*Rothamsted Report for 1968*, Part 2, 85); it is composed of angular quartz with as much as 20% felspar and a heavy mineral suite containing mainly epidote, chlorite and amphiboles. The difference in amounts of Thanet Beds derived material in the sand and silt fractions results from wind transportation, because sand is not carried far by wind and is therefore mainly local in origin, whereas silt may be carried much further.

The fine silt and three clay fractions were analysed by X-ray diffractometry of lightly compressed powders and oriented aggregates; quartz, felspar, mica and free iron oxide were determined chemically. The contents of quartz and felspar decrease with decreasing particle size, and are progressively replaced by increasing amounts of layer silicates (mica, kaolinite and expanding minerals) and iron oxides. However, because they are composed mainly of montmorillonite, the fine clay fractions ($< 0{\cdot}1\ \mu$m) contain less mica, kaolinite and iron oxides than the medium clays (0·1–0·5 μm).

Mineral changes caused by weathering. Glauconite has disappeared from the sand and coarse silt fractions in the upper 45 cm of the profile, but the amounts and properties of the minerals in the fine silt and clay fractions do not change significantly with depth, so that they have not been appreciably affected by weathering. However, there are a few small changes in the expanding minerals that seem to result from weathering. The amounts of fine silt vermiculite decrease upwards in the highest 45 cm, and instead

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of an interstratified montmorillonite–vermiculite in the fine silts from the lower parts of the profile, an interstratified mica–vermiculite occurs in the higher parts. Montmorillonite is the only expanding mineral present in fine clay fractions below 45 cm, but above that depth there is a mixture of montmorillonite and interstratified montmorillonite–vermiculite; in the highest 20 cm these minerals give broadened basal X-ray reflections, indicating increased disorder of their constituent layers.

The illuvial horizons below 45 cm are 107 cm thick. They contain more total fine clay montmorillonite than the sum of the amount originally in 107 cm of unaltered loess and that eluviated from an overlying cover of unaltered loess 45 cm thick. This increase in the amount of fine clay montmorillonite in the profile as a whole could result from several processes, but we think that the most important was formation of fine clay montmorillonite by weathering of coarse silt glauconite, fine silt vermiculite and coarse clay montmorillonite in the 0–45 cm horizon.

The weathering changes in the profile probably occurred in at least two stages. In the first, mildly acid conditions removed calcium carbonate from the loess, and some montmorillonite was formed by weathering of glauconite; most of the translocation of fine and medium clay occurred during this stage. In the later stage the layer silicate minerals in the higher horizons were affected by more acid weathering, which resulted in the formation of fine clay minerals that are less freely expanding than montmorillonite. (Catt, Madgett and Weir)

Clay mineralogy of volcanic ash soils from the British Caribbean. The clay mineral of 20 surface soils from the Caribbean (Moss, P & Coulter, J. K. (1964) *J. Soil Sci.* **15**, 284–298) were examined. X-ray diffractometry of fractions separated from some of the samples gave very poor diffraction patterns and little indication of the presence of crystalline clay minerals. The samples were therefore all treated to remove allophane, and the kandite (halloysite and kaolinite) in many determined by selective chemical analysis. Removing allophane decreased the cracking in oriented aggregates, improved the orientation of the remaining minerals and allowed the layer silicate minerals in the samples to be identified.

The clays of the youngest soils, which were developed in recent volcanic ash falls of St. Vincent, were analysed in detail. By comparing the chemical compositions of the untreated clays with those of residues left after removing allophane and halloysite, and diffraction patterns obtained at each stage of the analysis, the mineralogical compositions of the clays were obtained. The clay fractions contain approximately equal proportions of allophane, halloysite and montmorillonite. Comparing these results with those of other young and some older soils shows that all samples contained three components, allophane, kandites and expanding 2 : 1 layer silicate minerals. With more acid weathering montmorillonite is replaced by interstratified minerals, and Al-chlorite and gibbsite are formed. Halloysite predominates in the youngest soils and kaolinite in the oldest; the conditions that govern the formation of these minerals are not well understood. Allophane, determined as NaOH-soluble silica and alumina, occurs in approximately equal amounts in all samples. These results indicate that the commonly held view, that allophane alone is the first weathering product of volcanic ash, is incorrect. Montmorillonite and halloysite are formed at the very earliest stages of weathering; later changes in the type and proportions of 2 : 1 and 1 : 1 layer silicate minerals depend on the conditions of weathering under which the profiles developed.

The soils are classified according to the severity of weathering of the ash, as judged by field examination of sand grains and estimation of soil textures. In the Caribbean the names allophanoid, kandoid and smectoid are given to soils depending on the amount of these minerals they are judged to contain from simple field tests. Clay mineral analysis confirms the use of kandoid and smectoid, and suggests the need for a further category, gibbsitic, for the intensely weathered soils containing this mineral. Analysis has not confirmed the validity of the allophanoid category, because the soils thus classified do not contain exceptional amounts of allophane; nor does clay mineral analysis indicate any mineralogical cause for the characteristically fluffy and greasy texture of the so-called allophanoid soils, which probably results from the interaction of organic matter with allophane. The soils must be mature enough to have lost the gritty texture of young soils, and the climate must favour the accumulation of organic matter, which becomes intimately mixed with, and protected by, allophane. (Ormerod and Weir, with J. K. Coulter)

Clay mineralogy of soils from N.A.A.S. Experimental Husbandry farms. The clay minerals in top- and sub-soils from plots of long-term experiments on the release of soil K at six Experimental Husbandry Farms were examined at the request of R. D. Russell and T. Batey of the National Agricultural Advisory Service.

The soils from Bridget's, High Mowthorpe, Trawscoed, Boxworth and Gleadthorpe Farms, were dispersed and divided into size fractions. The $< 2\ \mu$ and $< 0{\cdot}1\ \mu$ clay fractions were analysed by X-ray diffractometry and total non-exchangeable K determined by flame photometry.

The clay mineralogy of the top- and sub-soils is very similar; the most abundant minerals of the top-soils are listed below. The $< 2\ \mu$ fraction of the Bridget's soil contains dominant montmorillonite and some mica and kaolinite; the same minerals occur in the $< 0{\cdot}1\ \mu$ fraction, but mica is less abundant. The High Mowthorpe $< 2\ \mu$ fraction contains dominant montmorillonite, some quartz and a little vermiculite, chlorite, mica and kaolinite; the $< 0{\cdot}1\ \mu$ fraction contains montmorillonite, mica, more kaolinite than the coarser fraction, but not chlorite or vermiculite. The Trawscoed $< 2\ \mu$ fraction contains dominant chlorite, much mica and a little vermiculite and interstratified mica–chlorite. The $< 0{\cdot}1\ \mu$ fraction contains chlorite, much mica and interstratified mica–chlorite and mica–vermiculite. The Boxworth $< 2\ \mu$ fraction contains dominant montmorillonite, some mica and kaolinite and a little chlorite; there is less mica and no chlorite in the $< 0{\cdot}1\ \mu$ fraction. The Gleadthorpe $< 2\ \mu$ fraction contains dominant kaolinite, much mica and vermiculite and a little montmorillonite and chlorite, and the $< 0{\cdot}1\ \mu$ fraction kaolinite, much interstratified montmorillonite–vermiculite and a little mica.

The responses to fertilisers during long-term cropping showed that most native K is released by the Boxworth soil, intermediate amounts by Bridget's and High Mowthorpe, and least by Trawscoed and Gleadthorpe. Table 1 contrasts the abilities of the soils to supply native K with the amounts of clay- and clay mica–potassium they contain. This ability of all five soils is correlated with the K contents of the $< 0{\cdot}1\ \mu$ fractions, but for only four with the K-content of the $< 2\ \mu$ fraction. The exception is the Trawscoed soil, which is developed in terrace deposits containing mica and chlorite-rich Silurian shales. This soil contains much clay mica, which occurs mostly in the 2–0·2μ fraction, and the soil contains very little fine clay potassium. Thus the ability of the Trawscoed soil to release native K to crops correlates with fine clay potassium, but not total clay potassium. (Ormerod and Weir)

TABLE 1

K-contents of clay fractions as percentages of the whole soil

	$<2\ \mu$ clay		$<0{\cdot}1\ \mu$ clay		Relative ability to supply K to crops
	% clay	% K	% clay	% K	
Bridget's	21·9	0·26	15·8	0·16	++
High Mowthorpe	29·4	0·32	15·9	0·15	++
Trawscoed	33·8	0·98	3·4	0·07	+
Boxworth	39·1	0·80	22·6	0·36	+++
Gleadthorpe	7·7	0·16	2·2	0·03	+

Clay physics

Clay orientation and pore-size distribution. Microscopic examination of thin sections of soils is a useful technique, provided that the sections faithfully preserve the structure of the original moist soil. Current methods of preparing thin sections of soils involve drying and impregnating the specimen with a resin; this greatly decreases the void ratio and contracts the voids by shrinkage. As a result there is considerable risk of introducing spurious features, and because the voids become smaller, penetration of the dried sample by the resin is slow and incomplete. A detailed study of the water-soluble polyethylene glycols of molecular weights 6000–20 000 showed that their aqueous solutions rapidly impregnate moist soils and permit excellent thin sections to be made. They cause only about half the shrinkage produced by drying and impregnation with resin. This is a substantial improvement, but it is obviously desirable to decrease the shrinkage still further. It is also desirable to dry moist soils with minimal shrinkage to be able to measure the pore size distribution and specific surface area. For these reasons we are studying the interaction of clays with organic compounds, with the object of understanding the mechanisms involved during water replacement.

The degree of clay orientation in thin sections is commonly merely observed and recorded photographically, and a less subjective assessment is desirable. Clay orientation can be measured by attaching a photoelectric cell to a petrological microscope and measuring the light transmitted by a clay section at different orientations between crossed polars. This method can be extended to thin sections of soils, provided the area viewed is large in relation to the largest sand grains in the field. (Chapman and Greene-Kelly)

Pore structure of solvent-treated clay aggregates. The methods developed for measuring pore structure, outlined in last year's Report, were applied to studying the effects of particle size, mineralogy, cation saturation, dispersion and solvent treatment, on the pore-size distribution of dry clay aggregates. Aggregates of clays of small particle size can be prepared with pore volumes associated with pores smaller than 10^{-7} m in excess of 1 ml/g. As expected the clay sedimentation volumes in different solvents, measured under carefully controlled conditions, correlate with the pore volumes of the resultant dried aggregates, and clay sedimentation volumes can therefore be used to assess the relative properties of solvents in conferring gel strength by promoting strong particle–particle adhesion. Although pore and sedimentation volumes tend to be greater with solvents of small dielectric constant, as the diffuse double-layer theory predicts, there is better inverse correlation with their spreading coefficients on water. Consequently the type of compound likely to produce minimal shrinkage during replacement of water in clays can be predicted.

The pore-size distributions of aggregates of coarser particles are relatively unaffected by the solvent used in their preparation, because their floc structures are easily destroyed by small stresses, such as those generated by centrifuging. These clays, and soils in which they occur, require careful handling to preserve their original structure.

The way water is replaced by a solvent had no significant effect on the gel strength. However, the gel strength depends on the type of water-miscible solvent used for the initial flocculation, whatever subsequent solvents are used in preparing the aggregates. (Gallavan and Greene-Kelly)

Soil geochemistry

The variability of soils within a soil series. Comprehensive studies on the geochemistry of British soils are few. As part of an examination of the variability of soils within three areas mapped as Denchworth series on Oxford, Kimmeridge and Gault clays in Oxfordshire, Buckinghamshire and Berkshire (see Report of the Soil Survey of England Wales *in Rothamsted Report for 1968*, Part 1), the major and minor element distribution in samples from 30 profiles are being determined. Qualitative analyses by X-ray fluorescence spectrometry show considerable differences between profiles, and also changes with depth within profiles. (Brown and Carolyn Williams)

Toxic elements in municipal composts. We continued to collaborate with Dr. K. R. Gray of Birmingham University, and the Soil Association, in investigating toxic elements in municipal composts (*Rothamsted Report for 1968*, Part 1, 71). Much of the resources of the optical spectrochemical section was devoted to this project.

Before embarking on the plant analyses, the precision of the analytical procedure for the elements was tested. This was necessary because the concentrations of some of the elements (e.g. Co and Sn in potato tubers) are near their detection limits, where precision deteriorates. Replicated analyses of separate sub-samples of plant materials were made, so that both sampling and analytical errors were included. The approximate detection limits are: Cr, Cu, Mo, Ni, 0·01 ppm; Co, Pb 0·02 ppm; Sn, 0·03 ppm; B, 1 ppm; Zn 2 ppm (dry matter).

The results so far available on the 1968 crops of dwarf beans, potatoes and spinach beet show that those grown on plots treated with 100 tons municipal composts/acre contain significantly greater concentrations of some elements than crops from untreated plots. Boron, molybdenum and zinc were significantly increased in beans, and copper and zinc in potato tubers. Spinach-beet leaves showed similar enhancement of cobalt, chromium, nickel, tin and zinc with one or other of the composts; the greatest increase was in cobalt, chromium and tin from one of the Leicester composts. Averaged over four replicated treatments, the increases amount to about 50–100%, probably not yet reaching toxic amounts. Analyses will be made over several years. (Le Riche)

Soil chemistry

Residual effects of fumigation on the mineralisation of soil organic matter. Work on the residual effects of fumigating field soils with formaldehyde (*Rothamsted Report for 1968*, Part 1, 72) was extended to other sites and to include the effects of methyl bromide. Table 2 shows the results obtained with soils from Pastures, Butt Close and Broadbalk sampled, respectively, 6 months, 3½ years and 22 months after fumigation. Except for the soil sampled 6 months after fumigation, unfumigated and field-fumigated soils respired and mineralised nitrogen at similar rates when incubated in the laboratory. In contrast, after exposure to chloroform vapour in the

TABLE 2

Effects of fumigation on the mineralisation of soil organic matter

	Pastures Field treatment with formaldehyde		Butt Close Field treatment with formaldehyde		Broadbalk Field treatment with methyl bromide	
Laboratory measurement*, mg/100 g soil	None	1966 (twice) and 1967	None	1963, 1964 (twice) and 1966	None	1967
Not exposed to chloroform vapour						
O_2 consumed	30·9	34·5	12·2	12·4	24·6	21·9
CO_2 evolved	9·8	10·4	—	—	—	—
N mineralised	0·77	1·14	0·54	0·48	0·11	0·17
Exposed to chloroform vapour						
O_2 consumed	79·1	54·6	23·6	18·3	54·9	38·9
CO_2 evolved	24·3	17·0	—	—	—	—
N mineralised	4·30	2·88	1·23	0·97	2·18	1·63

* Soils incubated for 10 days at 25°C.

laboratory the field-fumigated soils respired less rapidly and mineralised less nitrogen then chloroform-treated soils that had never been fumigated. This difference between fumigated and unfumigated soils was persistent; it was observed in Pastures soil 3 years after fumigation and in Butt Close soil 5½ years after fumigation. It is attributed to a section of the soil biomass being eliminated during field fumigation and not restored completely after several years.

Less nitrogen is mineralised after a second fumigation than after the first, so that when nitrogen limits crop growth, a second fumigation will be less effective than the first, quite apart from any effect on plant pathogens. (Jenkinson and Powlson)

Effects of chloroform vapour, formaldehyde and γ-ray irradiation on soil metabolism. Chloroform vapour was used to demonstrate long-lived changes in the biomass of soils fumigated in the field (see above). Treatment with formaldehyde and γ-ray irradiation gave results broadly similar to those obtained with chloroform, but there were some important differences. Formaldehyde could not be completely removed from soil and its residues were metabolised during incubation. This caused the immobilisation of nitrogen, a pronounced lag phase in respiration, and a rapid evolution of carbon dioxide that tended to mask differences between the evolution of carbon dioxide by different soils. Respiration was slightly greater after irradiation than after exposure to chloroform vapour, but less nitrogen was mineralised. The reason for this difference is not known. (Jenkinson and Powlson)

Bromine residues in Broadbalk from fumigation with methyl bromide. The scorched zones in the crop after fumigation with methyl bromide in September 1967 (*Rothamsted Report for 1968*, Part 1, 72) reappeared in 1969. Wheat plants taken from a scorched zone of plot 3 (unmanured) in July 1969 contained 0·25% bromine; wheat taken in July 1968 from the same place contained 0·42% bromine. Soil from this zone contained 20 ppm bromine in the top 15 cm when sampled in August 1969, whereas soil from an adjoining unfumigated area contained only 5 ppm. Two wet winters were obviously not sufficient to leach the bromine residues from this soil. (Brown and Jenkinson)

Radiocarbon dating of soil organic matter. Table 3 gives eight new measurements of natural and bomb-derived radiocarbon in soils (*Rothamsted Report for 1968*, Part 1, 73). One soil already examined by the National Physical Laboratory was dated by Isotopes Inc.; the agreement was within experimental error. The assumption underlying last year's turnover calculations, that under steady-state conditions the equivalent age of soil organic carbon does not alter with time, was confirmed for plot 3 on Broadbalk; samples taken in 1881 and 1944 differed little in age or carbon content. The incorporation of bomb-radiocarbon into soil continues; the equivalent age of the 1969 sample from Broadbalk plot 3 is less than that of the 1966 sample. The amount of carbonised material

TABLE 3

*Radiocarbon dating of organic matter in Rothamsted soils**

Site	Plot and cropping	Sampling date	Organic, C %	N, %	Carbonised material, %	Equivalent age, years
Broadbalk	Continuous wheat, unmanured (plot 3)	1881	0·94	0·105	0·018	1450 ± 95
Broadbalk	Continuous wheat, unmanured (plot 3)	1881	0·94	0·105	0·018	1385 ± 140†
Broadbalk	Continuous wheat, unmanured (plot 3)	1914	0·83	0·097	0·020	1545 ± 95
Broadbalk	Continuous wheat, unmanured (plot 3)	1944	0·93	0·100	0·016	1305 ± 95
Broadbalk	Continuous wheat, unmanured (plot 3)	1966	0·96	0·107	–	875 ± 120†
Broadbalk	Continuous wheat, unmanured (plot 3)	1969	0·93	0·101	0·025	520 ± 95
Broadbalk	Continuous wheat, with N, P and K (plot 8)	1944	1·03	0·109	0·027	1450 ± 95
Broadbalk	Continuous wheat, with N, P and K (plot 8)	1969	1·09	0·113	0·022	550 ± 95
Barnfield	Near drain gauge: mixed arable	1870	1·40	0·148	0·054	1550 ± 100
Barnfield	40 inch drain gauge: fallowed 1870–1969	1969	0·76	0·086	0·018	1480 ± 105

* All soils sampled 0–9 inches (0–23 cm): all decalcified with dilute hydrochloric acid before analysis.

† Measured by the National Physical Laboratory: all other radiocarbon measurements by Isotopes, Inc.

such as coal or charcoal is less than 0·03% in all the Broadbalk samples so far dated.

The Barnfield drain gauge results are puzzling. The drain gauges are 4 sq m areas of undisturbed land from which weeds were removed as they appeared, since 1870. In 1870 the decalcified soil contained 0·148% N and in 1969 0·086% (Table 3). If in 1870 the soil contained a stable fraction, together with a larger decomposable one, as is usually assumed, the 1969 sample should give a greater age than the sample taken in 1870. However the equivalent age of the soil carbon has changed little, despite the loss of organic matter. Assuming that the entry of fresh organic matter, and hence of bomb radiocarbon, is negligible in the drain gauge soil, these results suggest that the organic matter decomposed between 1870 and 1969 must have been of roughly the same equivalent age as that remaining in the soil in 1969. (Jenkinson)

Soil organic matter–trace element reactions. Continuing our study of trace element–organic matter interactions (*Rothamsted Report for 1968*, Part 1, 74), the rates of dissolution of the oxides of Fe, Mn, Cu, Co, Ni, Zn and Pb by aerobically decomposing lucerne were measured. Very little water-extractable Fe or Mn is formed. Except for Cu, the extent of solution of the other elements is more or less constant after 1 month's incubation. Large amounts of extractable Cu are formed during the first month but about half of this reverts to an insoluble form during the second month, presumably because of fixation on insoluble organic matter. Continued incubation for 4 months causes no further change in the amount of Cu mobilised.

On the basis of the number of atoms, the extent of mobilisation under aerobic conditions varies as Cu > Ni > Co > Zn, Pb ≫ Mn, Fe, which is quite different from the order obtained with the corresponding anaerobic system (*Rothamsted Report for 1958*, 67).

The small amount of extractable iron is completely non-dialysable against water (Visking cellulose). For the other elements, throughout 6 months' incubation, between $\frac{1}{4}$–$\frac{1}{3}$ of the dissolved metals are in a non-dialysable form.

The influence of the insoluble organic matter in fixing dissolved metals was eliminated by reacting the oxides with water extracts of lucerne previously incubated for 0–6 months. Judged by the amounts of metal dissolved in the presence of toluene in 4 weeks, very little Fe is dissolved by extracts of either fresh or rotted lucerne. Relatively large amounts of Ni, Co, Cu, Zn and Pb are dissolved by an extract of undecomposed lucerne (as much as 11 mg Ni/g lucerne), but except for Cu the activity of the extract decreases sharply during the first 2 months of rotting, thereafter remaining more or less constant. With Cu the activity of the extract increases steadily for the first 3 months and then decreases sharply. In these reaction solutions, the absolute amounts of non-dialysable Cu, Zn and Ni (the only elements for which results are at present available) do not differ significantly between the 0–6 month preparations, despite the large difference in the total amount of dissolved metal. As the amount of humified material increases during rotting, this observation supports the view that the importance of pre-formed humose material as a mobilising agent is less than that of the labile intermediates involved in the process of humification.

Table 4 gives the amounts of the various elements dissolved from their oxides by lucerne and wheat straw after rotting for 10 months, and the proportions of dialysable metal in the extracts.

TABLE 4

Solution of trace metal oxides during aerobic incubation with lucerne or wheat straw for 10 months

μg metal/g original plant matter

	Lucerne			Wheat straw		
		% dialysable			% dialysable	
	Total dissolved	H_2O	0·05 N acid	Total dissolved	H_2O	0·05 N acid
Fe	93	Nil	44	46	Nil	23
Mn	39	14	47	—	—	—
Cu	1530	13	95	20	Nil	65
Ni	2320	30	95	—	—	—
Co	1660	20	60	960	58	98
Zn	1410	27	94	400	76	93
Pb	570	27	81	270	22	53

Relatively large amounts of the elements are immobilised by reaction with the insoluble organic residues (Table 5). To obtain these values the organic residues were separated from the bulk of unreacted oxide by sedimentation in water and washed with hot water to remove microbial gums. After drying from methanol-benzene the remaining traces of oxide were removed by repeated centrifugation in carbon tetrachloride.

TABLE 5

Metal contents of lucerne residues before and after extraction with 0·1N acid

μg metal/g dry residue

	Total	After 0·1 N acid
Mn	3660	2530
Cu	3760	740
Ni	5670	860
Co	4560	860
Zn	3140	240
Pb	1450	190

Because the appreciable water-solubilities of the oxides preclude their use in experiments such as these, metallic Mo and V were used in preparing solutions of these elements. Both were very reactive, and approximately 60 and 40 mg respectively of Mo and V were mobilised per g lucerne during 6 months. In contrast to the other elements, the dissolved Mo and V were completely removed by dialysis against water, and V also dialysed completely against dilute acid. Much Mo remained after dialysis against dilute acid, but this was completely removed by subsequent dialysis against neutral ammonium acetate.

In experiments with pea plants grown in acid-washed quartz, in collaboration with E. C. Humphries, Botany Department, manganese dissolved by anaerobically decomposing lucerne was completely available to the seedlings, whereas the non-dialysable fraction of aerobically mobilised Mn seemed to be unavailable—Table 6.

TABLE 6

Uptake of Mn by pea plants

Mean of 12 plants

Source of Mn	Weight of plant, g	Mn content of plant, μg
$MnSO_4$	1·51	184
Anaerobic Mn	1·65	156
Aerobic Mn	0·96	73
No Mn	0·93	76

A Ca-saturated ferruginous soil clay sorbed trace metals from the extracts, to the extent of several mg/g clay. Humic, as opposed to fulvic, acid is preferentially sorbed by the clay, and removing humic acid in this way significantly increases the absolute amount of fulvic acid in the residual solution. A possible explanation of this effect is that fulvic acid is coprecipitated with humic acid when the extract is acidified. (Bloomfield, Kelso, Maria Piotrowska and Pruden)

The oxidation of pyrite in relation to the formation of acid sulphate soils and of ochre in field drains. Enrichment cultures of Fe^{2+}- and S^{0}-oxidising microorganisms were obtained from acid sulphate soils from Malaya, and from ochre deposits in field drains in Britain. The oxidation of FeS_2 was promoted by these cultures, just as by a pure culture of *Thiobacillus ferrooxidans* obtained from the National Collection of Industrial Bacteria. *T. thiooxidans* seems not to exert any such action.

Moist pyrite oxidises readily when exposed to the atmosphere, but much more slowly than in the presence of *T. ferrooxidans*. Ferrous iron persists in solution for long periods in the chemical process, but little or none can be detected when *T. ferrooxidans* is active. In relation to the $Fe^{2+} : Fe^{3+}$ ratios of the reaction products, the rate of oxidation of pyrite in a Malayan acid sulphate soil and a sand from Lincolnshire were compared before and after γ-ray sterilisation and inoculation with *T. ferrooxidans*. It seems that bacterial oxidation was the dominant process with the sand, but not with the Malayan soil, from which ferrous oxidising bacteria were isolated only after a very long lag phase. This soil was previously air-dried; this may have affected the activity of the bacteria and our results may not reflect the behaviour of the soil in the field.

Although ochre formation is widely recognised as a problem in draining pyritic soils, the concomittant danger of acidification does not seem to receive adequate attention. At one site in Lincolnshire, a horizon of pyritic sand underlying a 5–6 in. layer of surface peat had a pH value around 3, and large bare patches of soil have developed since drains were installed. It is interesting to note that deposits of jarosite as extensive

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as those of the tropics were observed in spoil from drainage ditches in this area.

Pons and Zonnenveld (*Publs int. Inst. Ld Reclam. Improv., Wageningen* (1965), No. 13) remark that irrigating pyritic soils with brackish water causes less acidification than irrigating with fresh water. We find no significant difference between the acidities developed by a pyritic soil aerated in the presence of distilled water or 1·2% NaCl solution.

We hope to collaborate with the Field Drainage Experimental Unit of the Ministry of Agriculture in measuring the rate pyrite oxidises in undisturbed soil cores, and the effects of liming in limiting acidification, and on immobilising iron within the profile. (Bloomfield, Poon and Pruden)

Sulphur compounds in the mud of Lake Victoria. It has been suggested that Lake Victoria mud contains abnormally large amounts of organically combined sulphur (Hesse, P. R., *Hydrobiologia* (1957) **11**, 29). This suggestion was based on the determination of organic sulphur as sulphate formed by oxidation with hydrogen peroxide, so that pyrite sulphur would be included. This possibility was noted by Vallentyne (*Limnol. Oceanogr.* (1963) **9**, 16), who failed to detect pyrite in the mud. The abnormally small C : S ratios that are implicit in Hesse's values, and the apparent absence of pyrite from material such as this, seemed to justify re-examination of the mud.

No pyrite was detected in a microscopic examination of the untreated mud (kindly supplied by Dr. J. Okedi of The East African Freshwater Fisheries Research Organisation), but a few spherules were seen after dehydrating the mud with methanol.

Fractionation according to particle size and density gave a slight concentration of sulphur in the heavy fraction (s.g. $> 2{\cdot}3$) of the $< 53\ \mu$m fraction, but the sulphur content of the supposedly purely organic light fraction was still considerable. Pyrite was detected, microscopically and by X-ray diffraction, in the residue left after digesting the light fraction with hydrochloric and hydrofluoric acids. The sulphur content of this residue accounted for 57·5% of that of the original light fraction, although some pyrite must have been lost during the acid digestion; the organic sulphur content of the mud is therefore much less than it was thought to be, and there seems no reason to assume that the organic matter possesses any unusual features. (Bloomfield, Brown and Catt)

Anthocyanins of conifer seedlings. Conifer seedlings grown in soils deficient in potassium form anthocyanins at the tips of their shoots during the spring. Similar pigment production ('purpling') occurs during the autumn in plants grown on potassium-rich soils. At the request of the Forestry Commission, pigmented Lodgepole pine plants were examined to identify anthocyanins formed during autumn and the results compared with those obtained with plants grown on potassium-deficient soils.

The plants chosen were grown at Kennington, Oxford, from seeds originating in Alaska and the west coast of the U.S.A. The potassium content of plants selected for weak, medium and strong purpling showed little variation from plant to plant, ranging from 0·57% to 0·66%, with no correlation between potassium content and degree of purpling. Four anthocyanins were identified, and the amounts obtained after extracting the plants with methanol/HCl depended on the origin of the seeds. Comparing these results with those previously obtained with Sitka spruce plants grown on potassium-deficient soils, it seems that the pigments may be the same. Delphinidin 3-glucoside, cyanidin 3-glucoside, cyanidin 3,5-xyloglucoside and peonidin 3,5-xyloglucoside, were isolated from Lodgepole pine. There was too little Sitka Spruce material to examine the nature of their pigments in detail.

Lodgepole pine plants obtained from seed originating in Central British Columbia contain twice as much autumn-formed pigment as plants grown from the western United States seed, although the average dry weight of the latter is 1·4 times larger. Values of these two properties for the plants grown from seeds of the other regions are intermediate between these extreme values. (King)

Apparatus and techniques

X-ray diffraction. A new Philips X-ray generator, PW 1011 and diffractometer, PW 1050, was installed during the year. After some initial difficulties the instrument has been in use for 6 months and more than 1000 diffraction patterns were made in connection with the mineralogical work of this department and for the Soil Survey of England and Wales. (Brown)

X-ray fluorescence spectrometry

Mercury content of wheat seeds. Mercury is a component of fungicides used as dressings on cereal seeds, and there has been concern about the uneven distribution of fungicide on different seeds. A quick method of moderate precision was required to measure the Hg in enough individual wheat seeds for the distribution from seed to seed within a batch to be determined. We find that when softened by treatment with dilute ammonia or water, individual seeds ranging in weight from 10 to 40 mg, can be pressed between steel plates on to discs of filter paper to produce thin film specimens for examination by X-ray fluorescence spectrometry. Tests with filter papers impregnated with known amounts of a mercury salt showed that a sensitivity of about 0·1 μg Hg could be obtained by measuring the intensity of the HgL radiation using a molybdenum anode X-ray tube and a LiF (200) crystal in a total counting time of 200 seconds. This was confirmed by adding standard amounts of mercury solutions to untreated seeds. Both peak and background count rates must be measured because the background count rate is proportional to the weight of the wheat seed. The method is rapid enough to analyse more than 100 seeds per day.

More than 700 seeds representing batches of treated seeds were analysed; the Hg content of individual seeds ranged from less than 0·1 μg–1 μg per seed, with occasional values as large as 5 μg. There is no chemical information by which the accuracy of the method can be estimated, but the

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reproducibility of points on the calibration line obtained with samples prepared by adding mercury to untreated seeds indicates an accuracy of about ± 0·1 μg. (Brown and Harden with Lord, Insecticides) See also Insecticides Report.

Determination of cation exchange capacity. We frequently need to determine the cation exchange capacity of small samples of clays or similar materials. Methods using ammonium ions as the exchanged species have been used but these may be inaccurate because replacement of other cations by ammonium is sometimes incomplete. The use of divalent cations is preferable, and the determination of total Sr in thin films of Sr-saturated samples was studied. Sr-saturated clays were dispersed and filtered on to a weighed membrane filter. The resulting filter + clay was dried, reweighed to obtain the weight of clay, mounted between two layers of thin Mylar film and used as the sample for spectrometry. The intensity of Sr $K\alpha$ radiation was compared with standards. Less than 10 mg of clay is needed and the lower detection limit is less than 0·01 μg equivalents. Because the weight varies with the relative humidity, the main error in determining cation exchange capacity by this method is in weighing 5–10 mg of clay accurately. Investigations are continuing to find the best standard conditions for weighing. (Brown, Newman and Carolyn Williams)

The determination of major elements in silicates. The two computer programmes used to obtain element percentages from X-ray intensities were combined into a single programme written by R. Kanaris-Sotiriou for the ICL 1907 computer at the University of Hull. The combined programme was modified to run on the ICL 4.70 computer which will be at Rothamsted next year. In conjunction with punched tape output from the spectrometer, this programme allows the computer to calculate and print results corrected for dead time and matrix effects. (Brown and Coles)

Miscellaneous analyses. X-ray fluorescence analysis was used to determine trace elements in the experiments of Bloomfield *et al.* described above. V, Mn, Fe, Co, Ni, Cu, Zn, Mo, Pb and U were determined directly on the extracts by comparison with standard solutions in water. Detection limits are in the range 0·4 to 3 ppm. The direct analysis of the extracts takes much less time than chemical methods, which involve considerable pretreatment.

The Zn (900–2300 ppm), Hg (8–38 ppm), As (2–84 ppm), Se (1–11 ppm) and Cd (not detected) in 40 samples of town composts was determined. The determination of these elements by optical emission spectroscopy is difficult or impossible. (See report by H. H. Le Riche.)

Mg, Al, P, S, K, Ca, Mn, Co, Ni, Cu and Zn were determined in samples of rye grass, onion and liquid amber grown in pots containing soils inoculated with fungi and bacteria. Only semiquantitative analysis was possible because of the small amount of material. (For Soil Microbiology Department)

Our method for determining total sulphur in soil (*Rothamsted Report for 1967*, 80) was applied to mud from Lake Victoria, and to six soils from Wareham, for the Chemistry Department. (Brown, Carolyn Williams and Harden)

Liquid nitrogen level controllers. Measurements of nitrogen sorption by compact clay aggregates often require many hours to reach equilibrium. Two automatic liquid nitrogen level controllers were made that enable our adsorption microbalance to be used during the night. Their operation depends on the increase of resistance of a semi-conductor diode when immersed in liquid nitrogen.

Recorders. Flat-bed potentiometer recorders suitable for attaching to amplifying systems with negative feedback were evaluated. The choice of recorder is extremely critical and the amplifier and recorder require careful matching. When this is not done, expensive filter circuits have to be inserted between the two to prevent interaction.

Soil consolidation apparatus. To prepare soil samples reproducibly for clay orientation studies, a soil consolidation apparatus was built. The soil sample, enclosed in a 6·35 cm diameter ring, is immersed in water and subjected to known loads by compression between porous discs. The degree of consolidation is measured by a clock gauge. (Chapman, Gallavan and Greene-Kelly)

Determination of molecular weight with Sephadex gels. Earlier attempts to fractionate leaf extracts and decomposition products of plant material with the dextran gel Sephadex were reported last year. It was hoped that fractions of increasing molecular weight would be isolated by passing an aqueous solution of the test material successively down columns of Sephadex G-10, G-15, G-25, G-50 etc. The capacity of the more tightly cross-linked gels (e.g. G-10, G-15) to adsorb certain components of the extracts, particularly polyphenols, made the method unworkable. Promising results were obtained by using 50% aqueous acetone instead of water as the eluent, and by using only Sephadex G-25 (Medium) gel (Somers, *J. Sci. Fd Agric.* (1967) **18**, 193–196). Adsorption effects were greatly decreased with this system, but model compounds that from their molecular weights were expected to be retained, were excluded from the gel. Titan yellow, M.W.695, was one such substance. Sephadex LH-20, a gel made specifically for use with a wide range of organic solvents, behaved in the same way.

The scanty literature dealing with the separation of polyphenols and flavonoid compounds on Sephadex G-25 with 50% acetone as eluent, or comparable concentrations of alcohol, assumes that the gel just excludes a compound of molecular weight about 2000. Our experiments show that this is not so. To determine the molecular weight that would just be excluded, the elution volumes of a series of model compounds of *M* 126–695 were determined, and the results plotted as Elution volume (Ve)/Column bed volume (Vb), as ordinate, against log molecular weight, as abscissa. Compounds excluded from the column at the void volume (Vo), i.e. the volume of eluent required just to elute a solution of Blue Dextran, *M* 2 000 000, give a constant value for Ve/Vb, which is then Vo/Vb. When a compound is excluded, the line joining points of different Ve/Vb will meet the horizontal line Vo/Vb, giving the required molecular weight. See Table 7.

TABLE 7

Behaviour of model compounds on Sephadex G-25 with 50% acetone as eluent

Weight of Sephadex G-25: 64 g
Bed volume (V_b): 175 ml
Void volume (V_o): 62 ml

Compound	*M*	log *M*	Ve/Vb
Pyrogallol	126	2·1004	0·596
2,2′-Dipyridyl	156	2·1931	0·548
Gallic acid	180	2·2553	0·538
PAR	237	2·3747	0·428
Catechin	290	2·4624	0·486
m-Digallic acid	342	2·5340	0·383
Phenol red	354	2·5490	0·397
Aluminon	473	2·6749	0·378
Bromo cresol purple	540	2·7324	0·355
Bromo thymol blue	624	2·7952	0·355
Titan yellow	695	2·8420	0·355
Chinese gallotannin	approx. 1800	—	0·355

Vo/Vb = 0·355

Most of the points fall satisfactorily near the Ve/Vb line that cuts the abscissa at about *M*. 510. This value is surprisingly small; possibly much of the material previously considered to be of large molecular weight may contain components of molecular weights as small as 510.

Small adsorption effects do not interfere with the method, and compounds that are adsorbed can be recognised by their anomalous Ve/Vb values. (King)

The semi-micro analysis of clay minerals (major elements). Existing methods and colorimetric reagents used to analyse silicate minerals were investigated and an improved scheme of semi-micro analysis for clay minerals developed.

Silica and alumina are determined as molybdenum blue and as the calcium-Alizarin Red S complex respectively, after fusing a 50 mg sample with sodium hydroxide. Titanium is determined with tiron, total iron with 2,2′-dipyridyl, calcium with glyoxal bis (2-hydroxy anil), magnesium with Titan yellow, phosphorus as molybdenum blue and manganese as permanganate, all on a hydrofluoric-sulphuric acid digest of a 50 mg sample. Sodium and potassium are determined flame-photometrically on the same digest. Ferrous iron is determined separately. Additional methods for determining total water, total sulphur and fluorine are indicated. Calcium is determined colorimetrically and specifically.

By improving the quality of commercial Alizarin Red S, the sensitivity of the aluminium determination was increased, doubling the length of linearity of the calibration graph. Because of its variable composition, Titan yellow has fallen into disrepute for estimating magnesium. It can now be easily synthesised in a reproducibly pure form.

The sensitivities of the determinations of SiO_2 and TiO_2 are improved by measuring the absorbancies of their complexes at the wavelengths of maximum optical density.

The scheme is applicable to samples of 100 mg minimum weight. (King and Pruden)

The assay of dithizone for use in determining zinc and lead. Dithizone (diphenyl thiocarbazone) is widely used for the colorimetric determination of zinc and lead. Commercial samples vary greatly in composition and often need purification. The usual method is to extract pure dithizone with ammonium hydroxide from a carbon tetrachloride solution of the crude material. The combined extracts from several treatments with ammonium hydroxide are acidified and the pure dithizone dissolved in fresh carbon tetrachloride. No determination of the concentration of pure dithizone so formed is recommended in the analytical literature; it is suggested that a 0·125% solution of the crude material be taken in the expectation that a 0·100% solution will remain after purification.

Various commercial samples of dithizone were examined by thin layer chromatography and by spectrophotometry to see whether purification was necessary. Thin layer chromatography on activated Kieselgel G with benzene as solvent resolves crude dithizone into a green spot (dithizone), a yellow spot (oxidised dithizone) and a yellow-green spot, probably a partly-oxidised product. The relative sizes of the spots indicate the purity of the sample.

In carbon tetrachloride solution the spectrum of dithizone in the visible region gives maxima at 440 and 617 nm, the ratio of the lower- to the higher-wavelength peak being 65%. At 617 nm the optical density of 1 mg pure dithizone in 100 ml carbon tetrachloride is 1·25. The oxidised dithizone has no maximum at 617 nm but absorbs strongly at 409 nm; the optical density at 617 nm is therefore a measure of the purity of the product.

The purities of eight commercial samples of dithizone were determined spectrophotometrically. Values ranged from 39 to 98%; the best sample was labelled merely as a metal indicator, not as an analytical grade colorimetric reagent. The smallest acceptable purity was not determined, but samples of 86% purity can be used without treatment; the lengthy purification process could often be avoided if a spectrophotometric assay were made. (King and Pruden)

Staff and visiting workers

J. A. Catt attended the 8th INQUA Congress in Paris. Mrs. Maria Piotrowska returned to Poland after a year's work on trace element–organic matter reactions. Dr. J. Walczyna, of the Institute for Land Reclamation and Grassland Farming, Falenty, Poland, spent 3 months in the department, studying the fractionation of soil organic matter. Dr. J. Thorez of the Geology Department of The University of Liege worked for 6 weeks in the Pedology and Soil Survey Departments, studying the techniques of making thin sections of soils. Mr. Y. C. Poon, of Harrisons & Crossfield (Malaysia) Ltd., spent 8 weeks in the department, studying acid sulphate soils.