Report for 1970 - Part1

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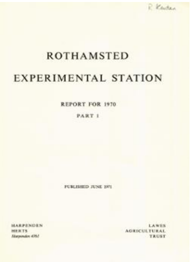

Pedology Department

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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.

Alkali feldspars and micas are the commonest K-bearing minerals in soils, but only micas are considered to release appreciable amounts of K on weathering. K-release in soils should therefore be related to the behaviour of mica-group minerals when subjected to a stress, for example a concentration gradient, that tends to withdraw K from the structure. We have studied the reactions under K-stress of clay fractions from British soils developed on various parent materials, and compared their behaviour with that of individual minerals. Soil mica particles $>1\ \mu m$ behave similarly to mono-mineralic micas, whereas fine clays, $<0{\cdot}5\ \mu m$, often differ from coarse clays, both structurally and in their ability to release potassium, and we are investigating fine clay fractions of different reactivities.

To assess how, or whether changes in agricultural practice affect soil structure, methods are needed to detect incipient breakdown of the structure. So that pore-size distributions and other physical properties can be measured on the soil in its field state, we are seeking methods of drying samples without causing significant structural changes.

Geochemical studies of variability within a soil series continue, in collaboration with the Soil Survey of England and Wales. Work on molybdenum and vanadium casts doubts on the statistically based assumption that organic matter is chiefly responsible for these elements accumulating in sediments.

Our long-term investigations of the effects of fumigants on respiration and on the decomposition of organic matter in soils is continuing; bromine can be retained for a long time after a soil is fumigated with methyl bromide; the amount of bromine retained immediately after fumigation is correlated with the organic content of the soil. Wheat grown three years after fumigation contained much bromine. The very small amounts of carbon disulphide released by some kinds of rubber bung can prevent nitrification in incubated soils.

Mineralogy

Interstratified clay minerals. A clay mineral assemblage may consist of a single mineral or a mechanical mixture of minerals in which each crystal is composed of identical layers. Because of the structural similarities of clay minerals, interstratified (or mixed layer) minerals exist, in which individual crystals are made up of elementary layers of two or more types. Minerals of this kind are a common component of soil clays and often occur as intermediate products of mineral alteration.

Using Fourier transforms, MacEwan (*Kolloid-Zeitschrift* (1956), **149**, 96–108) developed a method for analysing X-ray scattering from interstratified lamellar materials. The calculation gives a probability function, W(R), which is the relative frequency of finding layers separated by a distance R. This can be interpreted in terms of the nature and relative abundance of the component layers, and the sequence in which they are superposed. Although MacEwan's method has been widely used, its assumptions and approximations have not been critically evaluated.

Computer programs were written and used to calculate W(R) probability functions for several interstratified clays, to find the effect of including scattering from small amounts of impurity phases not recognised as such, of using different models for the structure of the layers, and of the effect of small or zero values of the layer structure factor. We also compared the results obtained by MacEwan's treatment, which uses single peak intensities only, with a more rigorous treatment that uses the continuous intensity distribution. Different results are obtained depending on the choice of variables, and consequently unique solutions are not obtained. The results are all approximations to the true distribution, and the best procedure is to make several calculations based on the various possibilities, and to deduce the most probable distribution function from the range of results.

The methods were applied to an interstratified mica–montmorillonite from the Old Red Sandstone, Monmouthshire, and to two nearly regularly interstratified chlorite–montmorillonites from Llanvirnian breccia from the Huy region, Belgium. They were also used to analyse diffraction patterns from material formed when potassium is resorbed on altered micas; the results of these calculations confirm previous intuitive interpretations. (Brown, Madajdik and Rayner)

Formation of chlorite from biotite in the laboratory. A widespread pedogenetic mineral alteration in moderately acid soils involves the development of chlorite-like minerals from micas by replacing the potassium of micas by aluminium hydroxide interlayers of various degrees of perfection. These interlayers confer important properties on the clay complex; for example, they can affect the cation exchange capacity, the sorption of potassium and the buffering action of the soil. In soils, these minerals are usually produced from dioctahedral micas and are rarely, if ever, pure enough for detailed study. The relative ease with which potassium can be removed from biotite by cation exchange suggested that materials analogous to those formed in soils might be prepared by treating biotite with aluminium chloride solutions at a pH at which the aluminium is considered to be unpolymerised.

Biotite was altered in boiling 0·2*M* $AlCl_3$ solution, pH 3·6, renewing the solution nine times in 112 hours. This treatment extracted almost all the potassium from the biotite. The product is a chlorite-like mineral with hydroxy–aluminium interlayers. Its basal spacing of 14·0 Å is not changed by ethylene glycol treatment or by potassium saturation. Heating at increasing temperatures produces increasing collapse, reaching 10·1 Å spacing at 750°C. Material heated in air to 550°C or less rehydrates readily. The interlayer material cannot be exchanged by washing with salt solutions, but it can be extracted by boiling in sodium citrate solution at pH 7·3. This treatment produces a vermiculite-like product, having a 14·4 Å spacing when Mg saturated and a 10·3 Å spacing when K saturated. The properties of the artificially altered biotite are similar to those of the mineral intermediate between chlorite and vermiculite that has been found in various soils.

Another series of alteration experiments determined how duration of treatment in boiling $AlCl_3$ affected the degree of development of aluminium hydroxide interlayers. Three samples were extracted for 1, 5 and 22 days respectively. When heated, the interlayer material collapses less readily with increasing time of treatment; this probably reflects increasing structural regularity of the interlayer hydroxide. (Brown, Nagasawa and Newman)

Alteration of potassium minerals in soils

Muscovite. Mica-like minerals in clays and fine silts are often dioctahedral, so that muscovite is probably a better reference mineral than the trioctahedral biotite–phlogopite group. Our preliminary work therefore included extraction of K from muscovite with Na- and Ba-tetraphenylboron (*Rothamsted Reports for 1966*, 64 and *for 1967*, 66) and with aqueous solutions of Li, Na, Mg, Ca, Sr and Ba salts at several temperatures. At room temperature the apparent order of effectiveness is Na > Ca = Mg > Li > Sr > Ba; the order is reversed at boiling temperatures, when Ba is most effective. Replacement of K is very sensitive to K impurities in the reagent, and some anomalies previously encountered were traced to impure reagents. The importance of this factor was appreciated only since we acquired the Perkin Elmer flame spectrophotometer, which permitted the purity of the reagents to be determined. As boiling $BaCl_2$ solutions are most effective for exchanging K from muscovite, this reagent was used in the work with soil clays. Boiling seems not to affect the structure of micas adversely and there was no evidence that muscovite was partially degraded to boehmite, as reported by von Reichenbach and Rich (*Clays & Clay Min.* (1969), **17**, 23). In addition to exchanged mica, a white reaction product sometimes forms with boiling NaCl solutions; infra-red examination showed this to be an amorphous silicoalumina. This product never formed with $BaCl_2$.

Feldspars. Three potash feldspars were treated with boiling $BaCl_2$ solutions to see whether this would extract K from feldspars under the conditions used to extract K from muscovite. The feldspar extracts contained only a tenth to a twentieth as much K as those from muscovite, showing that mica is preferentially attacked.

Barium-saturated clays. Very little is known about the structure and properties of Ba-saturated clays, so X-ray diffraction traces were taken of some Ba-saturated reference minerals, to assist in identifying the products formed by treating soil clays with $BaCl_2$ (Table 1).

TABLE 1

Basal spacings of Ba-satured layer silicates (Å)

	Air dry	Wet	Heated to 300°C	Ethylene glycol treated
Wyoming bentonite	12·36	18·9	9·85	16·96
BH 137 montmorillonite	12·45	18·4	9·98	16·68
Altered muscovite	12·22	14·25	—	13·4*

* After 4 hours, non-rational; expands further after longer treatment.

Soil clays. Ten soils containing 2–5% K in their clay fractions were selected; to avoid the need to destroy organic matter, samples from lower horizons were used. Whole clay fractions (<2 μm) were separated by sedimentation, using minimal amounts of 'Calgon' and brief ultrasonic agitation to disperse the clays. Each fraction was treated five times with $MgCl_2$ and the K in each extract determined. K removed in the first extract was equivalent to the conventional 'exchangeable' K and varied over a seven-fold range between soils; it was not related to the K content of the clay fraction. Exchange capacities of the clays were measured by extracting the Mg-treated clays with $CaCl_2$ and determining Mg in the extracts. X-ray diffraction traces of the clays before and after Mg/Ca treatment showed no detectable structural changes during cation exchange cycles. K was most concentrated in the first $CaCl_2$ extract, smaller in the second and third extracts, but did not decrease further in subsequent extracts. Activity ratios ($K/Ca^{1/2}$) in the third and fourth extracts ranged less widely between soils (two-fold range) than did exchangeable K.

After the exchange cycle, each clay was treated with $BaCl_2$ at boiling point (1 g clay per 2 litre solution); five such treatments extracted 35–60% of the total K in the clays. On the evidence of the X-ray diffraction traces, the original clays contained mica in amounts ranging from minor to dominant proportions; little mica remained after reaction and there was a corresponding increase in the content of high-charge swelling minerals, yet 25% or more of the original K remained in the clays. However, poorly crystalline materials, apparently interstratified layer silicates containing some mica layers, also occurred in most of the clays, and these were much less altered by the $BaCl_2$ treatment. The nature of these relatively unreactive clay minerals is being investigated. (Newman)

Ordering of octahedral cations in micas. The optical properties of micas and their abilities to exchange interlayer potassium depend on the cationic composition of the octahedral layers, which commonly may contain Li, Mg, Fe^{2+}, Al, Fe^{3+} and smaller proportions of Mn and Ti. This interrelationship has been explained on the probable groupings of these cations, three at a time, in the sites adjacent to the octahedral hydroxyls; with cations enough to occupy all or nearly all the octahedral sites, it has been assumed that these cations distribute randomly, but this assumption has the serious limitation that it generates appreciable populations of groupings, such as Al_3OH, that, for electrostatic reasons, seem improbable. We modified this model so that constraints imposed on a random distribution prevent the development of these improbable combinations. A computer program was written that generates a random sequence of symbols representing atoms in the required proportions, in effect, placing the symbols on a trigonal lattice. The lattice is scanned three cations at a time, and any cation that produces an impermissible combination is interchanged with a more suitable cation from the yet unscanned part of the lattice. Permitted combinations were decided after a detailed application to the mica structure of Pauling's rules for the structure of ionic compounds.

Probabilities of cation combinations calculated with these restraints differed from those expected from unconstrained random distribution, and a print-out display of the rearranged lattice showed that the trivalent atoms were partially ordered into chains based on vacant cation sites. These results may explain some of the properties of micas. (Newman, with Kzranowski (Statistics))

The determination of the structure of phlogopite mica by neutron diffraction. The neutron diffraction intensities from a phlogopite crystal (*Rothamsted Report for 1969*, 74) were analysed further. The calculations were extended from the 68 reflections in the *0kl* zone to the 293 reflections in the *0kl*, *hhl* and *1kl* zones with neutron intensities significantly greater at the 1σ level than the background. The previously proposed approximate structural model for phlogopite was altered by cycles of least squares refinement until the disagreement factor, R, decreased from 12% to 6·2%. This small R factor was for a model with a total of 67 variable parameters for the nine crystallographically different atom sites. The parameters described the position of the site in the cell, the anisotropic vibration of the atoms and the proportion of sites occupied. Statistical tests showed that the measurements were significantly better fitted by a model with sites not all quite filled, but at no one site was the proportion of atoms missing significantly different from that expected from the chemical analysis. The hydrogen atom site has an occupancy of 0·64 with a standard deviation of 0·05 calculated from the neutron diffraction measurements, and this is not significantly different from the expected proportion of $OH/(OH + F)$, 0·72 from the chemical measurements; all the hydrogen atoms are therefore probably at this one type of site.

The structure factors calculated for this model were compared with the measurements, using a computer program RANGER that groups the reflections to show whether any group has a systematically large error. This showed that errors for all the reflections were larger than would be expected were they from neutron counting errors alone, perhaps because of the slightly bent and split crystal that reflected some neutrons in the directions used to count the background intensity, and that the errors in the very weak reflections were even greater. The R factor for the 256 reflections with intensities more than three times the standard deviation in intensities expected from the counting statistics is 4·9%, but is 32% for those weaker reflections with intensities only 2–3 times the standard deviation.

The O–H bond length calculated from these positions is 0·926 Å, with a standard deviation of 0·017 Å. The hydrogen atom vibrates more than the heavier atoms, but its bond tends to confine it to a roughly umbrella-shaped region rather than the ellipsoid used in the model structure. Busing & Levy (*J. Chem. Phys.* (1957), **26**, 563) found that in $Ca(OH)_2$ the O–H bond length estimated from the ellipsoid models as 0·936 Å was better described as 0·984 Å when this motion was allowed for; so phlogopite probably has a bond length of about 0·97 ± 0·02 Å. The other near neighbours of the H atom are magnesium ions in the octahedral layer, at 2·36 Å, and three oxygen atoms of silica tetrahedra at 2·80 Å, very nearly in Van der Waals contact. The potassium ion is 3·10 Å distant, or 3·05 Å when corrected for vibration.

Computer program for crystallography. The Orion computer is soon to be given up and the crystallographic computer programs written for it will not be useable on the new ICL 4-70. Programs in Fortran with similar but improved facilities have been obtained—but the dialect of Fortran provided on 4-70 differs slightly from that of the programs.

Transfer to the 4-70 was made in two stages. The programs were amended to run on the IBM 360/50 at Edinburgh, using the link installed at Rothamsted. Most of the separate subroutines making up the programs were correct and acceptable to the 360/50 computer, but there were errors in the transfer of numbers between subroutines and errors also occurred when several programs shared the same files on the magnetic disc. Many test runs were needed to correct the errors but a set of three programs was developed and used to complete the calculations on the phlogopite neutron diffraction data.

Punched card copies of these programs are being compiled and attempts made to run them as part of the development of the 4-70 multijob system. The least squares program was compiled with only three changes, necessary because the subscripts were too complicated to be accepted by the 4-70 Fortran compiler. The final set of crystallographic programs will give a wider range of results, and the graph drawing and visual display of the new system will make it easier to consider the results of crystal structure determinations. (Rayner)

Beta horizons in Hertfordshire soils. Thin horizons of clay enrichment, formed at the junction between decalcified soil material and calcareous gravel or limestone, have been called Beta Horizons (Bartelli & Odell, *Proc. Soil Sci. Soc. Amer.* (1960), **24**, 388–395). In England they are sometimes developed in soils over chalk and other limestones, where clay is deposited from percolating water in the spaces left by dissolution of the limestone. We investigated the mineralogy and micromorphology of a dark brown clay that lines pipes and other solution hollows developed in the Upper Chalk beneath the sub-Tertiary surface at Castle Lime Works (TL 230025), near South Mimms, Hertfordshire. The hollows and pipes are filled mainly with basal Tertiary deposits, which here include (a) the Bullhead Bed, (b) thin brown sands, which mineralogically resemble the

Thanet Beds, and (c) multi-coloured Reading Beds clay. Where these deposits have collapsed into the solution cavities they are disturbed and intermixed, but the brown clay lining always follows the irregular chalk surface and is neither disturbed nor mixed with the collapsed Tertiary beds. This suggests that the clay was deposited after collapse, and therefore could have been derived either by dissolution of chalk forming the walls and bottom of the cavities, or by redeposition of clay translocated from overlying beds.

The clay linings contain at least 80% material <2 μm, but because they are very porous they have an unusually small bulk density (undisturbed dry density of 1·0 g cm^{-3}). In places they contain white, unworn flints, similar to those in the adjacent chalk. Their small contents of fine sand (50–250 μm) consist mainly of collophane, limonite, flint fragments, chalcedony and ferromanganiferous concretions, all of which were also derived from the chalk. In contrast, the clay fraction (<2 μm) contains very little chalk-derived material. It is composed of 60% montmorillonite, which shows in electron micrographs as small anhedral flakes, 20% mica, 10% kaolinite, and small amounts of quartz, apatite, goethite and lepidocrocite, whereas clay from acid-insoluble residues of the Upper Chalk contains lath-shaped montmorillonite crystals, and no kaolinite.

Thin sections of the clay linings show that the pores, which occupy up to 40% by area, are irregular equant or irregular prolate. The clay occurs partly in unoriented and almost isotropic patches, partly in randomly-distributed, weakly-oriented patches, and partly in strongly-oriented and moderately birefringent cutans around the pores. The unoriented and weakly-oriented patches are strongly impregnated with ferromanganiferous granules, 1–2 μm across, which have grown *in situ*, and disoriented clay that previously was probably quite strongly-oriented. The chalk immediately adjacent to the clay lining is also very porous, and thin sections show that the pores are either sub-spherical voids or elongate channels, possibly representing fracture planes widened by dissolution. Both kinds of pores are lined and sometimes almost filled with strongly-oriented laminated clay, which is yellow-brown and moderately pleochroic.

Strong orientation and lamination of the clay indicate that its constituent particles were deposited from suspension in percolating water. The formation of the Beta horizon thus involved, first, the dissolution of chalk along fracture planes and other places where water could penetrate; the voids so formed were then partly filled with the small amount of insoluble residue (flint, etc.) from the chalk, and with clay carried from overlying deposits by the water. Small blocks of chalk were later sealed in by encompassing layers of clay as dissolution proceeded, and these blocks were finally removed by slow diffusion of ions through the clay. However, further deposition of clay would then be impossible, so that voids of roughly equant shape developed in the clay as the blocks dissolved. The impeded drainage caused by the Beta horizon encouraged mobilisation and local reprecipitation of iron and manganese within the horizon, where it partly disoriented the translocated clay, and also above it, where it caused extensive mottling of the collapsed Tertiary deposits. (Catt and Weir, with Bullock, Soil Survey)

Soils on glacial deposits. Many soils in eastern England are formed from till, the unsorted and unstratified deposit left by glaciers. The weathering and erosional history of these deposits in East Anglia was long and complex, because they were deposited more than 100 000 years ago, during the Elsterian and Saalian glacial periods. However, in East Yorkshire the soil-forming till (the Hessle Till) is much younger. It overlies deposits dated by the radiocarbon method to approximately 18 500 years ago (*Rothamsted Report for 1968*, Part 1, 68), but it is older than deposits of Late Glacial Zone Ia (the Oldest Dryas period), which are dated to approximately 14 000 years ago. In the main areas of glacial deposition, such as Holderness, surface erosion since the Oldest Dryas period has occurred only locally, so that in most of the soils the duration of weathering and other processes is known fairly precisely.

We studied a profile in the Hessle Till at Tunstall (TA 314318) near Withernsea, which is typical of the imperfectly drained soils common in eastern Yorkshire. The soil is decalcified to a depth of 0·71 m, and gleying occurs below a depth of 0·33 m. Below the plough layer, which is dark greyish brown (10 YR 4/2) and 0·20 m thick, there is a paler brown (10 YR 5/3) horizon extending from a depth of 0·20–0·33 m. The calcareous horizons below 0·71 m are dominantly yellowish red (5 YR 4/6), but vertical fissures and other ped faces are grey (5 GY 5/1). A zone of carbonate accumulation between 0·71 and 1·40 m is shown by abundant impure carbonate concentrations up to 10 mm across.

The carbonate and organic matter were removed from samples of the main soil horizons, and the particle size distribution of the remaining material determined by sieving the sand fractions (50 μm–2 mm) at quarter Ø intervals, by pipette sampling three silt fractions (2–5 μm, 5–20 μm and 20–50 μm), and by centrifuging to separate two clay fractions (0·25–2·0 μm and $<$0·25 μm). The amounts of total clay (<2 μm) increase downwards from 20% in the plough layer to 37% between 0·33 m and 0·71 m depth, but then decrease slightly at greater depths. This suggests that some clay has been removed from the highest 0·33 m of the profile, and redeposited mainly just below this level. However, expressed on a clay-free basis, the amounts of the various silt and sand fractions do not change significantly with depth, except that the amounts of sand have increased slightly in horizons above 0·71 m depth by natural weathering and disaggregation of sandstone erratics larger than 2 mm.

The fine sand fractions (50–250 μm) contain mainly quartz and feldspar, with 0·5–1% heavy minerals (s g $>$2·9). The more resistant heavy minerals (zircon, garnet, rutile, tourmaline and epidote) occur in constant amounts through the profile, but the less resistant ones (biotite, apatite and augite) are much less abundant in higher than in lower horizons.

The fine silt, coarse clay and fine clay fractions are composed mainly of layer silicate minerals, with small amounts of quartz, feldspar, iron oxides and amorphous silica and alumina. The layer silicates are mica, chlorite, kaolinite, and various expanding minerals, which can be divided on the basis of their swelling properties into smectite, vermiculite and interstratified mica–vermiculite.

The similarity of resistant heavy sand minerals and the uniform pattern of particle size distribution in the 2 μm–2 mm fractions throughout the profile indicate the original homogeneity of the soil parent material. The mineralogical differences between lower and higher horizons are therefore attributed to weathering and other soil-forming processes during the last 14 000 years. These differences are found by comparing the mineralogical composition of the various size fractions from each of the four higher horizons (above 1·40 m depth) with the same size fractions of the almost unaltered till below 1·40 m.

Two effects of weathering easily detected in the field are the decalcification of the soil and the disruption of erratic stones ($>$2 mm) derived from clastic sedimentary rocks. Assuming that the whole soil originally contained the same amount of calcium carbonate (8% by weight) as the till below 1·40 m, less than 5% of the carbonate removed from horizons above 0·71 m was re-precipitated in the horizon of carbonate accumulation (0·71–1·40 m). The remainder was completely removed from the profile and lost in the groundwater. In the plough layer all stones, except the most resistant ones such as flint and hard quartzite, have weathered and disaggregated, and their constituent sand particles have been separated and mixed with the other soil material. Softening of stones by dissolution of their cementing agents also occurred in lower horizons down to 1·40 m depth, but here the soil has been less disturbed than in the plough layer, so the weathered stones are still recognisable in the field. However, the mild mechanical agitation used to disperse the soil in the laboratory easily separates their constituent particles.

The amounts of kaolinite, chlorite and smectite in the fine silt and coarse clay fractions decrease upwards in the profile, representing losses that are balanced by gains of the same minerals in the fine clay fractions of lower horizons. Weathering therefore made the particles of these minerals smaller, and the fine clay produced in higher parts of the profile was moved to lower horizons. Mica has also been made smaller and moved, but the loss from higher horizons is only partly balanced by the gain of fine clay mica at lower levels. In contrast, the amounts of fine clay vermiculite and interstratified mica–vermiculite between 0·33 and 1·40 m greatly exceed the amounts of these minerals lost from all size fractions in higher parts of the profile. An important weathering process in the highest 0·33 m of the soil was therefore the removal of potassium from mica; this produced fine-grained expanding minerals that were then moved to lower levels. The weathering of silicate minerals in higher horizons probably also released a little iron, because horizons above 1·40 m contain more free iron oxide than does the same thickness of unaltered till. Much of the free iron released was leached from horizons above 0·33 m, and redeposited as crystalline lepidocrocite and goethite between 0·33 and 1·40 m. (Catt, Madgett and Weir)

A new occurrence of sepiolite from Turkey. The Eschi Chehir region of Turkey is renowned for its deposit of pure sepiolite, which has important industrial uses. Field studies by Y. Turan near Yeni Douan, some 100 km distant, revealed basin deposits of sedimentary clay rocks of small density that were suspected to contain sepiolite. X-ray and chemical examination showed that samples from different horizons contained sepiolite. In some horizons the sepiolite is contaminated with much dolomite, but others, one of which is several metres thick, contain almost pure sepiolite with only small amounts of mica and organic matter. The sepiolite mineral is closely similar to that of the Eschi Chehir meershaum deposit. (Brown, Turan and Weir)

Clay minerals in weathered phonolite from Brazil. Phonolite, an alkaline igneous rock from near Rio de Janeiro, consists of feldspar, 75–80%, and nepheline, 15–20%. It is altered saprolitically to a depth of several metres. The clay fraction (<2 μm e s d) consisting of up to 50% of the residuum, was separated from three samples taken at different depths and found to consist of a dioctahedral mica, a mineral of the kaolinite group similar to that described by de Souza Santos, de Souza Santos and Brindley (*Am. Miner.* (1966), **51**, 1640–1648), and montmorillonite with a little feldspar. (Brown, Ormerod and Valença)

Soils from East Pakistan. A red soil from Dacca and two soils from tea plantations were analysed. The red soil, which had a pH of 5·4, contained 12% sand, 57% silt and 31% clay. Its clay fraction consisted of mica, kaolinite, vermiculite, interstratified vermiculite–smectite and an unusual 7 Å mineral. This mineral expanded from 7·2 to 7·5 Å after glycollation and gave a spacing of 7·5 Å after heating to 335°C. The spacing was unchanged after treatment with potassium acetate, so no intersalation complex resembling those obtained with kandites was formed. The mineral may be a swelling 7 Å chlorite, but it occurs in too complex a mixture of minerals to be identified with certainty. The two tea soils were very similar in their clay mineral composition; each had a pH of 4·3 and contained 13% clay composed of kaolinite, mica, smectite and vermiculite, with

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minor amounts of mixed layer expanding minerals, chlorite, quartz, goethite and feldspar.

Oxford Clay. Core samples from depths of 9 and 40 feet were obtained from the Oxford Clay at Stewartby. The upper sample contained 10% gypsum and small amounts of calcite, pyrite and organic matter, whereas the lower contained only 1% gypsum, but 21% calcite, 2·7% pyrite and 2·1% organic carbon. The clay minerals of both samples were similar; they consisted of mica, vermiculite, interstratified smectite–vermiculite, kaolinite and a little chlorite.

Ngala soil, Lake Chad, Nigeria. Samples from the top and bottom of this strongly cracking soil contained 67 and 85% clay, respectively. The clay fractions were composed of 33 and 38% kaolinite, 10 and 12% mica and 34 and 38% smectite and interstratified smectite–vermiculite. The soils contained very small amounts of sulphate sulphur, 0·01 and 0·04%, mainly in gypsum concretions up to 3 mm in diameter, but no detectable pyrite. A sample of salt efflorescence from a drainage ditch near the sampled profile contained crystals of gypsum and thenardite (Na_2SO_4). (Ormerod and Weir)

Clay physics

Pore size distribution in soils. The 'structure' of a soil is described by the way that its void volume is distributed between pores of different sizes. All the satisfactory methods of determining pore size distribution (p.s.d.) involve the removal of pore water and although this does not disturb the fabric of non-shrinking soils, soils that shrink appreciably will show not only smaller void ratios but different p.s.d. Measurements made on dried samples are therefore meaningless when it is desired to infer from them the original structure of the soil. We find that good results can be obtained by first exchanging the pore water with organic liquids that strengthen the soil fabric and so prevent excessive shrinkage. The sample can then be either embedded, ground and polished for microscopical examination, or the solvent evaporated off, preferably above its critical temperature, to allow suction (or mercury intrusion) and adsorption measurements to be made.

Polyethylene glycol 6000 (P.E.G.6000) is especially attractive as an embedding agent because, being miscible with water, it can be exchanged directly with the soil water. The shrinkage from the exchange and subsequent cooling of the molten glycol into a hard wax is one-half to three-quarters the shrinkage consequent on drying. We find that with P.E.G.6000 the infiltration and not the cooling step causes most of the contraction (contrary to the findings of Quigley, R. M. & Thompson, C. D., *Can. geotech. J.* (1966), **3**, 61–73), and that careful control of the concentration of the infiltering solution is needed to prevent the soil structure from being disturbed by osmotic stresses. We also find that the extent of shrinkage increases and the rate of infiltration decreases with increasing molecular weight of the P.E.G.; for example, samples treated with diethylene glycol, $O(CH_2CH_2OH)_2$, show negligible shrinkage, and when subsequently infiltrated with P.E.G.6000 the shrinkage is only one-third of that caused by direct impregnation. Thin sections of soils were prepared using this two-step procedure; the sections seem to be undisturbed and are therefore probably faithful representations of the original fabric. The smaller molecular weight and softer waxes, P.E.G.1500 and P.E.G.4000 were also successfully used as embedding agents, with advantages of less shrinkage and quicker infiltration.

More volatile solvents are preferable for the exchange when the sample is required for suction or adsorption measurements with non-polar substances. Most soils shrink little when water is replaced by a wide range of solvents, but when the solvent evaporates the shrinkage depends critically on the nature of the solvent and on the initial void ratios and drying/wetting history of the soil; the type of soil clay seems to be only of secondary importance. Some samples may appear to shrink little until examined microscopically, when they show many micro-cracks; these are usually caused by too rapid exchange or evaporation. (Greene-Kelly and Gallavan)

Soil geochemistry

Genesis of loess soils. Last year Catt, Madgett and Weir suggested that some clay in a buried soil in the loess at Pegwell Bay, Kent, may have derived from the weathering of glauconite, which occurs in the lower horizons of the profile, but not in the upper ones. As a development of this work, the distribution of trace-elements was studied to see whether this provides further evidence for the provenance of the clay that has accumulated in the lower horizons, Specimens of glauconite collected over a wide area of southern England were analysed to see whether any elements consistently occurred in large enough concentrations to characterise the weathering products of glauconite. A boron-range of 410–710 ppm in the glauconite, compared with 45–64 ppm in the soil, suggests that it may provide a suitable indicator. Specimens of glauconite from the Upper Greensand of Dorset, the Bracklesham Beds near Woking, the Cambridge Greensand near Barrington, Cambs. and the Thanet Beds at Pegwell Bay provided the data given in Table 2. (Le Riche)

TABLE 2

Range of trace-element contents found in glauconite (ppm)

B,	410–710	Mo,	<5
Ba,	33–110	Ni,	27–130
Co,	14–85	Pb,	<30
Cr,	196–650	Sn,	<30
Cu,	4–27	Sr,	37–190
Ga,	11–19	V,	71–370
Mn,	89–170		

Uranium in peaty soils from Co. Limerick. Qualitative X-ray fluorescence spectrometry of peaty soils, known to contain anomalously large amounts of Mo and Se, showed the presence of large amounts of U and Br. Quantitative XRF analysis of three soils (containing 20–40% organic carbon) gave the following results: U 70–550 ppm; Br, 70–130 ppm, Se, 190–485 ppm; Mo, 40–385 ppm (air-dry basis). The average U content of soil is 1–4 ppm (Vinogradov, A. P. (1959), *The geochemistry of rare and dispersed chemical elements in soils*. Second ed., New York: Consultants Bureau). These soils came from the site of a drained glacial lake; elements carried by ground water from the surrounding Clare shales (Lower Namurian black shales) are concentrated in the highly organic soils.

Because of the reported association of U with Se (Cannon, H. L., *Am. J. Sci.* (1952), **250**, 735–770) we examined other Se rich soils derived from black shales (Culm measure of Devon, and Namurian shales of the Meath–Dublin area) from poorly drained environments. All contained <10 ppm U. (Carolyn Williams)

Computer program. Siliancomb, a program used to process XRF results of major element silicate analysis, was modified to permit easier handling of the data. (Carolyn Williams with Coles, Computer Department)

Soil chemistry

Inhibition of nitrification in soil by carbon disulphide from rubber bungs. While working on soil fumigation, we noticed that soils nitrified much less in respirometers closed with rubber bungs than in all-glass apparatus. Thus a soil that produced 18 ppm NO_3-N when incubated for 10 days at 25°C in an all-glass respirometer produced only 2 ppm in a rubber-closed respirometer, although both produced similar amounts of carbon dioxide. The effect was traced to volatile material evolved by some types of rubber. This material inhibited the microbial oxidation of ammonium to nitrite, presumably by interfering with the activity of *Nitrosomonas* in soil. Gas chromatography showed that the volatile material was a complex mixture, containing components that could be resolved into at least 14 separate peaks. Activity against nitrifiers was associated with one peak alone; mass spectrometry showed that this peak was given by carbon disulphide. Probably an accelerator of the tetramethylthiuram or dimethyldithiocarbamate type was used in the manufacture of the rubber, which gave dimethylamine (also identified in our volatile fraction) and carbon disulphide as decomposition products. Although carbon disulphide has long been known to inhibit nitrification, the extreme sensitivity of *Nitrosomonas* to it seems not to have been recognised. Thus, in one of our experiments, adding 0·5 ppm of carbon disulphide to a soil decreased the amount of NO_3-N produced in 5 days from 104 to 22 ppm; 8 ppm of carbon disulphide stopped nitrification completely. (Jenkinson and Powlson, with Callow and Greenway, Insecticides and Fungicides Department)

Bromine residues in methyl bromide fumigated soils. The zones of scorched plants previously noted (*Rothamsted Report for 1969*, Part 1, 83) in wheat growing on soil that had been fumigated with methyl bromide reappeared in 1970. The above-ground parts of the wheat in one such zone contained 0·42% bromine in the first crop after fumigation (1968), 0·25% in the second and 0·09% in the third (1970). Thus three years were not enough to leach all the residual bromine from the soil.

Laboratory experiments showed that the amount of bromine remaining in soil after treating it with methyl bromide is correlated with the organic content of the soil. Thus a soil with 2·81% organic carbon contained 63 ppm bromine after fumigation with 500 ppm of methyl bromide for 24 hours, whereas an otherwise similar soil with 0·93% organic carbon contained only 25 ppm. The residual bromine was ionic and was completely extracted with N potassium sulphate, contrasting with the native soil bromine, which could not be extracted. (Brown and Jenkinson)

Radiocarbon dating of soil organic matter. Table 3 gives measurements of the radiocarbon contents of the hydrolysable and non-hydrolysable fractions of soil organic

TABLE 3

Radiocarbon dating of organic matter in soil from Plot 3 on Broadbalk

Sampling date*	Fraction	Organic C in fraction, g per 100 g oven-dry original soil	Equivalent age, years	δC^{14}
1881	Decalcified soil	0·95	1450	−165±10
	6N HCl hydrolysate	0·35	515	−62±12
	Residue from hydrolysis	0·35	2560	−273±13
1969	Decalcified soil	0·89	520	−63±11
	6N HCl hydrolysate	0·36	—	+8±13
	Residue from hydrolysis	0·38	1995	−220±10

* Sampling depth 0–23 cm in both cases

matter in soil samples from plot 3 of the Broadbalk Permanent Wheat Experiment; one sample was taken in 1881 after the field had carried its 37th successive wheat crop, and the other in 1969, while the 125th crop was growing. The hydrolysable carbon was younger than the non-hydrolysable, suggesting that the non-hydrolysable was the more biologically inert. The hydrolysable fraction from the soil sampled in 1969 had so much bomb-derived radiocarbon (see *Rothamsted Report for 1969*, Part 1, 85) that it contained more radiocarbon than the contemporary standard (δC^{14} was positive: Table 3). The non-hydrolysable residue also gained a little bomb-derived radiocarbon. (Jenkinson)

Respiration in partially sterilised soil. Chemicals used as fumigants in the control of soil-borne plant pathogens drastically alter soil metabolism, and the after-effects can still be detected several years after fumigation. We are investigating respiration and mineralisation of nitrogen in a range of fumigated soils that differ in pH, organic matter content, cropping history and mechanical analysis. Irradiated (2·5*M* rad) and air-dried soils were included for comparison. Excluding acid soils, all treatments increased respiration when the treated soils were inoculated with unsterilised soil and incubated at 55% of their water holding capacities. Irradiation and treatment with chloroform vapour have broadly similar effects on soil respiration, although there are some differences. The flush of decomposition after fumigation with chloroform vapour was almost over after 10 days incubation, but lasted longer in irradiated soil. Again, chloroform vapour-treated soil respired at about the same rate whether inoculated or not, whereas inoculation more than doubled the rate at which irradiated soil respired. Respiration in the uninoculated irradiated soil probably reflects enzymic activity in damaged cells incapable of dividing, whereas enough organisms survive exposure to chloroform to mask the effects of the inoculum.

Air-drying affects respiration differently from the other treatments, and sometimes stimulates respiration more and sometimes less than chloroform. The correlation between oxygen consumed during a 10 day incubation and the total organic carbon content was closer with air-dried than with irradiated or chloroform-treated soils. Air-drying was the only treatment that appreciably increased oxygen consumption in a soil so acid (pH 3·9) that there was little stimulation of respiration after such biocidal treatments as irradiation or chloroform. Irradiation and chloroform seem more specific than air-drying, which affects many different fractions of the soil organic matter. (Jenkinson and Powlson)

Reactions between soil organic matter and trace elements. Continuing this work we studied the reactions of Mo, V and U with humified organic matter. Solutions of the elements were prepared by the action of aerobically decomposing plant matter as described in the *Report for 1968*, Part 1, 74.

In the forms in which they occur in the reaction solutions, Mo and V are completely dialysable against water, in contrast to U and the elements previously studied. An appreciable proportion of the dissolved Mo is retained after dialysis against dilute acid, and the effect of pH on the ability of the three elements to pass through dialysis sacs was therefore studied in more detail. Vanadium remains completely dialysable between pH 2–8, but non-dialysable U persists above pH 1·5, with maximum retention around pH 6. With Mo, retention is greatest between pH 1–2, and persists up to pH 4. As would be expected, the proportion of non-dialysable Mo increases with increasing relative organic matter contents.

The availability of Mo to plants usually varies directly with the pH of the soil, although this element sometimes remains available in acid soils. Mitchell described an organic soil, pH 4·7, that carried herbage containing 30 ppm Mo (Bear, *Chemistry of the soil* (1955), Reinhold, New York). To explain the availability of Mo in these acid conditions, Mitchell suggested that it was complexed with organic matter in a manner that prevented its sorption by sesquioxides. Our results indicate that such an effect would be appreciable only under more acid conditions. Possibly in his soil the Mo-sorbing properties of the sesquioxides are masked by surface films of organic matter.

Filtration through millipore membranes of progressively smaller pore size showed that, at the pH of the reaction solution, Mo is not associated with organic matter of molecular weight >1000; over the same range of molecular weights, U is retained more or less equally by all fractions of the organic matter. Vanadium forms colloidal polymeric oxyanions between pH 2–12, so ultrafiltration is not applicable in the study of this element.

The behaviour of the dissolved metals towards cation and anion exchange resins proved that all three were in anionic forms. To explain the accumulation of these elements in organic-rich sediments, it has been suggested that Mo and V migrate as anions, but suffer ion-exchange reactions with organic matter after reduction to lower valency states, in which forms they exist as cations. Uranium is considered to migrate and exchange as the UO_2^{2+} cation (Szalay, A., *Geochim. cosmoch. Acta* (1964), **28**, 1605–1614; (1967), **31**, 1–6). Our results suggest that this mechanism could not operate under aerobic conditions. Further, we find that when dissolved under the strongly reducing conditions developed by anaerobically decomposing plant matter, U^6 and Mo^6 persist in anionic forms, as shown in experiments with exchange resins. V^5 is reduced to V^4 under these conditions, but above pH 2·5 this reoxidises too rapidly to allow further study. Dialysis experiments with V^4/organic solutions under an inert atmosphere gave no evidence of any significant fixation of V, but the results of such experiments are necessarily open to question. The ease with which V^4 compounds are hydrolysed suggests that precipitation rather than sorption would operate under all but very acid conditions, and should oxidising conditions supervene, it is to be expected that V^5 would be formed, in which state it would presumably no longer be retained by the organic matter. Together with the associated trace metals, the humose constituents of the aerobic reaction solutions are strongly sorbed by soil colloids, and this is a possible mechanism by which the metals could accumulate in sediments. However, the formation of sulphides would no doubt be the most important influence in anaerobic sediments.

Despite the relatively short duration of our incubation, the soluble organic products are of considerable complexity. Filtrates from 0·45 and 0·025 μm filters are distinctly lighter in colour than the original extract, and removing material of $M > 25\,000$ completely removes the original brown colour; compounds of very large molecular weight are thus involved. (Bloomfield and Kelso)

The soluble organic matter contains humic and fulvic acids, and polysaccharide. In preliminary work, acid hydrolysis of humic acid separated from a reaction solution yielded 15 of the 23 amino acids found by Bremner (*J. agric. Sci.* (1959), **46**, 247–256) in humic acid extracted from soil. (King)

General

Nematode cyst coatings. The females of some cyst-nematodes, attached to plant roots in soil, are covered with a layer of white material called the sub-crystalline layer. A sample of the white material was examined to see whether it was crystalline and to find its chemical nature.

Columnar structures visible under the polarising microscope broke up into fibres a few μm wide by 20–30 μm long, some pieces of calcite *c.* 20 μm and some pieces of non-birefringent material containing a few tiny crystals. An X-ray diffraction pattern from a whole coated cyst was of the type given by mixtures of crystalline powders, and showed three kinds of lines. The lines most broken up into spots came from the largest crystals, which were silt size crystals of quartz. Somewhat smoother lines were given by calcite, and the smoothest lines by crystals of a long chain aliphatic compound with an inter-layer spacing of 65·0–65·5 Å and principal side spacings, caused by the side by side packing of the chains, of 4·12, 3·70 and 4·57 Å. Another pattern from carefully selected coating material showed no quartz lines, only the strongest calcite line and a clearer pattern of the long chain compound.

Although no published diffraction data have been found to fit these results exactly, extrapolation of the spacings of calcium palmitate, 45·5 Å and calcium stearate, 50·4 Å (*Structure Reports* (1949) (Ed. A. J. C. Wilson), **12**, 343), predicts a spacing of 65·1 Å for calcium tetracosanoate $(C_{23}H_{47}COO)_2Ca$ which agrees with the value found. It is concluded that the coating is mainly a waxy long chain organic compound, perhaps calcium tetracosanoate, possibly associated with some calcium carbonate, although this may be accidental. Another biological wax found in soil by Himes & Bloomfield (*Pl. Soil* (1967), **26**, 383) was identified as triacontyl stearate by NMR and fragmentation mass spectroscopy; these methods should give further evidence on the chemistry of the so-called subcrystalline layer of cysts. (Brown and Rayner)

Apparatus and techniques

Mercury content of wheat seeds

Individual seeds. The method outlined in last year's report, in which the intensity of HgLα radiation is measured from samples prepared by pressing individual seeds on to filter paper discs, was refined. Procedures were developed to correct for the absorption of X-rays in the individual samples of seed plus filter paper support, and to allow for uneven distribution of mercury between the exposed and covered sides of the pressed seed. To take account of differences between the two sides of the sample, readings are made with the exposed side facing towards and away from the X-ray source. The relative absorption of each individual seed + filter paper support can be obtained by measuring the decrease in intensity of SeKα radiation when a pressed seed sample is placed over a second filter paper disc impregnated with selenium. The decrease in the intensity of SeKα from the substrate gives a measure of the absorption by the sample. This, together with the absorption of the filter paper, which can be measured separately, allows the Hg content to be determined more accurately. If all the seeds are about the same size and are flattened in a reproducible way with a hydraulic press, the variation in absorption between individual seeds is small, ranging ±5% from the mean. In these circumstances, a mean absorption factor for the seeds, determined for a limited number of untreated seeds using an Hg bearing substrate, can be used with a considerable saving in time when examining many seeds.

These improved methods were used to analyse 12 sets of 10 wheat seeds corresponding to those analysed last year. Applying the corrections increases the amount of Hg found by 10–20%. As a check, the sum of the individual Hg contents of the ten seeds was compared with the chemically determined total Hg contents of the same seeds. The two results were in reasonable agreement considering the uncertainties in both methods. The mean Hg content of the seed samples was in the range 75–110% of the target dose.

Another 40 wheat seeds and 20 barley seeds were analysed to assess the effectiveness of new seed-dressing methods. The Hg on the individual seeds was distributed more evenly than those tested previously; the total amounts of Hg were 84% and 97% of the target dose for two lots of 20 wheat seeds, and 87% for the barley seeds.

Mercury content of bulk samples of seeds. Chemical methods for estimating the mercury content of seeds and similar organic materials take much time and are often inaccurate because of the difficulty of removing organic matter without loss of mercury. The use of X-ray fluorescence analysis for the analysis of bulk samples was investigated. The mercury content of dressed cereal seeds is of the order of 10 ppm. Routine X-ray fluorescence analysis on samples prepared by grinding and compacting the ground powders can determine the mercury content to about ±10% of the amount present i.e. 10 ppm ± 1 ppm. A thin zinc filter in the primary X-ray beam decreased the background intensity much faster than the mercury fluorescent intensity, thereby doubling the sensitivity without increasing the analysis time. Zinc filters ranging in thickness from 0·0003 to 0·0016 in. were tested and a thickness of 0·0005 in. gave the best results. Using this filter the sensitivity for mercury in plant materials is about 0·4 ppm. X-ray fluorescence analysis can therefore be used for rapid analysis of plant materials such as dressed cereal seeds. (Brown, with Jeffs, Insecticides Department)

Heating stage for Philips diffractometer. Changes in X-ray diffraction patterns caused by removing water sorbed between the silicate layers are valuable diagnostic criteria for clay minerals. Dehydration is often reversible so that heating tests may give ambiguous results unless precautions are taken to prevent rehydration. A simple method of achieving this is to maintain the sample at temperatures up to 250°C while making the X-ray examination. A simple heating stage was made for use with the Philips vertical diffractometer. The stage can maintain samples at temperatures up to 270°C; it was designed to obviate modification to the standard goniometer other than making a new cover for the specimen chamber to accommodate the electrical heater leads. The heating stage is a direct replacement of the usual specimen holders and is held in position against the reference surface by the same retaining springs; this eliminates the need for realigning the instrument when changing between usual working and examinations at elevated temperatures. The change from one mode to the other can be made in a few minutes. The entire stage is small enough to fit inside the normal X-ray protection shielding supplied as part of the diffractometer. Efficient thermal insulation of the heated parts of the stage from the reference surface block and the main shaft of the goniometer and the use of a 15 watt heating element allow temperatures up to 270°C to be reached on the specimen surface without special alterations for cooling the goniometer. The temperature can be controlled by altering the applied voltage, and the stage is calibrated by determining the voltage necessary to melt substances of known melting points on the glass specimen support. Oriented clay films on glass, as used for normal X-ray examination, are used as specimens. (Brown, Ormerod and Weir)

Atomic absorption spectrophotometer. The new Perkin Elmer 290 atomic absorption spectrophotometer has proved capable of diverse applications. The precision, sensitivity and selectivity of K determinations are much superior to those obtained on the filter emission unit previously used, and without the new instrument the alteration of soil potassium minerals could not have been studied. Na, Ca, Mg, Mn and Fe are now determined with excellent precision on a routine basis, and during the year we determined exchangeable Ca and Mg in more than 100 ammonium acetate extracts for the Soil Survey. The range of application has recently been extended by a nitrous oxide–acetylene burner and excellent results for Ba and Al are obtained with this flame; atomic absorption seems to be the only simple method of determining Al in sodium citrate extracts with acceptable accuracy. We can also determine Cu, Mo, Co, Si and Ti, and other elements can be added to this list should the need arise.

The instrument can also operate in flame emission, which has proved invaluable in determining the K impurity in reagents, which could only be done in the atomic absorption mode if a similar reagent entirely free from K were available. Because the amount of impurity in analytical reagent grade chemicals is unpredictable, this reagent screening is essential in the study of soil potassium. (Newman)

Specific surface area apparatus. A simple apparatus was developed for measuring the specific surface areas of soils and other fine-grained solids by nitrogen adsorption at the boiling point of liquid nitrogen. Robust and compact, it requires neither pumps nor knowledge of high vacuum technique. The procedure is simple the calculation rapid, and the results compare very favourably with the much more involved B.E.T. method. A description of the apparatus with working drawings can be obtained on request. (Greene-Kelly)

Determination of boron by optical spectrography. A new method was developed to determine boron in plant ash and mineral materials. Determining boron directly in plant ash by dc arc methods is complicated by the large contents of alkali and alkaline earth salts, which greatly decrease sensitivity. This is overcome by mixing the ash sample with three times its weight of a mixture of one part of Al_2O_3 and two parts of carbon containing 0·05% beryllium, as BeO, as internal standard. Comparison standards in a simulated plant ash matrix are similarly mixed. The electrodes are of boron-free carbon, with outside diameter 4 mm and cavity 2·38 mm diameter × 4·5 mm deep. Anode excitation is used with an arc gap of 4 mm and a current of 14 amps. The arc column is imaged on to a screen with a slot through which light passes to the spectrograph, thus masking direct glare from the electrodes. A 7-stepped rotating sector is placed at the slit of the Hilger E.492 spectrograph with a lens that focuses the arc on to the collimator lens. The same procedure is used for mineral samples, using comparison standards in an appropriate matrix. The line pairs B 249·773 nm or 249·678 nm to Be 249·473 nm are used. The former boron line is more sensitive, but in mineral samples is liable to interference from Fe 249·782 nm. Photometry is by the standard blackening-curve separation method. The sensitivity is 10–20 ppm, with a coefficient of variation of about 7%; this is adequate for plant materials and samples of 15 mg of ash can be analysed, representing a detection limit of about 0·15 μg B. (Le Riche)

Lower molecular weight limits of compounds excluded by Sephadex G-25/aqueous acetone. Solutions of model compounds of molecular weight 120 to 695 were passed down a column of Sephadex G-25 (Fine) and the ratio Ve/Vb (elution volume/column bed volume) plotted against log (molecular weight of compound). The intersection of the straight line Ve/Vb with the line Vo/Vb (voil volume/column bed volume) gives the molecular weight at which the compound is just excluded from the gel. The lower limits of molecular weight were: 40% acetone, 900; 50% acetone, 500; 60% acetone, 300. These values are considered to be correct to within 50.

Each system was further tested by separating the components of tannic acid. Tannic acid consists almost entirely of gallotannin (*M* approx. 1800), trigallic acid (*M* 504), m-digallic acid (*M* 342) and gallic acid (*M* 180), but their relative proportions differ from sample to sample. Because of the diminished adsorption of phenolic compounds

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in the presence of aqueous organic eluents, with 60% acetone all the components of tannic acid, except gallic acid, should be excluded from the gel as soon as the void volume of eluent has passed down the column. Only gallotannin should be excluded at the void column with 40% acetone. This was found to be so. Gallic acid was adsorbed whichever eluent was used, but this is no disadvantage because gallic acid has the smallest molecular weight of the four compounds, and its sorption does not affect the running of the other three.

With 40% acetone the compounds separated well, in the expected order of decreasing molecular weight. Gallotannin trailed a little into the trigallic acid fraction, but a second run of the fraction should separate trigallic acid from the contaminant. The separation was confirmed by plotting the effluent volume against the optical density of fractions of the effluent treated with Folin–Denis reagent, and also by paper chromatography.

Sephadex G-25/aqueous acetone is useful for separating substances into broad groups, m. wts. up to 300, 300–500, 500–900 and >900 where, because of strong adsorption effects Sephadex G-10 or G-15, gels that nominally cover these ranges, cannot be used with water as eluent. The method should be useful in separating groups of components in plant extracts containing much polyphenolic material, and in investigating the molecular weight distribution of the components. Much material of small R_F, which is unresolved on paper chromatograms, is often referred to as being of large molecular weight. Experience with Sephadex G-25/aqueous acetone shows that a considerable amount of such material is not excluded from the gel, suggesting that the molecular weights of its constituents may be less than 900. (King and Pruden)

The purification of small quantities of dithizone by chromatography. A spectrophotometric method for estimating the purity of samples of commercial dithizone was described in last year's Report (p. 93). Work on dithizone was continued to find simpler methods for preparing small quantities of the pure reagent, other than by the standard lengthy procedure of shaking a solution in carbon tetrachloride with ammonia. A convenient and simple method for preparing milligram quantities is to chromatograph up to 50 mg of the crude reagent, in chloroform, as a band on a sheet of Whatman silica-impregnated chromatography paper (SG81), 50 cm × 45 cm, with benzene as solvent. After drying the developed chromatogram the pure dithizone is eluted with acetone, which is removed under vacuum. Alternatively a solution of crude dithizone in benzene can be chromatographed on a column of a mixture of equal parts of acid-washed silica (Kieselgel N) and Celite 545, with benzene as eluent. Oxidised impurities run ahead of pure dithizone. The quantity of dithizone that can be handled depends on the solubility of the crude reagent in benzene. In a sample that assayed spectrophotometrically as 83·3% pure, the solubility was 1·43 g/l.

The purity of the dithizone obtained using the chromatographic methods can be measured spectrophotometrically at 620 nm (revised maximum wavelength), by comparing the optical density with that of a sample of pure dithizone at a standard concentration. (King and Pruden)

X-ray fluorescence analysis. New applications for X-ray fluorescence analysis included the determination of Mo, U and Se mobilised by decomposing plant matter, Zn in composts, Br in soils and soil leachates, and S in soils and plants.

An attachment for measuring mass absorption was fitted to the scintillation counter; this allows differences in absorption caused by matrix variations in the samples to be measured, increases accuracy and simplifies the preparation of standards.

Foils of various elements used to filter the primary X-ray beam diminished the background radiation, and gave smaller detection limits for Se, Hg and Cu and other elements. (Carolyn Williams)

Staff and visiting workers

J. A. Catt and A. H. Weir attended the field study meeting of The Quaternary Research Association in The Netherlands.

Professor Keino Nagasawa of Nagoya University, Japan, arrived in February to spend a year studying the weathering of mica. D. Machajdik of the Slovak Academy of Sciences, stayed six months, as a Royal Society exchange scholar, studying methods used in the study of the structures of clay minerals. Dr. Yilmaz Turan of Canakkale Seramik Fabrikalari AS, Turkey, and J. Valença of the Federal University of Rio de Janeiro stayed for shorter periods, studying methods of analysing and characterising clays. Jürgen Lamp, Institute für Pflanzenernahrung and Bodenkunde, Kiel, visited the department in September to study the classification of soils by numerical taxonomy. M. H. O. Bellia, of the Sudan, Ministry of Agriculture, spent two months studying methods of soil analysis, under the auspices of the British Council. Dr. N. C. Kuhn, of the Swiss Forest Research Institute, arrived in November to spend a year working on the behaviour of sulphur compounds in reduced soils.

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