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Chemistry Department

G. W. Cooke

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CHEMISTRY DEPARTMENT

G. W. COOKE

W. B. Haines retired in September. K. Shaw resigned at the end of the year to take up an appointment with the National Agricultural Advisory Service. B. Harrington emigrated to Australia in October. Mrs. Mary P. Webster joined the staff in January and left in September. D. S. Jenkinson was appointed to the staff in October to work on soil organic matter and Miss Barbara M. Close to take charge of glasshouse experiments.

P. W. Arnold returned in August from a period of secondment to the West African Cocoa Research Institute. S. G. Heintze spent a year's leave of absence at the Galloway Laboratory, Hamilton, New Zealand.

J. M. Bremner was awarded a Rockefeller Foundation Fellowship tenable at Iowa State College and at the University of Illinois. P. W. Arnold spent a month in the U.S.S.R. as a member of an agricultural delegation invited by the Soviet Union Ministry of Agriculture. He visited the All-Union Research Institute for Fertilizers and Agro-Soil Science, as well as a number of other research institutes in Moscow. G. W. Cooke visited laboratories and experimental stations in Holland and France to discuss phosphate fertilizers. O. Talibudeen attended the International Conference on the Peaceful Uses of Atomic Energy organized by UNESCO and held in Paris in September.

P. W. W. Daborn of the Forestry Commission was seconded for a further year's work on nutrition problems in forest nurseries. Two members of the Colonial Agricultural Research Service were trained in soil fertility work and field experimentation: R. Webster left in September to take up an appointment in Northern Rhodesia, J. W. O. Jeffery joined the Department in October.

Professor S. W. Melsted of the University of Illinois worked in the Department until May while on sabbatic leave. Miss A. Stojkowska (from Yugoslavia), Mr. P. Arambarri (from Spain), Dr. S. N. Chakravarti (from India) and Dr. J. Rodriguez (from Spain) all joined the department as temporary workers during the year. Mr. L. Overrein (from Norway) worked here for several weeks during the summer.

NITROGEN FERTILIZERS

Times and rates of application for winter wheat (F. V. Widdowson)

A three-year series of field experiments on winter wheat which tested different rates of "Nitro-Chalk" applied as spring top-dressings is summarized in Table 1. In 1955 the rates of application were 52 and 104 lb. N/acre; in both 1956 and 1957 69 and 139 lb. N/acre were given. Tests were also made of splitting the lower rate and applying one-third of the dressing at sowing-time in autumn. Three varieties were compared in each experiment: Hybrid 46,

Minister and Heine 7. They behaved rather similarly in any one year, except that Minister tended to give higher yields than the other varieties when no nitrogen was applied and also that this variety was rather less responsive than the others. On average,

TABLE 1

The effect of different rates and times of application on yield and nitrogen content of winter wheat (averaging the results of three varieties and of all experiments in each year)

	1955	1956	1957
No. of experiments	3	4	4
Yield of grain, cwt./acre			
Yield without nitrogen	25.4	21.6	28.9
<i>Increase in yield from N fertilizer</i>			
From low rate... ..	8.2	7.0	4.6
From high over low rate	3.3	1.1	0.4
Gain from splitting low rate... ..	0.5	-0.3	-0.2
Per cent of N in grain			
Without nitrogen	1.57	2.02	1.87
<i>Increase from N fertilizer</i>			
From low rate... ..	0.05	0.17	0.16
From high over low rate	0.22	0.22	0.25

the low rate of nitrogen increased yields by over 30 per cent in 1955 and 1956, but in 1957 average yields were only increased by 16 per cent. The extra yield from the second dose of nitrogen gave a good return in 1955, but in the two later years this higher rate of dressing was unprofitable. There was no worthwhile gain from giving a portion of the nitrogen when sowing in autumn. The average percentage of nitrogen in the grain varied greatly from year to year, but in any one year all varieties tended to give rather similar values. The second dose of nitrogen gave a larger average increase in the nitrogen content of the grain than the first dose.

Forms of nitrogen fertilizers (F. V. Widdowson, A. Penny, R. J. B. Williams and G. W. Cooke)

Experiments on spring cereals compared ammonium sulphate and a Continental fertilizer grade of "calcium nitrate" (actually a double salt of calcium nitrate and ammonium nitrate). The results of three years' work are summarized in Table 2. Both fertilizers were tested when combine-drilled and when broadcast on the seed-bed at sowing-time. The low and high rates of ammonium sulphate combine-drilled increased yields of barley by about 30 and 40 per cent respectively, and the extra gain from the second level over the first level of manuring was profitable. In comparison with this well-marked general effect of nitrogen the differences between yields given by the two forms, and by the two methods of application, tended to be small. Where ammonium sulphate was applied by combine-drill consistently higher yields were obtained than by broadcasting (this confirmed the results of earlier work: *Rep. Rothamst. exp. Sta. for 1956*, p. 44). When calcium nitrate was applied there was no consistent gain from combine-drilling. When the fertilizers were combine-drilled ammonium sulphate gave higher

yields than calcium nitrate, but when they were broadcast the nitrate was best. (Calcium nitrate drilled with the seed at the higher rate checked germination and early growth; although the crops grew away from the check, it may have been responsible for a small

TABLE 2

The effects of two forms of nitrogen fertilizer applied in two ways on yields of spring barley and spring wheat (yields of grain in cwt./acre are stated after averaging all experiments on each crop)

	BARLEY (7 experiments)		WHEAT (5 experiments)	
	Combine- drilled	Broad- cast	Combine- drilled	Broad- cast
Yield without nitrogen ...	25.7		25.7	
<i>Increase from 34 lb. N/acre</i>				
As ammonium sulphate ...	7.6	5.9	2.8	3.1
As calcium nitrate ...	6.7	6.1	2.0	3.1
<i>Increase from 68 lb. N/acre</i>				
As ammonium sulphate ...	10.5	9.8	3.6	4.4
As calcium nitrate ...	10.1	10.6	3.5	4.6

loss of yield.) Wheat was much less responsive than barley, the low and high dressings of ammonium sulphate giving average increases in yield of 12 and 16 per cent respectively, and the extra gain in yield from the double as compared with single dressing barely paid for the fertilizer. Broadcasting the fertilizers on the seedbed gave higher average yields of wheat than drilling them with the seed; there were no consistent differences between the effects of nitrate and ammonium. The percentage of nitrogen in barley grain was increased by nitrogen fertilizer, and the form of the nitrogen and the way it was applied had little effect. The increases in nitrogen contents of wheat grain caused by fertilizers were rather smaller.

Potatoes. The results of three years' work (summarized in Table 3) emphasize that, for the restricted area covered by these experiments, there were marked seasonal effects on the general profitability of nitrogen. At present-day support-prices for potatoes the highest rate of dressing (1.5 cwt. N/acre) was justified in the 1955 experiments; but in 1956 and 1957 dressings higher than 0.5 cwt. N/acre were unprofitable on average. In each year calcium nitrate gave lower yields of potatoes than ammonium sulphate at all rates of dressing, nitrate tending to be markedly inferior at the high rate. Poor results obtained with calcium nitrate were partly due to damage to emergence and early growth; this effect was most marked in experiments where the fertilizers were broadcast over furrows prepared for planting which concentrated them near to the seed. At centres where the fertilizers were broadcast on flat land before planting by machine, nitrate did not cause a visible check to early growth and average yields given by calcium nitrate were only a little less than those given by ammonium sulphate. The urea used in the 1956 experiments was a granulated fertilizer grade material imported from the Continent. It contained over 4 per cent of biuret; this material damaged establishment and early

growth in all the experiments where it was spread over furrows prepared for planting, but even where fertilizer and soil were mixed before planting by machine the high rate of urea gave poor yields. In 1957 a pure form of chemical-grade urea was used containing little biuret; it caused a slight amount of damage where fertilizers were placed close to the seed, but it gave average yields similar to those given by ammonium sulphate.

TABLE 3
Yields of potatoes and kale (in tons/acre) given by three nitrogen fertilizers

	1955		1956			1957		
	Am- monium sulphate (7 experiments)	Calcium nitrate	Am- monium sulphate (8 experiments)	Calcium nitrate	Urea	Am- monium sulphate (7 experiments)	Calcium nitrate	Urea
POTATOES								
Yields without nitrogen	7.2		10.4			8.9		
<i>Increases in yield from:</i>								
0.5 cwt. N/acre ...	1.3	1.2	1.1	1.0	0.8	0.5	0.4	0.7
1.0 cwt. N/acre ...	2.1	2.0	1.2	1.0	0.5	0.5	0.4	0.5
1.5 cwt. N/acre ...	2.5	1.4	1.3	0.4	-0.4	0.5	0.3	0.6
KALE			(2 experiments in each year)					
Yields without nitrogen	16.3		9.4			19.0		
<i>Increases in yield from:</i>								
1.0 cwt. N/acre * ...	3.8	4.2	11.6	9.3	8.1	5.9	3.7	5.5
2.0 cwt. N/acre * ...	5.3	5.5	11.4	12.4	9.0	6.6	2.2	6.1
High rate, half early, half late ...	6.9	6.1	13.6	11.7	11.2	7.0	6.2	6.9

* 0.6 and 1.2 cwt. N/acre in 1955 only.

Kale. The average results of six kale experiments are stated in Table 3. In 1955 and 1956 calcium nitrate and ammonium sulphate gave similar increases in yields of kale, but in 1957 calcium nitrate was inferior, particularly at the high rate of application. Inferior results from calcium nitrate were associated in each year with damage to germination which often occurred when the heavy dressing of this fertilizer was used. At some centres sufficient plants were established to give a satisfactory crop, but at other centres germination was damaged so seriously that yields were reduced. The urea used in 1956 had a high biuret content, and it damaged establishment seriously and reduced yields. The purer material used in 1957 caused slight damage to establishment, but was not as dangerous as calcium nitrate, and it gave satisfactory yields. The kale experiments also tested split dressings, half of the heavy dressing being applied in the form listed in Table 3 before sowing, and half as a dressing of "Nitro-Chalk" in July. Divided dressings gave slightly higher yields than dressings applied wholly before sowing.

Concentrated organic nitrogen fertilizers for vegetables (R. G. Warren and G. W. Cooke)

A series of field experiments carried out over 12 years on vegetable crops to compare organic fertilizers with ammonium sulphate has now been summarized. For the crops grown crushed hoof and formalized casein (a waste product of the plastics industry) were roughly as effective as an equivalent amount of nitrogen as ammonium sulphate, the "organics" tending to be slightly inferior for

rapidly growing crops with a heavy nitrogen requirement (such as cabbage, tomatoes and potatoes) and slightly superior for crops (such as leeks, lettuce and onions), which required only small dressings of nitrogen in these experiments. Crushed hoof and formalized casein gave similar yields of most crops. There were no marked gains from treating hoof with formalin; a coarse (5–7 mm.) sample of formalized casein did not give materially different yields from the ordinary (2 mm.) product. Individual batches of processed leather wastes were tested in too few experiments to provide reliable average yields; the better batches behaved in much the same way as crushed hoof. Dried blood was tested in a few experiments, and there was no reason to suggest that it behaved very differently from ammonium sulphate or hoof. In one experiment the plots were treated continuously with nitrogen fertilizers for 10 years and were then cropped with grass for 3 more years without further manuring. The “residual effects” of unformalized hoof and of finely divided formalized casein were not larger than the “residual effects” of ammonium sulphate. Coarse formalized casein had much the same residual effect as the fine material; residues of formalized hoof gave slightly larger yields than did residues of untreated hoof. The extra yields of grass given by all nitrogen fertilizers after dressings had ceased indicate simply the difference between fertility levels of soils which had received nitrogen manuring for 10 years and of soils which had received no nitrogen for that period. The soil of unmanured plots lost about 6 per cent of its total nitrogen during the 10-year period, the nitrogen content was maintained at its original level on plots receiving hoof, formalized casein or ammonium sulphate dressings; there was a slight increase in soil nitrogen where formalized hoof had been applied for a number of years.

The experiments did not provide any clear and consistent indications that organic nitrogen fertilizers were either markedly superior or inferior to ammonium sulphate. For the crops grown the work gives no reason for using expensive organic fertilizers in preference to inorganic materials. Growers should work out correct methods of using cheap inorganic nitrogen for most kinds of vegetables grown in the open, and special attention should be given to the timing of the dressings. For glasshouse crops organic materials may have special merits where nitrate is quickly leached away by heavy watering, or where inorganic materials raise the salt content of the soil to dangerously high levels.

Formalized casein for grass (K. Shaw and F. V. Widdowson)

The experiment on Italian ryegrass laid down in 1956 (*Rep. Rothamst. exp. Sta. for 1956*, p. 46) was continued in 1957. There was little benefit from formalized casein applied in March 1957 at the first two cuttings, and marked increases in yield were obtained from this material only at the fourth and final cutting. Dressings of ammonium sulphate repeated before each cut produced higher and more consistent increases in yield at each of the first three cuttings. Formalized casein applied in March 1956 produced considerable increases in yield at the first cutting in 1957. The experiment also tested calcium nitrate and urea, both products giving slightly higher aggregate yields than ammonium sulphate or casein.

D

PHOSPHATE FERTILIZERS

Alternatives to superphosphate

A series of field experiments testing alternatives to superphosphate was initiated by the Fertilizer Conference of the Agricultural Research Council in 1951, when it appeared that supplies of sulphuric acid needed to make superphosphate would be restricted (*Rep. Rothamst. exp. Sta. for 1953*, p. 40). Although the shortage of acid did not persist, field experiments were continued from 1954 to 1957 to provide further information on the agricultural value of phosphate fertilizers which are insoluble in water. Two series of experiments were carried out. Both series tested dicalcium phosphate, which is important because it supplies the bulk of the phosphate in fertilizers made by using nitric acid instead of sulphuric acid to attack rock phosphate, also because it is formed when superphosphate is ammoniated. The first series of experiments tested two other products as well: a nitrophosphate (made in England on pilot-plant scale by the process described by d'Leny (*Proc. Fertil. Soc.* 24 (1953)), and compound fertilizers made by ammoniating superphosphate or triple superphosphate. The second series of field experiments tested Gafsa rock phosphate ground to the customary fineness for direct application (approximately 90 per cent through the 100-mesh B.S. sieve) and a more finely ground material (70 per cent passing the 300-mesh sieve). Continental workers have suggested that rock phosphates ground so that most passes the 300-mesh sieve are much more active than the coarser materials generally used. In both series of experiments all plots received the same total quantities of nitrogen and potassium.

The field experiments were carried out by Advisory Soil Chemists of the National Agricultural Advisory Service, the Macaulay Institute for Soil Research, the East of Scotland College of Agriculture and the Northern Ireland Ministry of Agriculture. The work was organized and co-ordinated from Rothamsted by G. W. Cooke and F. V. Widdowson.

The results of the work are summarized in Tables 4 and 5 after subdividing the groups of experiments on most crops according to the pH values of the soils used. In both series the division into "acid" and "neutral" soils was made at pH 6.5. Superphosphate was tested at 0.3 and 0.6 cwt. P_2O_5 /acre and the other materials at 0.45 cwt. P_2O_5 /acre. (All dressings were applied on the basis of the total P_2O_5 content of the fertilizers.) Yields stated in Tables 4 and 5 for superphosphate supplying 0.45 cwt. P_2O_5 /acre have been obtained by using the superphosphate response curve calculated for the appropriate group of experiments. Standard errors stated for the larger groups of experiments do not apply to yields obtained without phosphate fertilizer; they were calculated from the interaction between treatments and experimental centres. In experiments on barley (Table 4) the fertilizers were broadcast on the seedbed before sowing. Both dicalcium phosphate and ammoniated compound fertilizer gave average yields similar to those given by superphosphate, but nitrophosphate was inferior to the other materials tested. Nitrophosphate gave significantly smaller average yields of potatoes than superphosphate both on acid and on neutral

soils; dicalcium phosphate and ammoniated compound fertilizer were roughly equivalent to superphosphate. On average of the group of swede experiments on acid soils the other phosphates tested were significantly inferior to superphosphate, perhaps because water-soluble phosphate gave the crops a good start.

TABLE 4
Mean yields of barley, potatoes and swedes in experiments testing dicalcium phosphate, nitrophosphate and ammoniated compound fertilizer

	Barley	Potatoes		Swedes	
		All soils	Acid soils	Neutral soils	Acid soils
No. of experiments ...	4	11	8	10	3
	Grain, cwt./acre	Tubers, ton/acre		Roots, ton/acre	
Without phosphate ...	22.8	7.0	9.9	9.4	10.2
With superphosphate supplying:					
0.3 cwt. P_2O_5 /acre ...	26.1	8.6	11.6	14.0	18.2
0.45 * cwt. P_2O_5 /acre ...	27.4	9.1	11.9	15.0	18.8
0.6 cwt. P_2O_5 /acre ...	28.6	9.5	12.1	15.5	18.9
With 0.45 cwt. P_2O_5 /acre as:					
Dicalcium phosphate ...	26.9	9.2	12.0	14.0	17.7
Nitrophosphate ...	25.3	8.6	11.1	13.3	18.3
Ammoniated compound ...	27.4	9.2	11.6	14.0	18.7
Standard error † ...	—	0.14	0.21	0.33	0.55

* Calculated from the average response curves.

† Standard errors do not apply to mean yields obtained without phosphate fertilizers.

The results of the second group of experiments are summarized in Table 5. For grass there were no significant differences between mean yields given by dicalcium phosphate and by superphosphate on average of the group of experiments on acid soils and also on average of the smaller group carried out on neutral soils. The average yields of grass given by Gafsa rock phosphate were only slightly greater than those obtained with no phosphate at all; on average of the experiments on acid soils both grindings of Gafsa rock phosphate were significantly inferior to superphosphate. For kale grown on acid soils all three phosphates tested gave average yields similar to those given by two-thirds as much phosphorus applied as superphosphate. On average of the large group of experiments on swedes on acid soils dicalcium phosphate was as effective as superphosphate; both rock phosphates gave lower yields than superphosphate at equivalent rate and for the coarsely ground material the difference was significant. The two grindings of Gafsa rock phosphate gave very similar yields of grass, kale and swedes and there were no significant differences between them. For the crops tested, these experiments provide no justification at all for the extra cost of grinding rock phosphate for direct application more finely than is customary in this country.

The 1954-57 series of co-operative experiments confirm earlier

work on alternatives to superphosphate. Although phosphate fertilizers which are insoluble in water may be as satisfactory as superphosphate for certain crops and on certain classes of soil, no water-insoluble phosphate has been consistently superior to it. Under adverse conditions, such as on acutely phosphate-deficient soils, or in dry and cold weather, the stimulus to rapid early growth

TABLE 5
Yields of grass, kale and swedes in experiments testing dicalcium phosphate and rock phosphate

	Grass		Kale		Swedes	
	Acid soils	Neutral soils	Acid soils	Neutral soil	Acid soils	Neutral soils
No. of experiments ...	18	6	6	1	16	3
	Dry matter, cwt./acre		Total crop, ton/acre		Roots, ton/acre	
Without phosphate ...	42.0	36.4	13.9	23.0	9.8	15.4
With superphosphate supplying:						
0.3 cwt. P_2O_5 /acre ...	45.7	39.4	15.8	24.2	14.0	17.1
0.45 * cwt. P_2O_5 /acre ...	46.9	39.9	16.1	25.3	15.0	17.3
0.6 cwt. P_2O_5 /acre ...	47.8	40.1	16.3	26.3	15.5	17.4
With 0.45 cwt. P_2O_5 /acre as:						
Dicalcium phosphate	46.4	39.2	15.7	25.0	15.0	16.8
Coarse Gafsa ...	43.4	37.0	15.5	24.1	14.3	16.8
Fine Gafsa ...	43.7	36.5	15.6	24.2	14.5	16.8
Standard error † ...	0.55	1.14	0.39	—	0.24	0.46

* Calculated from the average response curves.

† Standard errors do not apply to mean yields obtained without phosphate fertilizers.

which is provided by water-soluble phosphate may result in higher yields being obtained from superphosphate than from water-insoluble materials. Of the fertilizers tested in this last investigation dicalcium phosphate was roughly equivalent to water-soluble phosphate for barley, potatoes, grass and kale grown on all kinds of soil. Phosphate fertilizers made by nitric acid processes and by ammoniating superphosphate are believed to contain anhydrous dicalcium phosphate; it is quite possible that the anhydrous salt incorporated in a granulated fertilizer may not act as quickly as the finely divided dicalcium phosphate dihydrate which was used in this work. The British-made nitrophosphate tested in the 1954-57 experiments was clearly inferior to superphosphate for barley, potatoes and swedes. The material used contained one-third of its total phosphorus in water-soluble form, and 91 per cent was soluble in 2 per cent citric acid solution. The ammoniated compound fertilizer which was used in 2 of the 3 years had about half of its total phosphorus in water-soluble form, and it was practically completely soluble in citric acid solution; the phosphorus it contained was nearly as effective as that in superphosphate for barley and potatoes, but the material was a little inferior to superphosphate in one group of swede experiments. Gafsa rock phosphate is attractive because

it is a cheap fertilizer; it was rather less effective than an equivalent amount of P_2O_5 as superphosphate for both swedes and kale, but it was of very little value for grassland, even on acid soils. These statements on the value of alternatives to superphosphate are based on results obtained in the year of application, unfortunately the work provided no good evidence on the residual values of the tested phosphates. Where the experiments were continued for more than 1 year, second-year effects were generally small and difficult to measure precisely; this is particularly true of experiments on arable crops, where phosphate residues were diluted with soil by ploughing and cultivating before another crop was grown.

G. W. Cooke, G. E. G. Mattingly and F. V. Widdowson carried out field experiments at Rothamsted using radishes grown on very small plots to obtain further information on the rate of action of granulated fertilizers containing dicalcium phosphate. Superphosphate gave much higher yields of radish (harvested 4 weeks after sowing) than any of the granulated nitrophosphates tested. Residual effects were measured on grass which was sown immediately after harvesting the radishes; the effectiveness of the nitrophosphates increased rapidly, and for a second cut of grass taken 16 weeks after the experiment was started only one of the three nitrophosphates was significantly inferior to superphosphate. Radish were also used to compare granulated nitrophosphates with the fine powders made by grinding these materials; powdered nitrophosphates acted much more quickly than the granulated products from which they were made. Solubility of nitrophosphates in 2 per cent citric acid solution and in solutions of neutral ammonium citrate and alkaline ammonium citrate (all of these solutions are used for valuing fertilizers of this type in other countries) were of no use in assessing the values of the fertilizers tested in these experiments. The work has emphasized that granular nitrophosphates are at a serious disadvantage where very rapid action is needed for a crop with a short growing season, but that they are much more effective for long-season crops. There is no useful chemical method for providing a certain valuation of dicalcium phosphate in granular materials; conventional solubility tests may be satisfactory when powdered materials are used, but when granulated fertilizers are applied much must depend on the rate at which the granules break down and allow phosphate ions to diffuse away.

COMBINE-DRILLING OF POTASSIUM FERTILIZERS

(F. V. Widdowson, A. Penny and G. W. Cooke)

Twelve experiments on spring-sown barley which have been carried out during the last 3 years to compare combine-drilling and broadcasting of potash fertilizers are summarized in Table 6. Average responses to potash were large in 1955 and smaller in 1956 and 1957. In each of the 3 years combine-drilling muriate of potash gave higher average yields than broadcasting at both rates of dressing; the advantage of combine-drilling was large in 1955 and smaller in the 2 later years. In each year drilling the low rate (0.25 cwt. K_2O /acre) produced higher yields than broadcasting twice as

much potash. The gain from combine-drilling as compared with broadcasting 0.5 cwt. K_2O /acre averaged 2 cwt./acre of barley over the 3 years. The experiments were carried out in Hertfordshire and Bedfordshire on ordinary mineral soils chosen as being deficient

TABLE 6
The average effects of broadcasting and combine-drilling muriate of potash in experiments on barley

	1955	1956	1957	All years
No. of experiments	4	4	4	12
Yields of barley grain in cwt./acre				
Mean yield without potash	25.8	30.8	23.8	26.8
Increase from 0.25 cwt. K_2O /acre:				
Broadcast	3.7	2.1	0.8	2.2
Combine-drilled	6.6	2.4	1.2	3.4
Increase from 0.5 cwt. K_2O /acre:				
Broadcast	4.6	1.8	0.3	2.2
Combine-drilled	7.3	3.6	1.6	4.2

in soluble potassium, and the work indicates that wherever potash fertilizers are justified for barley, they should be drilled with the seed to obtain the best returns from the dressing. Previous work has shown that there are very marked advantages from combine-drilling phosphate fertilizers for all cereals and that drilling ammonium sulphate with the seed gives higher yields than broadcasting this fertilizer. The practice of many farmers who drill a compound fertilizer with barley seed to supply all the nutrients needed by the crop appears to be well justified, and should lead to higher yields than broadcasting the same fertilizer before drilling.

MANURING OF CROPS

Flax (G. W. Cooke and R. G. Warren)

The results have been summarized of a series of 50 field experiments carried out during the War by Advisory Soil Chemists to examine the effects of manuring on total yields and quality of flax. The effects of fertilizers were small, on average of all similarly treated experiments the gains were:

	Yields in cwt./acre		
	Total crop	Green-scuthed flax	Retted-scuthed flax
No. of experiments	50	38	27
Mean yield of all experiments	46.8	5.28	4.37
Gain in yield from a dressing (per acre) of:			
1 cwt. ammonium sulphate	2.6	0.09	0.29
3.5 cwt. superphosphate	0.8	0.09	0.05
1.8 cwt. muriate of potash	0.7	0.22	0.08

Total crop yields were increased slightly by nitrogen, but the returns from phosphate and potash were very small. The experiments in 1940, 1941, 1942, 1943 and most of those carried out in 1944 were processed by a dry-scutching method which avoided retting; very

small average increases in yield of green-scutched flax were given by nitrogen and phosphate, but potash gave a somewhat larger increase. Such small crop responses make it difficult to justify any general recommendation to use fertilizers on flax. At present prices the extra yields of green-scutched flax were approximately sufficient to pay the cost of the nitrogen and potash fertilizers used, but the average return from superphosphate was not sufficient to pay for the dressing. The way in which the experiments were processed appeared to affect the returns obtained from fertilizers. The

Per cent of N in soil:	Response to ammonium sulphate, cwt./acre	
	Total crop	Scutched flax
To 0.2	2.8	0.14
0.21-0.3	3.0	0.00
Over 0.3	1.0	-0.07
History of land:		
Old arable	3.3	0.18
Ploughed from grass	1.5	-0.02

produce of some 1943 experiments and of all those carried out in 1944 and 1945 was processed by retting followed by scutching. On the basis of all experiments providing yields of retted-scutched flax, manuring with phosphate and potash lost money, but nitrogen was profitable.

Analyses of soils taken from the sites of the experiments were examined to see if chemical methods could be used to pick out the more responsive fields. The response to nitrogen fertilizer was examined by separating the centres according to the percentage of nitrogen in the soil and also, where possible, from knowledge of the previous history of the land. Groups of experiments which were

Soil analyses, mg. of P ₂ O ₅ (or K ₂ O) per 100 g. of soil	Response, cwt./acre	
	Total crop	Scutched flax
To superphosphate		
Citric acid soluble P ₂ O ₅ :		
“ Low ” (to 8)	3.0	0.49
“ Medium ” (9-16)	0.4	-0.03
“ High ” (over 16)	-0.1	-0.04
To muriate of potash		
Acetic acid-soluble K ₂ O:		
“ Low ” (to 10)	1.5	0.48
“ Medium ” (11-16)	0.6	0.21
“ High ” (over 16)	-0.1	-0.10

on old arable land or which were on soils containing less than 0.2 per cent N gave worthwhile responses to nitrogen fertilizer. Solubilities of soil phosphorus in 1 per cent citric acid and of soil potassium in 0.5N-acetic acid were used to provide the groupings of the above experiments.

By restricting dressings of superphosphate to those soils with “low” citric acid-soluble soil phosphorus manuring would have been quite profitable; experiments on groups of soils with “medium” and “high” soil phosphorus gave no return on average from phosphate

dressings. In the same way the average increase in yield of scutched flax from muriate of potash applied to the group of soils having "low" values for acetic acid-soluble potassium more than repaid the cost of the fertilizer, but dressings of potash given to soils which were "high" in soluble potassium would have resulted in a loss. The experiments showed that fertilizers were justified for flax only when there was evidence from chemical determinations, or from experience, that the soil was deficient in one or more of the major plant nutrients.

Oil-palm (W. B. Haines)

Examination of data from the West African oil-palm experiments (*Rep. Rothamst. exp. Sta. for 1956*, p. 49) has now been completed. It has yielded much new information on the possibilities of improving oil-palm yields by means other than manuring which may be of economic importance. The yields of individual palms show a very distinct rhythmic cycle, and peak yields stand out clearly and generally occur every 3 years. The average peak yield for each palm is about 80 per cent greater than the mean yield for the palm. It is suggested that this cycle is due to the fruiting phase having a shorter natural period than the weather. When the fruiting phase and suitable weather coincide, then peak yields are likely to be produced. The peak years appear to be the normal performance of palms which have suffered no check to fruiting. Poor yields which are obtained in years between the peaks may be regarded as losses which might be prevented if the vulnerable phases during the fruiting cycle can be identified. In the experiments the cyclic rhythm was not influenced by manuring treatments, by the sites used or the variety of palm grown.

SOIL NITROGEN

Fixed ammonium nitrogen in soils and clay minerals (J. M. Bremner)

The use of hydrofluoric acid for the extraction and determination of fixed ammonium-nitrogen in soil (*Rep. Rothamst. exp. Sta. for 1956*, p. 53) has been studied in detail. Experiments with vermiculite and other clay minerals containing fixed ammonium showed that neither hydrofluoric acid nor hydrochloric acid released as much ammonia as did mixtures of the two acids. Fixed ammonium was completely extracted from vermiculite by treating the mineral with a mixture of 1N-HF and 1N-HCl for 24 hours at room temperature. This acid-extraction procedure was applied to soil samples from various profiles and indicated that 3-8 per cent of the nitrogen in the surface soils, and 10-50 per cent of the nitrogen in the subsoils was in the form of fixed ammonium. The possibility that soil nitrogen compounds are decomposed by the HF:HCl mixture with formation of ammonia could not be tested directly, but experiments with organic soils, and with various organic nitrogen compounds, indicated that estimates of fixed ammonium obtained by this procedure are not seriously affected by such decomposition. However, a comparison of different methods of determining ammonium-nitrogen in hydrofluoric acid extracts of soils showed that techniques previously adopted for this determination

gave erroneous results due to decomposition of organic nitrogen compounds. Methods based on distillation with magnesium oxide at 25° or with a borate buffer (of pH 8.8) at 100° appeared to be reliable when they were modified to eliminate interference due to hydrofluoric acid. Experiments with vermiculite showed that ammonium-nitrogen fixed by this mineral was determined quantitatively by the Kjeldahl method.

While working at Iowa State College J. M. Bremner has shown that fixed ammonium-nitrogen can be extracted quantitatively from vermiculite by treatment with cation-exchange resins in the sodium or hydrogen forms. The use of this method for extracting fixed ammonium-nitrogen from other clay minerals and from soils is now being explored.

The results of these investigations on the occurrence of fixed ammonia in soils may help to explain the facts that a large proportion of soil nitrogen is liberated as ammonia by acid hydrolysis, and that the carbon : nitrogen ratios of many soils decrease markedly with depth in the profile.

Extraction of soil nitrogen compounds (J. M. Bremner)

Hydrated silicate minerals are believed to interfere with the extraction of soil organic matter. Further investigations on the effect of treating soils with hydrofluoric acid to destroy interfering minerals have shown that pretreatment with *N*-HF : *N*-HCl at room temperature has no significant effect on the quantity of soil nitrogen extracted subsequently by 0.5*M*-sodium hydroxide or neutral 0.1*M*-sodium pyrophosphate. This pretreatment dissolved a considerable amount of soil nitrogen, and over 90 per cent of the nitrogen in Rothamsted soils could be extracted with repeated treatments with *N*-HF : *N*-HCl and 0.5*M*-NaOH at room temperature. The acid reagent dissolved considerably more soil nitrogen than did neutral sodium pyrophosphate, and it proved to be more effective than 0.5*M*-NaOH in extracting nitrogen from some subsoils. A single pretreatment with *N*-HF : *N*-HCl dissolved 15–29 per cent of the nitrogen from surface soils and 30–68 per cent of the subsoil nitrogen. Hydrofluoric acid releases nitrogen compounds associated with clay minerals which are not extracted by the neutral and alkaline reagents generally used to extract soil organic matter.

Distribution of forms of nitrogen in soil profiles (J. M. Bremner)

The distribution of the forms of nitrogen in three soil profiles has been studied by determining the amounts of total-, α -amino- and ammonium-nitrogen released by acid hydrolysis. It was found that the proportion of soil nitrogen released by hydrolysis as acid-soluble- and amino-acid-nitrogen decreased with depth, whereas the proportion liberated as ammonia increased with depth. The proportion of soil nitrogen dissolved by 0.5*M*-sodium hydroxide or by neutral 0.1*M*-sodium pyrophosphate decreased with depth, whereas the proportion dissolved by *N*-HF : *N*-HCl increased with depth. The carbon : nitrogen ratios of both alkali and pyrophosphate extracts increased with depth in the profile.

Transformation and movement of fertilizer nitrogen (J. K. R. Gasser)

Concentrations of nitrate and ammonium in the surface soil of the plots of an experiment on sandy loam at Woburn were measured at intervals during the period April to October. Ammonium sulphate, calcium nitrate or urea were added to plots on which ryegrass was sown at the beginning of April, and also to plots which were uncropped. Under grass there was no loss of inorganic nitrogen from the soil for 5 weeks after sowing, thereafter uptake was rapid, and when the grass was cut in late July all the nitrogen applied as fertilizer had been removed. At subsequent samplings inorganic nitrogen levels under grass were the same on plots which had received nitrogen fertilizer in spring as on unfertilized plots. On uncropped land which received no nitrogen fertilizer $\text{NO}_3\text{-N}$ reached a maximum value of 15 p.p.m. in July, but with wet weather in July and August nitrate levels fell and were only 2 p.p.m. in October. Nitrification of added ammonium sulphate on uncropped land appeared to be hindered by dry weather, and was not completed until 20 weeks after the fertilizer was applied. All the urea applied to uncropped land had been transformed to ammonium 8 weeks after application, and the final transformation to nitrate was completed within 20 weeks. April was a very dry month, rainfall in May was below average, but it was slightly above average in June and July. There was no loss of nitrogen applied as fertilizer from the surface 6 inches of soil until late July. From the end of July onwards, nitrate in the top-soil decreased, and at the final sampling in October more than four-fifths of the nitrate applied to uncropped land in April had been lost from the top 6 inches. Deeper soil samples taken in October showed that nitrate had moved to a depth of 3 feet below the surface, the maximum nitrate concentration at that time being 1-2 feet deep. This work on the light soil at Woburn confirms that carried out on heavy land at Rothamsted in 1956 (*Rep. Rothamst. exp. Sta. for 1956*, p. 53). On uncropped land at both stations urea and ammonium sulphate were converted to nitrate much more slowly than had been anticipated; nitrate was not leached out of the surface layer of either soil by moderate summer rainfall, and leaching was only effective in prolonged wet periods. In each year where grass was grown both ammonium and nitrate were removed rapidly and practically all the fertilizer nitrogen had been taken up at the first cutting of grass.

Leaching of nitrate from soils (R. Webster and J. K. R. Gasser)

Laboratory experiments were carried out to study the way in which nitrate may be leached from columns of soils. A clay-loam soil from Rothamsted and a sandy loam from Woburn behaved similarly. Nitrate was leached more rapidly from fine (<2 mm.) soil than from coarser (2-10 mm.) fractions; the rate of loss was still smaller from unsieved soil. In other experiments the progress of nitrate down the columns during leaching was followed. These suggested that initially leaching water removed nitrate from the surface of structural units; later, when the soil mass was saturated with water, nitrate contained *inside* soil aggregates was lost.

Mineral- and mineralizable-nitrogen under winter wheat (J. K. R. Gasser)

Existing levels of mineral nitrogen and also "mineralizable"-nitrogen determined by an incubation procedure were measured on soil samples taken from the unmanured plots of four winter wheat experiments. $\text{NH}_4\text{-N}$ and $\text{NO}_3\text{-N}$ were determined on the fresh samples and also after incubation at 20° for 30 days. The total mineral-N content was high and fairly constant during dry weather in November and early December, averaging 22 p.p.m. When heavy rain fell during December the mean values fell to 6 p.p.m. $\text{NH}_4\text{-N}$ and 2 p.p.m. $\text{NO}_3\text{-N}$. The mean level of $\text{NH}_4\text{-N}$ then remained at about 5 p.p.m. until the following August. The mean $\text{NO}_3\text{-N}$ content was 2 p.p.m. until April, it fell to 1 p.p.m. during May and June, and at harvest in late August was again 2 p.p.m. The mean increase in total mineral nitrogen on incubation showed a marked rise in January following wet weather at the end of December. This higher level of mineralizable-nitrogen was maintained until late March, after which date a gradual decline occurred. By harvest the amount of $\text{NH}_4\text{-N}$ plus $\text{NO}_3\text{-N}$ produced on incubation was again at the level measured the previous autumn when the work began.

SOIL PHOSPHORUS

Phosphate concentrations in soil in relation to crop growth (G. E. G. Mattingly)

A group of soils from Rothamsted and from Forestry Commission Nurseries, which had different mechanical compositions and different manurial histories, were used in a greenhouse experiment to study the relationship between yields of ryegrass and soil phosphate concentrations (measured after equilibrating soils with 0.01M-calcium chloride). The grass grew more rapidly on the light forestry soils,

TABLE 7

Soil phosphorus concentrations before and after cropping, yields of dry matter and "A" values of soils used in pot experiments on ryegrass

	P concentra- tion $\times 10^{-6}$ M		Yield, g./per pot		"A", mg./P 100 g. soil	
	Before crop- ping	After crop- ping	1st cut	Total in 4 cuts		
Forest nursery soils:						
Wareham	{ without phosphate ...	5.2	0.03	1.24	2.14	1.2
	{ with superphosphate	13.1	0.07	3.56	7.58	3.4
Ringwood	{ without phosphate ...	2.0	0.03	2.93	9.54	5.4
	{ with superphosphate	6.9	0.06	4.21	15.54	9.6
Rothamsted soils:						
Hoosfield	{ without phosphate ...	0.3	0.03	0.89	3.59	3.4
	{ with superphosphate	4.0	0.12	4.13	17.02	30.8
Broadbalk	{ without phosphate...	0.3	0.03	1.71	6.87	5.7
	{ with superphosphate	3.2	0.17	4.18	16.58	30.0

which had high phosphate concentrations initially, than on the heavier calcareous soils from Rothamsted. Nevertheless, the Rothamsted soils produced higher yields of total dry matter in four

cuts of grass in spite of their much lower initial phosphate concentrations. Typical yield data are given in Table 7 together with "A" values and the phosphate concentrations measured before and after cropping. The experiment was continued for 4 months and at the end soil phosphate concentrations had been greatly reduced; in some of the lighter soils from forestry experiments concentrations were less than 1 per cent of the initial values, and they were very difficult to measure. Phosphate concentrations after cropping were invariably higher on soils that had previously received dressings of superphosphate in the field. The *initial* rate of growth of ryegrass in this experiment depended largely on the phosphate concentration in the soil, but the *total* yield obtained was approximately proportional to the total labile phosphate.

Isotopic exchange of phosphate in soils in relation to uptake by ryegrass
(G. E. G. Mattingly and O. Talibudeen)

The amounts of phosphate that undergo isotopic exchange in 24 hours (designated "rapidly labile" or P_{24}) and in 150 hours (designated "total labile" or P_{150}) were determined in 19 soils before and after cropping with ryegrass in greenhouse experiments. Differences between total labile phosphate are given in Table 8, together with the mean quantities of phosphate removed by the ryegrass. On average of the whole group of soils the amount of phosphate taken up by ryegrass corresponded closely with the decrease in total labile phosphate which occurred during cropping. The labile fraction of soil phosphate for the group of acid soils from forest nurseries was overestimated when compared with the phosphate taken up by ryegrass, perhaps because 0.001M-citrate was used to determine the values. The grass removed approximately half of the original total labile phosphate on average of this group of acid soils and of the group of calcareous soils from Rothamsted.

TABLE 8

Comparison of the phosphate removed by ryegrass with the changes in the total labile phosphate (P_{150}) caused by cropping (all measurements are of mg.P/100 g. of soil)

	No. of soils	Mean total labile P		Mean total P removed by ryegrass
		Before cropping	Decrease after cropping	
Forestry soils (acid)	10	9.72	6.97	4.69
Rothamsted soils (calcareous)...	9	12.46	6.27	7.38
All soils	19	11.02	6.64	6.02

In all soils except three the ratio of rapidly labile to total labile phosphate (P_{24}/P_{150}) was lower after cropping than in the original soils. This suggests that ryegrass uses rapidly labile phosphate preferentially. In three Rothamsted soils that have never received phosphate fertilizers, phosphate appeared to be taken up by ryegrass from the rapidly labile and total labile fractions in the same proportions, there being no decrease in the ratio P_{24}/P_{150} after cropping.

The total yields obtained from four cuts of grass taken over 4 months were related exponentially to values for the total labile phosphate (P_{150}) of the soils used.

Phosphate residues in Rothamsted soils (G. E. G. Mattingly)

Earlier work (*Rep. Rothamst exp. Sta. for 1954*, p. 44) showed that about one-third of the residual phosphate remaining in the slightly calcareous soils of the Hoosfield Exhaustion Land (which had received heavy dressings of superphosphate before 1901) undergoes isotopic exchange in laboratory and greenhouse experiments. This study was continued by measuring labile phosphate ("A" values) using ryegrass grown (in pots) on soils from Hoosfield Permanent Barley, Broadbalk Permanent Wheat and Barnfield Permanent

TABLE 9
"A" values of Rothamsted soils determined in pot experiments on ryegrass

	Total P, mg./100 g. soil	"A", mg./100 g. soil	Increase in "A" as per- centage of increase in total P
Broadbalk:			
No phosphate	60.5	5.7	
Superphosphate since 1843 ...	115.2	30.0	44
Hoosfield:			
No phosphate	52.0	3.4	
Superphosphate since 1852 ...	129.3	30.8	35
Barnfield:			
No phosphate	89.1	15.6	
Superphosphate since 1876 ...	125.0	27.0	32

Mangolds Experiments (Table 9). These soils, in contrast to those of the Exhaustion Land studied previously, receive annual applications of superphosphate and a slightly higher percentage of the residual phosphate in them is readily labile. Using these data, and the total amounts of superphosphate applied to the Exhaustion Land, it appears that in 1901, when manuring of this site stopped, the labile and total residual phosphate contents of these soils were about 20 mg. P and 60 mg. P/100 g. of soil respectively. R. G. Warren has shown, however, that since 1901 the total phosphate removed by crops from the Exhaustion Land soils containing superphosphate residues is about 40 mg. P/100 g. soil. It seems, therefore, that over a long period of continuous cropping more phosphate is taken out of the soil than was originally present in an isotopically exchangeable form.

Isotopic exchange of phosphate in Rothamsted soils (O. Talibudeen)

The influence of the other ions present in solution on values for isotopically exchangeable (i.e. labile) soil phosphate has been studied further by comparing the effects of 0.001M solutions of citric acid

and diethyl-barbituric acid. Temperature has been found to have some effect on values for labile phosphate, and measurements suggest that a change in the nature of isotopically exchangeable phosphate may occur between 35° and 45°. Graphical analysis has been used to subdivide total labile phosphate into "rapid", "medium" and "slow" fractions (with P. Arambarri).

Very small concentrations of organic anions markedly increase the specific rate of exchange of phosphate ions in the "rapid" and "medium" fractions; increasing the temperature above 35°, in the absence of organic anions, causes a marked increase in the specific rate of exchange of the "medium" and "slow" fractions.

DECOMPOSITION OF PLANT RESIDUES IN GRASSLAND SOILS

(K. Shaw)

Work on the decomposition of the mats which are formed on large areas of permanent pasture on marginal land has been completed. These mats retain many of the characteristics of plant material; they are unlike the organic matter of normal mineral soil, as they contain much cellulose and hemicellulose and their lignin has a high methoxyl content. Cellulose and hemicellulose contents decrease down the mat profile and the lignin-like material increases, but the methoxyl content of the lignin fraction remains unaltered. When the mats were decomposed in the laboratory, the hemicellulose fraction remained constant but cellulose rapidly disappeared and the lignin fraction increased. The organic compositions of the mature grasses from which the mats were formed were very similar to those of good agricultural grasses which rarely seem to form mats. The mats used in this work had formed over very acid soils and were themselves very acid and very deficient in bases. When the pH was raised to neutrality by adding lime the mats decomposed rapidly in laboratory incubation experiments. Adding phosphate and inorganic nitrogen salts to the incubating mats decreased the rate at which CO₂ was produced, but these treatments increased the rate of decomposition slightly when lime was added as well. Phosphate increased the rate of mineralization of the organic nitrogen in the mats both in the presence and in the absence of lime. Decomposition was very slow at 2°, but increased with increasing incubation temperatures. The amount of moisture present did not have a large effect on rate of decomposition, although each mat examined appeared to have an optimum moisture content at which it decomposed most rapidly. The organic nitrogen present was converted to ammonia quite readily, even under water-logged conditions. Mixing the underlying mineral soils with the mats decreased their rates of decomposition slightly.

The persistency of these mats in the field appears to be due mainly to their high acidity and low base status. In improving such land adequate liming will be essential to promote decomposition of surface mat. In addition, the mats must be treated mechanically to disintegrate them and to mix the organic layers thoroughly.

THE EFFECTS OF CROPPING AND MANURING ON SOIL FERTILITY
Arable rotation at Saxmundham (G. W. Cooke, G. E. G. Mattingly
and R. J. B. Williams)

The Rotation I Experiment at Saxmundham was carried on for many years by the East Suffolk County Council; recently it has been in the charge of the National Agricultural Advisory Service. Wheat, mangolds, barley and a legume have been grown in a four-course rotation with constant annual manuring which has compared all combinations of sodium nitrate, superphosphate and potassium chloride; bone meal and farmyard manure have been tested as well. There have been large responses by all crops to phosphate fertilizers; nitrogen has increased yields of all non-legumes, but responses to potash have been smaller. The soils were sampled and analysed after 56 years of continuous cropping and manuring. Farmyard manure applied at 6 tons/acre each year has increased the total nitrogen and carbon in the soils by about 50 per cent (as compared with plots receiving fertilizers); plots which have had nitrogen and phosphate fertilizers now contain slightly more organic matter than plots which have not had these fertilizers. The total amount of soil phosphorus has been built up by farmyard manure and by bone-meal dressings and, to a lesser extent, by annual dressings of 2 cwt./acre of superphosphate. "Soluble phosphate" estimated by several methods differentiated clearly between plots dressed with phosphate and those which had received none. 0.3N-HCl gave very high values on plots treated with bone meal. This extractant is satisfactory for most Rothamsted soils, but it is known to be unreliable when used on soils containing residues of bone meal or rock phosphate. The amounts of phosphate dissolved by 0.5M-NaHCO₃, and those which were in equilibrium with 0.01M-CaCl₂, placed the soils of all the plots in the same order, which agreed qualitatively with differences in the estimated amounts of phosphorus removed by the crops during the 56-year period. The total potassium content of the soils is too high for the effects of either potash manuring or removal of potassium by crops to be detected. The values for exchangeable potassium in the soils of the plots were closely related to the losses or gains of soil potassium calculated from the known manuring and the estimated uptake by crops. It is possible that potassium deficiency would develop on the plots of this experiment which do not receive potash fertilizers if heavier crops were grown by using higher rates of nitrogen.

The effect of nitrogen manuring of grassland on soluble potassium in soil (R. J. B. Williams)

An experiment at Rothamsted comparing various forms of nitrogen fertilizers for Italian ryegrass provided an instance of the severe drain imposed on soil potassium supplies when grassland is manured heavily with nitrogen fertilizer. A basal dressing of potash fertilizer (0.83 cwt. K/acre) was applied over the whole area and the grass was cut four times during the season. Soil samples taken from individual plots at the end of the season had the following amounts of potassium soluble in 0.3N-HCl:

	Mg. K/100 g. soil	Total K removed by crop, cwt./acre
Without nitrogen	9.8	0.46
With ammonium sulphate supplying:		
0.2 cwt. N before each cut	7.4	0.97
0.4 cwt. N before each cut	4.9	1.46

Heavy nitrogen fertilization had reduced soluble potassium to half of the amount present on plots which had received no nitrogen, and at the end of the season grass on plots receiving nitrogen was showing potassium-deficiency symptoms.

ANALYTICAL

Fluorine (A. C. D. Newman)

Investigations on the development of a reliable method of determining fluorine have been completed. The effect of fluoride on the colour reaction between quinalizarin and aluminium salts was further investigated. A water-soluble sulphonate of quinalizarin (1 : 2 : 5 : 8-tetrahydroxyanthraquinone) was prepared and its U.-V. and visible molecular extinction curve recorded. The reaction of this derivative with aluminium was investigated spectrophotometrically, and it was found that a complex was formed which exhibited two absorption peaks, one at 265 m μ and one at 495 m μ . The latter absorption peak was used to examine the influence of fluoride ions on the complex; at pH 3.9 the absorption was markedly decreased by fluoride. A procedure was developed to use this bleaching to determine small quantities of fluoride, and it was applied to the estimation of fluorine in rock phosphates. This application showed, however, that the absorption of the reagent was dependent on pH to an extent which made the method accurate only when very close control of pH (± 0.01) was possible. However, its simplicity enabled the method to be applied to the semi-quantitative analysis of large numbers of solutions per day.

The classical method of determining fluorine by titration with thorium nitrate suffers from interference by aluminium, ferric ion, calcium, phosphate and sulphate, all of which may be present when rock phosphates are dissolved. It was found that fluoride may be separated from phosphate and the anionic metal chelates of ethylenediaminetetra-acetic acid by absorption on, and elution from, an anion-exchange column containing a strongly basic resin. Development of this principle was shown to provide a simple and accurate method of removing interfering ions. It is a satisfactory alternative to the distillation of fluorine (as fluorosilicic acid) which is generally employed. The procedure developed was used to determine fluorine in rock phosphates and gave values similar to those obtained by standard methods.

Iron (S. N. Chakravarti and O. Talibudeen)

The bright-red complex produced by the reaction between *o*-phenanthroline and ferrous sulphate has been used to estimate iron. The method has been adapted to work at very low concentrations (0.04–6 p.p.m. Fe) and was used to determine ferric and ferrous iron in the aqueous phase of acid soils. The colours produced were stable, and there was no interference from acetate buffer solutions of various pH values or from phosphate up to 50 p.p.m.