

ISMA* Technical Meetings

Madrid, Spain
23-28 September 1957

**In 1982, the name of the International Superphosphate Manufacturers' Associations (ISMA) was changed to International Fertilizer Industry Association (IFA).*

THE INTERNATIONAL SUPERPHOSPHATE MANUFACTURERS' ASSOCIATION

AGRICULTURAL COMMITTEE
AVENUE FRANKLIN D. ROOSEVELT
PARIS (8E)
TEL. BALZAC 57-25

CENTRAL OFFICE
44 RUSSELL SQUARE,
LONDON W.C.1
TEL MUSEUM 8927

LE/913

TO ALL MEMBERS:

TECHNICAL MEETINGS - SPAIN

SEPTEMBER 1957

This paper will be presented at the Technical Meetings in Madrid and Santiago de Compostela from 23rd to 28th September, 1957. It must not be published prior to that date, and, in any case, it must not be published without the permission of the author.

ANALYTICAL CONTROL IN THE MANUFACTURE OF FERTILIZERS

by E. W. Schwehr,
Fisons Limited.

Summary. The problems facing the chemist are discussed and the type of basic information necessary for the inception of a control scheme discussed. The paper lists the tests carried out in the factories of Fisons Limited in the control of manufacture of single superphosphate, phosphoric acid, triple superphosphate and granular compound fertilizers. It presents evidence of the type and extent of the variations which can occur in the manufacture of compound fertilizers by a rotary granulation process from solid raw materials. The essential legal regulations covering the sale of fertilizer in the United Kingdom are reviewed in an appendix. A method is devised for the setting up of control charts for use in the manufacture of granular compounds.

It is not the purpose of this paper to discuss in detail analytical techniques practised in the laboratories of Fisons Limited, but rather to show where and how analytical control can be applied to the manufacture of fertilizer. It discusses the ways in which variations in the analysis of the fertilizers produced may arise and attempts, in some cases, to assess the magnitude of these variations. The word "analytical" will be interpreted in its widest sense and will not be confined to those tests which are necessarily made in the confines of a specialist laboratory.

GENERAL CONSIDERATIONS

1. The Objects of Analytical Control

Analytical control is carried out to ensure:-

- A. Efficient use of raw materials and plant.
- B. Compliance with sales specification of the product.
- C. Compliance with minimum legal requirements and civil agreements in respect of product quality.
- D. Compliance with minimum legal requirements and civil agreements in respect of any gaseous or liquid effluent produced by the manufacturing process.
- E. Prevention of hazards to health within the factory.

The chemist must consider each of these objects separately and decide on the type of sample, and the analysis required on the sample, which will give him the information necessary to fulfil each object.

To the control chemist, the fertilizer industry presents a difficult problem. He is concerned with reactions between solids and liquids in, often, a non-homogeneous mass. Faced with the knowledge that if, for example, he is attempting to fulfil the first object mentioned above, then he will always be testing material at some intermediate stage when the reaction is not completed. He must therefore forecast from his results and in the light of his knowledge of the subsequent rate and progress of reaction, whether or not adjustments to materials or process are necessary. Even worse, the product being manufactured may not enter into true chemical reaction, so control tests may be designed to assess the efficiency of plant operation and equipment rather than the progress of reaction.

In spite of all this, fertilizers are sold throughout the world on a standard based on a chemical analysis, and the need for analytical chemical control is, therefore, paramount.

2. Factors Influencing the Choice of a Control Testing Procedure for a Process.

A. The Process

The most important factor in establishing any procedure of control testing is to have an intimate and accurate knowledge of all stages within the process and to have established the effect of known variations on the operation of the plant and on the product. To build up this knowledge requires repeated and thorough plant investigation. It is the only way to answer such questions as:-

- (i) Where can a sample be taken, so that the results of a test made on that sample can be interpreted into plant operation, and, if necessary, modification of that operation?
- (ii) How representative is the sample likely to be?
- (iii) What size need the sample be?
- (iv) What will be the effect on subsequent stages of the process if a modification to plant operation or materials feed is made at any given point?

B. Legal Requirements

The process may give gaseous and/or liquid effluents which must comply with certain regulations. Regular control tests of these "by-products" of the process must be carried out. Fortunately, such tests are mainly for record purposes, and their priority can be lower than that of other tests. The product may also be required to comply with certain legal standards.

C. The Quality of the Product

If the sales specification is "rigid", then the degree of variation allowed in control tests will be smaller than if there is an appreciable tolerance in the specification.

D. The Choice of Analytical Test

Can it be a physical test or is a chemical test necessary? Must it be carried out by a skilled analyst or can it be made part of the routine of the plant operators? Can a less accurate method of assessment be accepted in order to obtain a more speedy result? How often must the test be carried out? How does the chosen test relate to those laid down

by legal requirements or in the sales specification? Has the test a definite bias when compared to other more generally accepted methods of test? Is it one which has a distinct operator bias?

When the answers to such questions are available, the chemist can put forward a control test procedure. The chemist must be responsible for laying down the standard, or mean value, for any test and applying to it the permitted limits of variation outside of which corrective action must be taken. Any such procedure must have the approval of the management and it must be backed by an agreed procedure for communication of the results and an acknowledged scheme for responsibility for any action taken in the event of necessary corrective measures.

Having done this, the chemist's responsibility is not over, for he must continually watch the results of his tests, if the efficiency of the factory is to be maintained, and devise means by which such results can be simply conveyed to both plant management and operators. In this respect, the use of control charts and statistical methods of interpretation must not be ignored.

The routine adopted in a control laboratory must always be heavily weighted in favour of tests carried out during the process to prevent production of off-specification material. It is then merely necessary to monitor goods ready for despatch to ensure that errors are not occurring in the factory and to provide records for identification of sales consignments.

3. Sampling

No control analysis has any value unless the sample on which the test is conducted is fully representative of the material being processed at the time the sample is drawn. It is felt that no review of this nature can be complete without reference to the subject of sampling, which is a complex one; the degree of complexity being dependent on the homogeneity of the material being sampled.

No hard and fast rules can be laid down and every process stream must be sampled on its merits. The drawing of a representative sample at any stage of a process seldom receives the attention it demands. Recent tests conducted by the author, the results of which were presented to the Fertiliser Society in Great Britain⁽¹⁾, have illustrated the high degree of analytical variation which can arise between samples drawn by different, but recognised and approved, methods of sampling from the same batch of material.

It is difficult to generalize over the way in which samples should be drawn, but it is probably correct to accept, a priori, the following two maxims when sampling solids:-

- A. Never take increments at regular time intervals if they are to be combined to give one sample for analysis. There is always the possibility that the time period chosen will coincide with some periodic fluctuation of the plant, so that a biased sample will be produced.
- B. Always take a large sample. Sample dividers are available which give a truly representative sub-sample of 1/16th of the original sample in a single pass. The time spent on sub-sampling is amply repaid by the increased reliance which can be placed on the test results obtained on such samples. It permits the acceptance of smaller tolerances, since sampling errors are reduced.

For process control purposes, a "spot" sample, i.e. one which is taken almost instantaneously is required. For monitoring purposes or for materials efficiency assessments a sample composed of a series of increments taken at random over a definite period of the operating cycle or day is preferable, since it can be expected to iron out the normal small fluctuations which are superimposed on the main process. The commonly accepted periodicity of such samples is that of the operating "shift". However, care must be taken that the increments which make up such samples are of equal size or are always in the same quantity relationship to the material flowing at the time of sampling, in order to prevent bias in the sample.

APPLICATION OF CONTROL TESTS TO MANUFACTURE OF FERTILIZERS

The following sections set down the type of tests suggested as necessary for control of the manufacture of single superphosphate, phosphoric acid, triple superphosphate and compound granular fertilizers.

In order to follow the reasons for such tests, it is essential for the reader to appreciate not only the legal regulations covering the sale of fertilizers in the United Kingdom (briefly summarised in Appendix A), but also the fact that the majority of fertilizers are manufactured to a definite pre-determined analysis, which is stated on printed forms, circulated to customers as a statutory statement, and which may be printed on the bags in which the fertilizer is packed.

The price of superphosphate is based on its water soluble P_2O_5 content to the nearest whole or half unit, which may be either above or below its actual determined water soluble P_2O_5 content.

1. The Manufacture of Single Superphosphate

In the manufacture of single superphosphate, the essential requirements are a knowledge of:-

- A. The correct acid/rock ratio to give the degree of conversion to water or citrate solubility required,
- B. The acid strength and acid temperature required to give the desired consistency of the slurry leaving the mixer and entering the den,
- C. The degree of fineness of grinding of rock necessary to achieve the conversion required in the time desired,
- D. The retention time in the den to ensure satisfactory condition of the superphosphate for "cutting out".

All of these factors can be established for a given type of rock, mixer and den by analysis of the rock and standardized tests in the laboratory before the rock is used in the manufacturing plant.

Once the conditions are established, it is merely necessary to carry out certain control tests to ensure that the required conditions are being maintained.

We consider the following tests are sufficient to control the manufacture of single superphosphate to produce a material of uniform analysis:-

(i) Process Control Tests

- (a) Degree of fineness of grinding of the rock. Once per eight-hour shift.
- (b) Acid strength and temperature. The frequency will depend on whether the acid is fed from a stock tank or directly from a small capacity tank fed from the acid dilution plant.
- (c) Weight of rock being fed to the mixer. The frequency of test will depend on whether the mixer is of the continuous or batch type and whether the rock feeder is a volumetric one or of the belt weigher type.
- (d) The quantity of acid being fed to the mixer. The frequency of test will depend on the type of equipment used to meter the acid to the mixer and whether the equipment records the total amount of acid being fed to the plant.
- (e) The free acid on an ex den sample. Once per hour.
- (f) The water soluble P_2O_5 and total P_2O_5 and moisture content of an ex den sample. Once per eight-hour shift.
- (g) The Ca/SO_4 and Ca/P_2O_5 ratios on ex den samples. Once per shift on composite samples in order to check the acid/rock ratio.
- (h) A full analysis of the rock. The frequency of test will depend on factory conditions such as the possibility of contamination of raw material in store, size of consignments of raw rock, etc. A given type of rock is normally of uniform analysis and analysis on a weekly basis is probably adequate.
- (j) Gaseous exit from scrubbers. Not less than once per shift.
- (k) Liquid Effluent. Any need for control is dependent on the existing requirements applying to the discharge of the effluent from the factory. pH meters, dosing controllers and recording instruments can be used to check and record such factors as acidity of the effluent. An automatic sampler can be installed to provide samples for laboratory assessment.

(ii) Monitoring Tests

The water soluble P_2O_5 , total P_2O_5 , free acid and moisture content of samples of matured single superphosphate. Samples of material are drawn from that portion of the bulk heap to be bagged for sale or to be transferred for use to the granulation plant. As such, samples will normally be tested on a once-daily basis.

(iii) Illustrations of the Value of the Tests

Control of rock and acid feeds

Measurement of rock feed. Table feeders have been shown to vary by as much as $\pm 8\%$ once in four hundred times, even when the same type of rock of essentially the same grist size is being fed. The variation is due to the aeration of the ground rock, both into and out of storage hoppers. On the other hand, the variation of a belt weigher need be no more than $\pm \frac{1}{2}\%$ on the same basis of assessment.

Measurement of acid feed. Rotameters are available which will give a high degree of accuracy for the metering of sulphuric acid. Alternatively, cup feeders of equal accuracy can be used. In fact, a case can be made out for the use of cup feeders rather than rotameters on the grounds that they can be geared to the belt weigher feeding the rock, they can be physically checked for accuracy more easily and they can be simply integrated to give the total amount of acid feed in a given period.

The combined effect of controlling rock and acid feeds is shown in Table I. The table shows quite clearly that by having the most accurate means of proportioning available, distinct advantages result, especially if the superphosphate is required in a "green" state for use, say, in a granulation plant. As is expected, this advantage is partially lost after the material has been allowed to mature.

TABLE I
Value of Control of Rock and Acid Feeds in the Manufacture of Single Superphosphate

Rock Feeder	Acid Feeder	Control Test	Control Operation	Type of Sample	No. of Samples	Mean w/s P ₂ O ₅	Standard Deviation	Type of Rock
Table Feeder	Rotameter	Free acid ex den	Manual on acid feeder	Ex den	272	15.86%	1.220	Morocco
Belt Weigher	Rotameter	Free acid ex den	Manual on acid feeder	Ex den	53	16.31%	0.360	Morocco
Table Feeder	Rotameter	Free acid ex den	Manual on acid feeder	Matured super	61	18.57%	0.561	Morocco
Belt Weigher	Rotameter	Free acid ex den	Manual on acid feeder	Matured super	67	18.36%	0.625	Morocco
Belt Weigher	Cup Feeders	Free acid ex den	Adjustment of variable speed drive on acid feeder	Matured super	51	18.10%	0.322	Morocco
Belt Weigher	Cup Feeders	Free acid ex den	Adjustment of variable speed drive on acid feeder	Matured super	89	16.18%	0.342	Gafsa

N.B. Comparisons between mean water soluble P₂O₅ values should not be made, since no information of the actual acid/rock ratios for the periods reviewed is available. The acid/rock ratio did not change during each period of operation reviewed.

2. The Manufacture of Phosphoric Acid

Phosphoric acid is produced by a wet process in the Dorr Plant. The reaction is controlled to produce calcium sulphate in the form of gypsum, which is separated on belt filters. Some of the slurry is passed to the filters, while a portion is recirculated to the head of the reaction system. Filtration is controlled to produce some 32% P_2O_5 acid which is concentrated in vacuum evaporators before being used in the manufacture of triple superphosphate. The remainder of the acid is washed from the gypsum on the filters and recirculated to the head of the reaction system.

Phosphoric acid is produced solely as a raw material for other processes and is not sold. There is therefore no need to consider analytical tests other than those required for control purposes.

(i) Tests carried out on the reaction system

- (a) Rock feed. The zero on the belt weighers is checked once per shift and the actual delivery of rock physically checked at random intervals by process operators.
- (b) Fineness of grinding of rock. This is checked twice per shift by process operators.
- (c) Sulphuric acid feed. This is carried out by means of cup feeders whose actual delivery is checked at random intervals.
- (d) Sulphuric acid strength and temperature. This is checked from samples drawn from the large stock tanks once per shift by process operators. A sample is titrated for actual H_2SO_4 content.
- (e) Excess H_2SO_4 in slurry fed to filters. The aim is to keep this at 2½% to ensure complete precipitation of calcium, and since the solubility of gypsum in mixtures of phosphoric acid and sulphuric acid is at a minimum at this concentration of sulphuric acid. The frequency of test is once every two hours and the test is carried out by process operators.
- (f) Determination of phosphoric acid in slurry. If the strength of the phosphoric acid rises above 32% P_2O_5 , then, according to the Lehrecke Diagram, the formation of the hemi-hydrate of calcium sulphate is promoted and filtration efficiency is decreased. On the other hand, if the concentration of phosphoric acid falls, an extra load is thrown on the evaporators. The test is carried out once every two hours by process operators. The normal working range is 30½ - 31½% P_2O_5 .
- (g) Specific Gravity of recirculating liquor. This is carried out to check the constancy of the reaction mixture. The test is made once every two hours by process operators. The normal working range is 1.59 - 1.60 at 75°F.
- (h) Crystal size of gypsum. A sample of slurry is filtered, the crystals washed and examined under the microscope. The test is carried out once per shift by the main laboratory. An even crystal size is required and during normal working operations 90% of the crystals will lie between 10 u and 100 u in size.
- (j) Temperature Control. The temperature of the mixture in the reaction vessels is recorded. It is maintained at 75 - 78°C, by use of cooling air. Above 78°C, some of the calcium is precipitated as the hemi-hydrate of calcium sulphate.

(ii) Tests Carried Out on the Filtration System

To ensure balanced working of the filtration equipment, the following tests are carried out.

- (a) Gypsum cake. A composite sample is tested every four hours for moisture content and for water soluble and total P_2O_5 .
- (b) Acid strength. The three grades of acids recovered from the filters are tested for phosphoric acid content every two hours. Samples are drawn from the holding tanks.
- (c) Wash water. The wash water used in the filters is metered to each filter unit and the quantity of wash water used is recorded hourly.

(iii) Tests carried out on the Evaporators

- (a) Concentrated acid. A composite sample is tested once hourly for phosphoric acid content. Sulphuric acid content, calcium and sulphate content are tested once per day in the main laboratory.
- (b) Steam consumption. The steam consumption of each evaporator and the quantity of condensate flowing from the evaporator is recorded. These tests indicate the amount of scale formation in the evaporator and so indicate when the unit should come off-stream for descaling.
- (c) Condensate return. This is continually checked for variations in pH and a daily sample is checked for P_2O_5 content in the main laboratory. This control prevents damage to boilers and indicates any leakage in the tubes or end boxes.

(iv) Gaseous and Liquid Effluents

- (a) Gaseous exits. The stack passing the cooling gases to air after scrubbing are checked daily for acidity by the main laboratory.
- (b) Liquid Effluent. The liquid effluent from the wash tower is fully analysed daily, while all washdown drain points are piped to a common exit which is sampled and tested daily for its P_2O_5 content. This test is carried out in the main laboratory.

3. The Manufacture of Triple Superphosphate

Triple superphosphate is produced in two forms, either as a granular product of low moisture content by reacting 38% P_2O_5 phosphoric acid and rock in a slurry system according to the Dorr process, which is followed by drying of the granules, or by reacting 50% P_2O_5 phosphoric acid in a suitably modified Broadfield mixer and den to give a powder product of high moisture content. Both these products are sold as fertilizers or used in the manufacture of granular compounds.

A. Granular T.S.P.

(i) Process Control Tests

- (a) Fineness of rock. This is checked on a composite sample twice per shift by process operators. It is important in that the ultimate conversion of P_2O_5 to the water soluble form is dependent on it.

- (b) Rock Feed. The zero on the belt weigher used is checked once per eight-hour shift by process operators. The actual delivery of rock is checked at random intervals.
- (c) Acid feed. The phosphoric acid is metered to the plant by cup feeders, which are checked at random intervals and set independently of the rock feed, according to acid strength and temperature.
- (d) CaO and P₂O₅ Content. The CaO and P₂O₅ content of the slurry ex the reaction vessels is tested twice per shift by the main laboratory to check the acid/rock ratio.
- (e) Reactor temperatures. These are controlled between 90°C and 95°C.
- (f) Ex drier temperature. The temperature of the granules ex drier is kept below 130°C to prevent loss of water soluble P₂O₅.
- (g) Screening tests ex drier. The total percentage of material above and below the accepted product size range is determined once per shift in order to establish the recycle load on the plant.
- (h) Gaseous exit tests. The gas from the drier is water scrubbed and the gaseous exit tested daily. This test is made by the main laboratory.
- (j) Liquid effluent. The liquid effluent from the wash tower is tested daily for P₂O₅ content to measure the carry-over of P₂O₅ in the form of dusts to the scrubbers. This test is made by the main laboratory.

(ii) Monitoring Tests

A composite daily sample is tested for total, water soluble and citrate soluble P₂O₅, moisture and free acid. The citrate solubility is normally less than 1%, figure in excess of this indicating under acidulation. It is important to control the degree of acidulation, since excessive free acid content at the low moisture contents at which the material is produced cause bag rot. Under acidulation prevents full financial realisation in the sales value of the fertilizer.

B. Powder T.S.P.

As far as control testing is concerned, this is essentially the same as for the manufacture of single superphosphate.

(i) Process Control Tests

- (a) Fineness of rock. This is checked twice per shift by process operators.
- (b) Rock feed. The zero on the belt weigher is checked once per shift and the actual delivery of rock is measured at random intervals.
- (c) Acid feed. The strength of the phosphoric acid used in conjunction with any one type of rock is important and must be carefully controlled. Cup feeders which are independently calibrated at random intervals are used.

- (d) Ex mixer samples. The CaO and P₂O₅ contents of ex mixer samples are determined once per shift to check acid/rock ratios.
- (e) Ex den samples. The free acid content is determined twice per shift by process operators, the control figure depending on the type of rock, the acid/rock ratio and the type of product required after maturing. The results are taken in conjunction with the results for (d) above to adjust the acid feed.
- (f) Gaseous exit. The den gases are water scrubbed and the gaseous exit tested for acidity on a daily basis by the main laboratory.
- (g) Liquid effluent. The wash tower effluent is checked for P₂O₅ content daily to control the carry over of material from the den.

(ii) Monitoring Tests

As for granular T.S.P.

It should be noted that the results obtained for all process control checks made by process operators are cross-checked by the main laboratory. "Spot samples" are drawn once per shift for this purpose.

4. The Manufacture of Granular Compound Fertilizers

In the manufacture of granular compound fertilizers from salts of ammonia and potash, triple and single superphosphates, the required quantity of each ingredient is proportioned by weighing on a batch principle. The batch is then mixed and passed to a rotary conditioner where the raw materials are sprayed with water in order to form granules. The granules are dried and cooled in conventional equipment. After drying, oversize granules are separated, while the fines or small granules are separated after cooling.

The oversize may be crushed to a size range below that of the smallest granule required and added to the fines which are always returned to the head of the conditioner, sometimes, but not necessarily, through the batch mixer. Alternatively, the oversize may be "cracked" to produce a mixed stream of cracked material consisting of particles which are still oversize or are within product size range or are fines. The cracked oversize stream may be returned to the head of the drier for re-drying (in which case any fines produced during cracking are removed with the normal process fines and any material which is still too large is removed on the oversize screen) or may be added to the material leaving the drier so that it is rescreened (in which case oversize is again rejected and any fines made rejected after cooling).

The product passes to store in pens which may take up to 2,000 tons and which are normally filled by ploughing material from an overhead conveyor. Material is reclaimed by mechanical shovel or overhead grab from the pen, fed to a bagging plant and filled into bags for despatch.

It is perhaps advisable to consider the sources of variation of analysis which can arise in any such process. At the same time, the necessity to comply with the Regulations to the Fertilisers and Feeding Stuffs Act must be remembered.

A. Raw Materials Analysis and Formulation

It is essential for any such process that the formulation, i.e. the quantities of each raw material required, is based on the known analysis of the raw materials being used. The first control test, therefore, in the manufacture of granular compounds must be the analysis of the raw materials and the formulation of the compound based on the determined analyses. Dr. Manning, in a paper entitled: "The Act and the Fertiliser Manufacturer" presented to the Fertiliser Society, showed the amount of the permitted tolerance of analysis which would be consumed by the normal variations in analysis which occur in consignments of, supposedly, the same grade of raw material. It is therefore necessary to make adjustments to the formulation if the amount of "error" to be introduced in the analysis of the product by small variations in the analysis of the raw materials is to be kept to a minimum.

B. Plant Variations

By repeated sampling of the product to a definite procedure as it leaves the process stream, sufficient results can be collected together to enable reliable estimates of the variations which occur during processing to be made. Each granulation plant must be treated on its own merit and, as is to be expected, the circuit employed in disposing of oversize and fines streams will have an appreciable effect on the variation of analysis of the samples.

IT IS OUR PRACTICE to take eight-hourly shift samples from each granulating plant. Each shift sample is composed of eight increments. The variance for each plant food in shift samples for each compound can then be calculated from the analytical results. In Table II the range of the variance for results returned for 12 granulating plants is shown. All the variances refer to the same compound and each one is based on between 40 and 250 individual results.

This variance is a true estimate of the variations occurring during a shift in the manufacture of granular compound fertilizer and must be considered in designing any control scheme.

TABLE II

Range of variance for plant foods in shift samples of No. 31 fertilizer (9;9;15) as shown by analytical results from 12 granulating plants.

	Plant Food		
	N	w/s P ₂ O ₅	K ₂ O
Maximum variance	0.23	0.20	0.30
Minimum variance	0.05	0.04	0.06

C. Bagging Plant Variations

In the type of granulation process previously described in this paper, it is well known that there are very marked differences in analysis between granules of different sizes.

In Table III, a series of analytical results which illustrate this fact are set out.

TABLE III
Variation of Analysis with Granule Size

Size of particles as B.S.S. screen sizes	Analysis			% sample in size range
	N	w/s P ₂ O ₅	K ₂ O	
Above No. 5	<u>6.4</u>	<u>11.2</u>	<u>12.6</u>	2.5
Between Nos. 5 and 8	9.0	7.9	14.8	30.0
Between Nos. 8 and 14	<u>10.1</u>	<u>7.0</u>	14.2	49.0
Below No. 14	<u>10.4</u>	<u>5.8</u>	15.8	18.5

The complete sample analysed 9.10% N, 8.35% w/s P₂O₅ and 14.45% K₂O, which was within the limits of tolerance allowed in the United Kingdom for a sample of a fertilizer for which a statutory statement of 9.00% N, 8.25% w/s P₂O₅ and 15.00% K₂O was given. Yet all the results underlined are outside the limits permitted.

This illustrates that any sample drawn must also be fully representative of the stream from which it is drawn, as far as particle size distribution is concerned, before the analysis can be correct.

This effect which is specific to this method of manufacture of granular compounds has an even more serious implication. When heaps of compound fertilizers are formed by ploughing from an overhead belt to a heap below, a natural segregation of particles of different sizes occurs. The big granules run down the outsides of the heaps and the small particles congregate in the centre. If this material is then reclaimed by mechanical means without further remixing of the different sized granules, then the analysis of a batch of material drawn from the heap will not be representative of that heap, since the particle size distribution will not be representative.

Tests have been conducted to estimate the increase of variation in N,P,K analysis which occurs during the process of forming a heap and reclaiming fertilizer from it for bagging purposes.

In Table IV, the calculated variances of analysis for each plant food in each compound for samples taken from the granulation plant and for samples taken from individual bags of fertilizer are shown. The granular fertilizer in the bags was reclaimed by mechanical shovel from heaps formed by ploughing from an overhead belt.

TABLE IV

Comparison of Variances of Analytical Results for Plant Foods in Samples from the Granulating Plant and from Individual bags

Grade	Nitrogen			w/s P ₂ O ₅			K ₂ O			
	Production Var.	Bagging Var.	Ratio	Production Var.	Bagging Var.	Ratio	Production Var.	Bagging Var.	Ratio	
No. 1	0.056	0.1367	2.44	0.0873	0.0533	0.63	0.1185	0.2049	1.73	
No. 2	0.0538	0.2137	3.97	0.0686	0.0075	0.11	0.0974	0.1261	1.30	
No. 5	0.0473	0.0284	0.60	0.1669	0.0391	0.24	0.2629	0.1153	0.44	
No. 6	0.0976	0.0790	0.81	0.1347	0.1375	1.02	0.0767	0.4458	5.81	
No. 7				0.0561	0.1598	2.85	0.0982	0.2889	2.94	
No. 31	0.1062	0.1735	1.63	0.0665	0.2117	3.18	0.5411	0.5928	1.09	
No. 33	0.1167	0.5218	4.47	0.3300	1.1519	3.49				
D.G.	0.0395	0.1726	4.37	0.0579	0.0581	1.00	0.0974	0.0800	0.82	
Average Ratios			2.61				1.56			

At a conservative estimate, the variance of analysis of each plant food in fertilizer in a single bag must be expected to be twice as much as that of the granulating plant material.

D. Variance due to Analytical Method

This is a subject which cannot be fully discussed in a paper of this nature. The choice of analytical method is not normally left to the manufacturer. The Regulations covering the sale of fertilizer usually specify the methods of analysis which must be used. It is unfortunate that the majority of the methods specified are not those which give a result in the shortest possible time, nor are they necessarily the most accurate. The manufacturer requires a result quickly, so that he can make adjustments to his process and prevent the manufacture of off-specification material. There is nothing to prevent a manufacturer using any method of analysis he desires for control purposes, providing that he knows the extent of the bias between his selected method and the official method by which he is judged. He must also know the relative accuracy of the two methods, and whether or not there exists a significant "between laboratories" variance in either of the methods.

The following comments relate the accuracy and reproducibility of the various alternative methods of analysis for each plant food.

(i) Nitrogen

- (a) Ammoniacal Nitrogen. Straight distillation of a solution of the sample with light magnesium oxide is to be preferred. The use of sodium hydroxide may lead to the evolution of nitrogen from compounds such as urea. The method has a high degree of reproducibility within a given laboratory, i.e. the "within laboratories" variance is low. However the method has a high "between laboratories" variance and mean results obtained by two different laboratories may differ by as much as 0.25 units at a 9 unit level. If consistent results are to be

obtained, then great attention must be paid to design of the apparatus and to distillation times, etc. It is always desirable to carry out "blank" determinations on the reagents.

- (b) Nitrate Nitrogen. As a method, the Devarda alloy reduction of nitrate nitrogen, followed by distillation with sodium hydroxide, has a large analytical variance. It is however as consistent as any of the newer methods, such as that due to Cotte and Kahane or the A.O.A.C. method. The oxidometric method, based on the oxidation of ferrous sulphate, is as consistent as the Devarda alloy method and has the advantage of giving results in a very much shorter time. Unfortunately neither this method nor the method based on discharging the colour from a standard solution of indigo-carmin can be accepted as a statutory method, since neither is specific to the nitrate ion.
- (c) Organic Nitrogen. The Kjeldahl reduction of organic nitrogen in the presence of mercury has been found to be the most reproducible method for the determination of organic nitrogen.

(ii) Phosphates

The determination of phosphate was fully reviewed in a paper LE/600B(d) entitled "Recent Advances in the Determination of Phosphate in Fertilizers" presented to the Technical Meeting of this Association held in Aarhus in September 1955.

Subsequent work has confirmed the superiority of the Wilson citric quinoline molybdate method for the determination of all forms of phosphate in fertilizer. The colorimetric method based on the formation of a coloured ion with vanado-molybdate is now established as a routine method of analysis in many fertilizer factories.

(iii) Potash

The determination of potash as its platinichloride salt by the procedure due to Perrin has been shown to be far more accurate and reproducible than the older methods, based on perchlorate finishes. However, there is sufficient evidence to suggest that, unless adequate washing of the precipitate by a solution of ammonium chloride saturated with potassium platinichloride is carried out, the result obtained may be biased on the high side.

The use of comparatively simple flame photometers has given excellent analytical results. Comparative tests have shown that not only the total variance but both the "within laboratories" and "between laboratories" variances of this method of analysis of potash are less than those for the Perrin method. Potash values given by this method are approximately 0.1 units lower at an 18 unit level than those given by the Perrin method.

With a detailed knowledge of the extent of the variations of the process given above, the chemist is able to use his own analytical results for samples drawn at any stage of the process to predict the number of consignments of material whose analysis is likely to be outside any legal or sales tolerances. Alternatively, he can set himself a target of maximum failures and so calculate the variation from statutory statement that he can tolerate in any type of sample drawn from the plant. In Appendix B, theoretical basis for the establishment of the control limits for a shift sample from a granulating plant product stream is laid down.

E. Control Tests

The control tests recommended for granulating plants are as follows:-

(i) Process Control Tests

- (a) Raw Materials Analysis. The raw materials used are tested by the main laboratory at least once per shift.
- (b) Raw Materials Proportioning. The zero on each weigh pan is checked at least once per shift, and the actual quantity checked against the scale at random intervals.
- (c) Ex drier material. The granules are not allowed to exceed 120°C in temperature to prevent excessive reversion of water soluble P_2O_5 . The product stream is sampled and a grading carried out to determine the relative ratios of the oversize, product and fines fractions. This indicates fluctuations in granulation efficiency and loading of screens and return streams of material for reprocessing. This test is made once every two hours by process operators.
- (d) "Spot" samples of Product. A full N,P,K analysis and moisture determination is carried out on a "spot" sample once per shift by the main laboratory (see note below).
- (e) "Shift" samples of Product. A full N,P,K analysis and moisture determination is carried out on a shift sample by the main laboratory. A shift sample is normally composed of eight increments. A full grading analysis of this sample is also made.
- (f) Gaseous effluent. The acidity of the gaseous exit after water scrubbing of the ex drier and ex cooler gases is made once per shift by the main laboratory.
- (g) Liquid effluent. A daily sample is tested for total solids and N,P,K content by the main laboratory. In this way, the losses of plant food in the form of dusts which have passed the cyclones can be controlled. If it is necessary to control the pH of the effluent, either pH meters and recorders are used, or samples are checked regularly by plant operators.

(ii) Monitoring

At random, but on at least two occasions each day, five-ton consignments of fertilizer from each bagging plant are sampled and fully analysed in the main laboratory.

Note. A "spot" sample is defined as one which is composed of eight increments drawn at five-minute intervals, each increment being of the same size as that which forms the "shift" sample. It has been proved, both during planned tests and in routine work extending over many months, that the variance of plant foods in a series of "spot" samples taken in this way is no greater than that in a series of shift samples. Furthermore, providing that the formulation is corrected for variations occurring in the analysis of raw materials, then there is no significant difference in the mean values of the corresponding plant foods in "spot" and "shift" samples.

CONCLUSION

The chemist's task in carrying out analytical control in the manufacture of fertilizers is not a simple one. He is faced with a continuous process which may produce many tons of off-specification material in the comparatively short time taken to complete his laboratory tests. He must at all times be a "works" man rather than a "bench" operator. He must be capable of designing and perfecting tests which may appear to the pure chemist to be unorthodox, and of interpreting such tests into terms not only of finished product quality but also of plant performance. He must continually watch his sampling procedures and assess the usefulness of the analytical result obtained on the samples taken. Above all, he must organise the work in his laboratory so that the required results are produced in the minimum time.

APPENDIX AThe Legal Requirements Covering the Sale of Fertilizers
in the United Kingdom.

The Fertilisers and Feeding Stuffs Act, 1926, requires every manufacturer of fertilizers to give a statutory statement in respect of each parcel or consignment of fertilizer. In the case of superphosphates, this statutory statement must contain a declaration of the water soluble P_2O_5 content of the material, while in the case of compound fertilizers, whether granular or powder, the manufacturer must declare the total nitrogen content (as % N), the water soluble and water insoluble phosphate content (as % P_2O_5) and the potash content (as % K_2O).

It is the responsibility of either the County or County Borough to administer this Act and Inspectors are appointed for the purpose of drawing samples to be analysed by a County Analyst appointed for that purpose. A farmer may request the Local Authority to sample and have tested any consignment of fertilizer he purchases. The Regulations to the Act define the number of bags which shall be sampled or increments which shall be drawn from any consignment according to its size and according to whether it is in bags or in bulk. The same Regulations prescribe the procedure which shall be used to take the sample and the analytical methods to be used in its assessment; in fact, several alternative methods are given for the analysis of both phosphate and potash contents.

Inspectors appointed under the Act have the right of entry into manufacturers' premises for the purpose of sampling any material on the premises which has been prepared for sale.

The Regulations lay down certain limits of tolerance for variations from the statutory statement. The following table gives a brief indication of these tolerances:-

<u>Type of Fertilizer</u>	<u>Limits of Tolerance</u>
Superphosphates	Water soluble P_2O_5 : $1/20$ th of declared content up to a maximum of $\pm 2\%$.
Compound Fertilizers	(a) For declarations of N, w/s P_2O_5 , insol. P_2O_5 or K_2O content up to 5%, then the permitted tolerance is $\pm 0.5\%$.
	(b) For declarations of N, w/s P_2O_5 , insol. P_2O_5 or K_2O content up to 8%, then the permitted tolerance is $\pm 0.75\%$.
	(c) For declarations of N, w/s P_2O_5 , insol. P_2O_5 or K_2O content above 8%, then the permitted tolerance is $\pm 1/10$ th of declaration, up to a maximum of 1.75%. (If the consignment sampled is less than 1 ton, then the permitted tolerance is increased to $\pm 1/8$ th of declaration)

It is emphasised that these tolerances apply either side of the declaration and excesses are considered as serious as deficiencies.

A manufacturer is considered criminally responsible if variations in excess of these limits are found in samples taken on or leaving his premises. In all other cases (e.g. samples taken on road or rail or on a farmer's premises), he is expected to make financial restitution for any deficiencies, and, although he cannot be criminally prosecuted he is often required to give an explanation in respect of the way in which any variations from the statutory statement may have arisen.

APPENDIX BA Method for the Setting up of Control Charts in the
Production of Granular Compound Fertilizers

Let us suppose that the variance of analysis of nitrogen for a shift sample, composed of 8 increments, is "y".

Variance "y" is made up of errors arising due to:-

- (i) production and sampling,
- (ii) "within laboratories" analysis.

Let the "within laboratories" variance be "a",

Then variance due to production and sampling is (y - a).

Now a shift sample is composed of 8 increments, and hence the variance of the analysis of nitrogen in the individual increments due to production and sampling only is:-

$$\sqrt{8(y - a)}$$

The variance of a bag sample is twice that of an increment sample, therefore the variance of a nitrogen sample from one bag is:-

$$2 \times \sqrt{8(y - a)}.$$

For a 5-ton consignment, we must sample 7 bags (Fertiliser Act requirements).

Therefore the variance of nitrogen in a 5-ton consignment due to production and sampling is:-

$$\frac{2 \times \sqrt{8(y - a)}}{\sqrt{7}} + c$$

where "c" is an estimate of the error due to sampling the consignment.

But this is tested by two laboratories and we must therefore add back the total analytical variance, say "b".

Therefore the variance of nitrogen as a result of a test by a referee analyst on a 5-ton consignment of fertilizer is:-

$$\frac{2 \times \sqrt{8(y - a)}}{\sqrt{7}} + c + b$$

Now, suppose we set a standard such that not more than one 5-ton consignment in 50 which leaves our works shall be outside the limits of tolerance laid down by the Regulations:-

$$\text{then:- } 2.32 \times \sqrt{\frac{2 \times \sqrt{8(y - a)}}{\sqrt{7}} + c + b} = \text{permitted tolerance for nitrogen in the compound}$$

Now "a", "b" and "c" and the permitted tolerance can be found or are known. Hence "y" can be calculated and "y" has been defined as the variance of shift samples from the plant.

(iii)

Hence, plant samples must not depart from their mean value by an amount which exceeds $1.65 \sqrt{y}$ more than 1 in 10 times, nor which exceeds \sqrt{y} more than once in 3 times. The mean value must also equal the statutory statement.

Control charts can now be set up and regular plots made of the analytical results. If the analytical method used is biased to the official method, then the mean value must be adjusted for the value of that bias.

The analytical monitoring of 5-ten consignments of fertilizer will enable the control charts to be checked.