

# ISMA\* Technical Meetings

Cambridge, United Kingdom

15-17 September 1953

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

# THE INTERNATIONAL SUPERPHOSPHATE MANUFACTURERS' ASSOCIATION

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TECHNICAL MEETINGS 1953  
Paper (d) 2

September 1953

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## RECENT BRITISH STUDIES ON THE VARIABILITY OF FERTILISERS

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### SUMMARY AND CONCLUSION

Owing to the increasing attention which is being given everywhere to the production of food and, therefore, to the provision of fertilisers, it is to be expected that government regulations concerning composition and analyses will become everywhere more detailed and more stringent. The British fertiliser industry, through the Fertiliser Manufacturers Association Limited, recognising this probability some years ago, began in 1945 (a) investigations into the variations in composition during the production over a number of weeks of a particular straight fertiliser or a particular compound mixture and (b) comparisons of analyses of an identical sample in different laboratories. In 1949 a further series of tests was begun in which, following a recommendation of an F.M.A. delegation which visited the United States and Canada in 1947, analyses of a particular compound fertiliser were made in a number of laboratories throughout the industry. In this paper a description is given of the methods of procedure adopted in these series of investigations.

The conclusion reached up to the present is that on account of (i) the real variation from time to time in the composition of a mixture in continuous or batch production and (ii) the differences in the analytical results obtained by different laboratories using the same methods on the same subject material, the limits of variation hitherto allowed in British Regulations under the Fertilisers and Feeding Stuffs Act need widening.

## ORGANISATION OF THE INVESTIGATION

The investigations have been carried out on the instructions of the Council of the Fertiliser Manufacturers Association Limited, working through their Fertilisers and Feeding Stuffs Act Committee under the chairmanship of Mr. W.G.T. Packard.

### PART I

#### STATISTICAL INVESTIGATIONS ON FACTORY PRODUCTION

The statistical studies have been designed, and their results collated and reported on by statisticians, Mr. W.L. Stevens, whose services were lent to the Association by Messrs. Imperial Chemical Industries Limited in 1945, Mr. D.V. Lindley of the Mathematics Division of the National Physical Laboratory, in 1948, and Mr. J.G. Hayes of that Department from 1949 onwards.

In the following description of what has been done the words of these statisticians have been used wherever possible.

The investigations fall into four classes as follows:-

#### 1. Tests on powdered superphosphate.

Four firms co-operated in carrying out a sampling scheme according to the instructions drawn up by Mr. W.L. Stevens in April 1946. In all cases the superphosphate was sampled from bags which were ready for sale and distribution. In order to study the connection between variability of the sample and the size of the consignment the samples were drawn from:-

- (a) one bag at a time
- (b) five consecutive bags at a time
- (c) twenty-five consecutive bags at a time.

They were taken at random times in the morning and in the afternoon of one day in each of four weeks, by means of a spear, the separate portions thus taken from each of the groups (b) and (c) being thoroughly mixed and a sample of 2 to 4 lbs. drawn from the mixture. Each sample was duplicated, one set being analysed in one firm's laboratory and the other sent to a second firm who reciprocated by sending their duplicate set in return. Thus 48 analyses were obtained for each firm's product.

From this first test it was established that:

- (1) The greater part of the variability in the composition of the fertiliser was caused by the variation in the percentage of  $P_2O_5$  actually present in the material in the bags at the time of sampling.
- (2) A second major cause of variability of results arose from variations in the chemical analysis of each sample. This variation was of two sorts. Firstly there was, in one case, a definite bias between two different laboratories so that one consistently quoted a percentage composition lower than the other. Secondly there was the accuracy of analysis, i.e. the amount of variation in any laboratory.
- (3) The sampling error was negligible in comparison with these two errors. Furthermore the more complicated methods of sampling in which samples of five and twenty-five bags were compounded produced no reduction in the overall variability and can therefore be regarded as unnecessary, and future investigations used the simplest sampling method.

2. Tests on powdered superphosphate and powdered compound fertilisers from a larger number of factories.

Eight firms took samples of their superphosphate and seven firms of their powdered compound. Again the samples were taken from bags ready for sale and distribution, each being drawn from a single bag at a time and on a day chosen at random once during each of eight weeks. A spear was employed except in one instance when coning was used. Each sample was duplicated, one set being analysed in one laboratory and the other in another laboratory. Thus 16 analyses were obtained for each firm for each of the constituents, soluble and insoluble P<sub>2</sub>O<sub>5</sub> as well as, in the compounds, N and K<sub>2</sub>O.

The instructions were drawn up by D.V. Lindley and read as follows:

"(a) The method of sampling.

"Two samples are taken once a week for eight weeks. These would normally be eight consecutive weeks but it is of no consequence if, as a result of shut-downs in packing, the weeks are not consecutive. The time of sampling is chosen at random in each week, in a way explained below. At the designated time of sampling, two consecutive bags of fertiliser are taken from the packing line. These must be consecutive in the sense that one is filled immediately after the other from the same filling apparatus or same belt or same automatic weighing machine, according to the circumstances. The point of sampling can be left to the judgement of the manufacturer, to suit his own convenience provided all these requirements are satisfied.

"A sample from 2 lbs to 4 lbs in weight is drawn from each bag by means of a spear.

"The samples are put in canisters labelled A and B respectively. The label must also indicate date and time of sampling, type of spear used, name of product and name of manufacturer. Other relevant information could usefully be added, such as the filling apparatus used. Rather give too much information than too little.

"(b) Method of assuring random sampling.

"In order to achieve the aim of random sampling, a series of randomly chosen days and times is given below. This gives a day, morning or afternoon, and hours and minutes from the beginning of the morning or afternoon work, as shown in Table I.

(Extract from) TABLE I

Th. m 0:45	F. a 0:15	Tu. a 1:00
W. m 2:15	W. m 3:15	F. a 1:45
M. a 3:30	Tu. a 1:45	M. a 0:45
F. a 0:30	M. m 0:00	Tu. m 1:15
Tu. m 1:45	M. a 0:30	F. m 0:15

M. = Monday                      m = morning  
 Tu. = Tuesday                    a = afternoon  
 W. = Wednesday  
 Th. = Thursday  
 F. = Friday

"If any indicated day is impossible, ignore the entry and go on to the next. If any indicated time is impossible, add or subtract two hours. The table may be interpreted quite freely in order to obtain times to suit the factory routine.

"In some factories, packing is carried on at irregular intervals. In such cases the selection of the time of sampling each week can be left to the person in charge, as long as he does not adopt any systematic plan, such as always sampling on the same day or at the same time, or at the beginning of each batch of production. The idea of a "snap" sample at a randomly chosen moment is probably familiar to most chemists and it is unnecessary to make these instructions more precise.

"In some factories, packing takes place through a number of automatic machines, filling apparatus or belts as the case may be. It is important that all points of supply should be represented in the final data. Thus, if there are four machines filling bags, they should be sampled in turn over the eight weeks:- 1,2,3,4,1,2,3,4; this should be indicated on the canister label.

"(c) Chemical analysis.

"The method of analysis should be one of those quoted in the Regulations to the Fertilisers and Feeding Stuffs Act, 1926, (Statutory Rules and Orders 1932, No. 658). In order to keep the quantity of work within bounds, duplicate analyses are not requested. A single determination of each sample will be sufficient. It is anticipated, nevertheless, that some laboratories will follow their usual custom and make duplicate analyses. When this is done, the results of the two determinations should be forwarded for statistical examination. The data forwarded should be complete. If, for example, comparison between duplicates reveals a gross error, and a third analysis is made, the results for all three analyses should be sent, with a note to the effect that a gross error has been suspected. All information of this kind is of value, although, in order to economise the time of the analyst as much as possible, he is not asked to carry out the analyses in duplicate. To provide an opportunity of checking anomalous results it is advisable to keep a portion of each sample until the survey is complete.

"It is better, in recording the results of chemical analysis, to give too many 'significant' figures than too few. The last figure should not be rounded off, even if the analyst does not think it is worth very much. The accuracy will in any case be determined by the statistical analyses, and the extra computational labour occasioned by the extra digit, is negligible. This suggestion is offered because it sometimes happens that the chemical analysis is more accurate than is supposed, in which case the rounding-off of the last digit may appreciably diminish the accuracy of the data.

"The analyst's report should contain all the information on the canister labels, together with the results of all the analyses and the type of analysis used. The results of the eight-weeks' survey of each product should be forwarded together at the completion of the work."

Results of this second series of tests. The following quotations are taken from the report of J.G. Hayes in September 1949, the tables quoted dealing mainly with soluble  $P_2O_5$ ,

"(i) Variation in Composition.

"The variations in composition given in Tables II and III in the results for soluble  $P_2O_5$  are reasonably consistent from firm to firm both in the superphosphate and in the compounds. The results for the other constituents show variations in composition that are not so consistent from firm to firm. That is, the variation in composition has distinct differences among the various firms.

NOTES ON TABLES II AND III

(a) The variations are given as standard deviations in units of percentage of total bulk (like the chemical analyses).

(b) The effect of the analytical bias has been removed from the variations.

(c) The analytical bias given is the estimate of the amount by which the analyst given first gives an average result greater than the analyst given second.

(d) The analytical bias is also given as a percentage of total bulk.

TABLE II

Summary of Superphosphate Results - Soluble P<sub>2</sub>O<sub>5</sub>

Manu- facturer	Analysts	Variation in composition (standard deviation)	Analytical bias	Analytical + sampling variation (standard deviation)	Total Variation (standard deviation)
I	I & II	0.16	-	0.15	0.22
II	I & II	0.21	-	0.06	0.22
III	III & IV	0.12	+ 0.35)	0.24	0.27
IV	III & IV	0.20	+ 0.32) + 0.30)	0.09	0.22
V	V & VI	0.19	+ 0.24)	0.08	0.21
VI	V & VI	0.30	+ 0.19) + 0.15)	0.07	0.31
VII	VII & VIII	0.20	-	0.19	0.27
VIII	VII & VIII	0.21	-	0.22	0.30

TABLE III

Summary of Powdered Compound Results - Soluble P<sub>2</sub>O<sub>5</sub>

Manu facturer	Analysts	Variation in composition (standard deviation)	Analytical bias	Analytical + sampling variation (standard deviation)	Total variation (standard deviation)
A	A & B	0.17	+ 0.04)	0.05	0.18
B	A & B	0.22	+ 0.06) + 0.08)	0.08	0.24
C	C & D	0.27	-	0.20	0.34
D	C & D	0.20	-	0.12	0.24
E	C & E	0.11	-0.31	0.23	0.25
F	E & F	0.18	+ 0.27	0.17	0.25
G	C & H *	0.30	-0.36	0.17	0.34

\* Firm H participated only as an analyst.

"(ii) Analytical Bias.

In addition to the analytical variation, a definite analytical bias between the two analysts concerned with the same product has been detected in about half the cases; that is, the average result of the one analyst is greater than that of the other by such an amount as is unlikely to have occurred by chance effects. There are several instances of this where the bias is greater than 0.3%. It is likely, however, that analytical bias is almost universal.

"(iii) Tolerances Desirable under the Act.

As for the variation in composition, the total variation in the results for soluble P<sub>2</sub>O<sub>5</sub> is reasonably consistent from firm to firm, both in the superphosphate and in the compounds. Thus, in these two cases, we can consider the products of the different firms as having, at any rate approximately, the same true total variation, and so we can lay down tolerances (given in Table IV) which are sound ones, in that they satisfy the practical requirement that they are neither so strict that they cannot be satisfied, nor so wide that it is practicable to produce fertiliser differing consistently from its declared composition.

TABLE IV

Tolerances (in percentage of total bulk) for powder.

	Super-phosphate	Powdered Compounds					
		Soluble P <sub>2</sub> O <sub>5</sub>	Soluble P <sub>2</sub> O <sub>5</sub>	Insoluble P <sub>2</sub> O <sub>5</sub> *		N	K <sub>2</sub> O
				all firms	omitting firm G		
Fine	0.51	0.54	0.58	0.50	0.53	0.57	
Guaranteed	0.77	0.80	0.87	0.75	0.79	0.85	

\*The content of insoluble P<sub>2</sub>O<sub>5</sub> in the powdered compound of firm G is so very much larger than the contents of the other firms that its inclusion in determining the limits for insoluble P<sub>2</sub>O<sub>5</sub> may not be justified. Two pairs of limits have therefore been given, one including and one excluding firm G.

"These tolerances are multiples (referred to later) of our estimate of this true total variation (approximately the square root of the average of the squares of the standard deviations of the individual firms).

"The total variations for insoluble P<sub>2</sub>O<sub>5</sub>, nitrogen and potash contained in the compounds, however, are not so consistent. That is, in these cases, we cannot regard the firms as having the same true total variations. Nevertheless, tolerances have been calculated for these constituents in the same way as for soluble P<sub>2</sub>O<sub>5</sub>, and are given in Table IV, but they can only be regarded as sort of average tolerances for the firms. If they were adopted it would mean that some firms could consistently produce to narrower limits than these, while others might not consistently be able to meet these limits unless they were able to reduce the variability of their product. It is not possible in these cases, therefore, to give tolerances which entirely satisfy the requirements.

"No limits of variation are laid down in the Statutory Rules and Orders for percentage of insoluble P<sub>2</sub>O<sub>5</sub> contained in super-phosphate. Consequently, this has not been dealt with in Table IV.

The total variations in this case also are not very consistent. The average tolerances, as we have called them, are:  
Fine, 0.93; Guaranteed, 1.39

"(iv) Further Notes on Tolerances

"The two tolerances which have been given for each constituent have been called 'fine' and 'guaranteed'. This was the nomenclature introduced by Mr. Stevens and the multiples of our standard deviation that have been used to obtain these are the simple multiples two and three respectively. These are such that, if the distribution of results we are concerned with is what is called "normal", only about one in twenty and one in four hundred bags respectively will give an analytical result lying out side these two limits from the mean content of the whole period's production. There is no reason to believe that our distribution does depart very far from "normality" and so the proportions quoted should be at least of the right order. It is presumably the 'guaranteed' tolerances which are of importance, since the incidence of failure to meet the 'fine' tolerances is fairly high, and it is probable that Mr. Stevens was aiming at a one in a hundred proportion of failure for the 'guaranteed' limits, which is often used, but used the multiple, three, to give ample allowance for any departure from normality of our distribution.

"The British Statutory Rules and Orders 1932, No.658 gives limits of variation for the composition of compound fertilisers which vary with the percentage content claimed for the fertilisers. There has been no evidence in this investigation, however, that the amount of variation in the fertiliser is any smaller for lower percentage contents. The limits given in Table IV should consequently be taken as referring to all the fertilisers, no matter what their content.

"(v) Summary.

"The figures for variation in content and for total variation for content of soluble  $P_2O_5$  in both superphosphate and powdered compounds show no distinct differences among the different firms. Those for all other constituents, however, do show real differences.

"The analytical variation varies from analyst to analyst.

"There is, moreover, evidence of almost universal 'bias' coming into the chemical analyses.

"The 'fine' and 'guaranteed' tolerances given are such that only a small proportion of bags (of the order of one in twenty and one in four hundred respectively) will give chemical analyses which lie outside these distances on either side of the mean content of a period's production."

3. Tests to Determine Whether in an Investigation on Granular Fertiliser Products Sampling by Spear is Adequate.

A preliminary experiment was designed to compare sampling by spear with sampling by coning and quartering and was carried out in a number of co-operating factories. The same general procedure as had been used in earlier series of experiments was followed, except that all the analyses were made by one laboratory. The opportunity was taken in these tests to compare the variability of granular fertilisers made by continuous rotary mixing with the variability of the product of batch mixing, and also to compare the variation in sampling from one bag with that obtained in sampling from nine bags at each time. The following conclusions were reached:



(a) There was a slight bias in samples obtained by spear as compared with those from coning and quartering. The mean bias amount to:

+0.03% P<sub>2</sub>O<sub>5</sub>  
 -0.09% Nitrogen  
 -0.06% K<sub>2</sub>O

(b) The variability of the product of continuous mixing was greater than that of material made in batches.

(c) Bag to bag variation, i.e. variability over a few consecutive bags, in granular compounds is not negligible as it was in powdered compounds, sampling from one bag giving an appreciably greater variability than sampling from nine bags for soluble P<sub>2</sub>O<sub>5</sub>.

On the basis of these results the main series of tests on granular fertilisers was designed, the samples being drawn by coning and quartering, and material being taken from one bag only at each time and place.

4. General Statistical Investigation of Analyses of Granular Fertilisers

In January 1951 a general series of tests on granular compound fertilisers was begun on the lines indicated above, i.e. a random time schedule, the use of coning and quartering to derive duplicate samples from a single bag on each occasion, samples drawn once in each of eight weeks, the "A" set of duplicates being analysed in the producer's laboratory and the "B" set in a laboratory of another co-operating manufacturer. Twenty-three firms took samples of their granular fertiliser, each deciding itself which particular compound formulation it would use. In order to obtain more information about analytical bias, the "A" and "B" sets of samples were not exchanged between pairs of Works but the "B" samples from each firm were sent to an analytical laboratory other than that of the firm from whom a set of "B" samples was received.

Results for Soluble P<sub>2</sub>O<sub>5</sub>

The individual numerical results for the twenty-three firms which have taken part in this survey are given in Table V.

TABLE V

Manu- facturer	Analysts	Variation in true compo- sition (standard deviation)	Analytical Bias	Analytical variation (standard deviation)	Total Variability (standard deviation)
1	1,8	0.16		0.27	0.32
2	11,2	0.13		0.16	0.21
3	3,1	0.14	0.34	0.14	0.20
4	4,18	0.29	-0.20	0.12	0.32
5	5,15	0.10	-0.16	0.10	0.14
6	6,11	0.42		0.10	0.44
7	7,17	0.15		0.25	0.29
8	8,14	0.17	-0.40	0.25	0.30
9	9,13	0.16	0.20	0.12	0.20
10	10,16	0.17		0.12	0.21
11	11,10	0.30		0.15	0.34
12	12,4	0.16		0.23	0.28

TABLE V (Contd.)

Manu- facturer	Analysts	Variation in true compo- sition (standard deviation)	Analytical Bias	Analytical variation (standard deviation)	Total variability (standard deviation)
13	13,2	0.14	-0.30	0.08	0.16
14	14,6	0.02	0.38	0.24	0.24
15	15,3	0.33	-0.28	0.09	0.34
16	16,7	0.33		0.15	0.36
17	17,12	0.53		0.18	0.56
18	18,20	0.39	-0.33	0.17	0.43
19	19,5	0.14		0.16	0.21
20	20				(0.58)
21	24,9	0.70	-0.05	0.04	0.70
22	8,4	1.09		0.18	1.10
23	25,7		-0.86	0.35	0.27
"Average" (i.e. root mean sq.)		0.37		0.18	0.42
"Average" omitting 17,21,22		0.22		0.19	0.29

- NOTE:** (a) The variations are given as standard deviations in units of percentage of total bulk.
- (b) The effect of the analytical bias has been removed from the variations.
- (c) The analytical bias given is the estimate of the amount by which the analyst given first gives an average result greater than the analyst given second.
- (d) The analytical bias is also given as a percentage of total bulk.
- (e) Dashes in the columns for variation in composition indicate that the estimate of the total variation has proved to be less than the estimate of one of its component parts, the analytical variation. All that can be said in these cases about the variation in composition is that it is small compared with the analytical variation.
- (f) Complete results for firm 20 have been received from only one analyst. The figure in the last column for this firm has been obtained only from these results and has been omitted in calculating tolerances.

The conclusions given by J.G. Hayes, August 1952, read as follows:-

"The various firms differ considerably amongst themselves both in variation in the true composition of the fertiliser and in analytical variation, and consequently also in the total variation.

These variations are all much greater on the average for K<sub>2</sub>O than for the other constituents.

There is evidence of a consistent "bias" coming into the chemical analyses of many of the analysts. This is also generally much larger for K<sub>2</sub>O than for the other constituents.

Since some firms can produce fertiliser which is much less variable than others, it is not possible to lay down limits of variations which are really satisfactory for all the firms at once.

Limits have nevertheless been calculated using an average value for the total variation, and these are given in Table VI. Some firms, however, will not be able consistently to meet these limits, while others will be able to produce consistently well within them.

These limits are appreciably larger than the corresponding earlier ones for powdered compounds. Much of this appears to be due, for each constituent, to a few firms having much greater variability than the others. If these firms are omitted, the limits of variation (also given in Table VI) are then only slightly greater than the ones for powdered compounds. This does not apply, however, to content of  $K_2O$ , which is still much more variable than previously.

The "fine" and "guaranteed" tolerances, or limits of variation, given are such that only a small proportion of bags (of the order of one in twenty and one in four hundred respectively) will give chemical analyses which lie outside these distances on either side of the mean content of a period's production.

Some difficulty will, however, be encountered in determining this mean content, in order to stamp it on the bags, if an analytical bias is involved as large as some of those which have been observed.

TABLE VI

Tolerances (in percentages of total bulk)  
in granular compounds.

	N.	Sol. $P_2O_5$	Insol. $P_2O_5$	$K_2O$
Fine	0.75	0.83	0.71	1.24
Guaranteed	1.12	1.25	1.06	1.87

As above, omitting some results which showed  
obvious inaccuracies.

Fine	0.59	0.58	0.54	0.94
Guaranteed	0.88	0.87	0.81	1.40

PART II

ROUTINE CHECK ANALYSIS SCHEME

An F.M.A. delegation (Messrs D.J. Bird, E.P. Hudson, A.E. Sell, A.T. Vernon) which visited the U.S.A. in 1947 reported as follows:-

"An interesting recent development is the Analytical Check Service by which State Analytical Laboratories and Fertiliser Manufacturers are able by regular routine analysis of standard samples to check their methods of analysis and possible analytical error.

At regular periods a standard sample prepared by an external commercial laboratory is sent to all subscribers for analysis; the results are sent back to the laboratory for tabulation and circulation. By this means consistent plus or minus variations from standard provide an indicator of differences in analytical technique or method and enable corrections to be made.

It is a service which might well be operated to advantage in Britain and it is recommended that the F.M.A. should consider the possibility of initiating such a service amongst its own members."

The Council of the F.M.A. adopted the recommendation and Messrs G. Taylor and J.H. Hamence of Dr. Bernard Dyer and Partners (1948) Limited have been since 1949 periodically preparing and despatching to members of the Association test samples, seven different materials having been sent out up to date. All results are assembled and circulated under a code letter so that the extent of the variation can be seen by all members of the Association. The first samples were, on the suggestion of Mr. Taylor and Dr. Hamence, sent out in the form of liquids, i.e. water solutions containing soluble nitrogen, phosphoric acid and potash. By this means some assessment was immediately obtained of the methods of analysis in use.

Eighteen laboratories analysed the first sample sent out and the number has increased progressively to twenty-nine analysing the seventh. The compositions of the samples are given in Table VII.

TABLE VII

Sample	Date despatched.	C O M P O S I T I O N				
		Nitrogen	Soluble Phosphoric Acid.	Insoluble Phosphoric Acid.	Total Phosphoric Acid.	Potash.
		%	%	%	%	%
1	16.5.49	3.23	5.60			5.03
2	9.49	3.02	4.90			4.18
3	26.5.50	calcium phosphate			44.80	
4(dry)	21.9.50	7.30	8.25	0.55	8.80	8.15
5 "	8.5.51	7.10	6.25	0.65	6.90	11.25
6 "	27.12.51	9.50	4.10	0.65	4.75	8.85
7 "	15.9.52	6.85	9.30		9.90	10.00 9.85

The primary purpose of the Routine Check Analysis Scheme is to enable laboratories to assess the accuracy of their work by relation to the results obtained elsewhere and thus to obtain, where necessary, a stimulus towards improvement. An improvement has in fact taken place, most noticeably in the elimination of wild or exceptional results. The standard deviation between the laboratories in each set was worked out by Mr. W. Spendley of Imperial Chemical Industries Limited, for the first five tests and his conclusions are given in Table VIII.

TABLE VIII

<u>Set</u>	<u>Nature of Sample</u>	<u>Component</u>	<u>S.D. * between Labs.</u>
1. (17 labs.)	Solution	N P <sub>2</sub> O <sub>5</sub> K <sub>2</sub> O	N 0.06 P <sub>2</sub> O <sub>5</sub> 0.57 K <sub>2</sub> O 0.32
2. (29 labs.)	Solution	N P <sub>2</sub> O <sub>5</sub> K <sub>2</sub> O	
3. (27 labs.)	Solid calcium phosphate	Total P <sub>2</sub> O <sub>5</sub>	0.39
4. (28 labs.)	Solid	N Soluble P <sub>2</sub> O <sub>5</sub> Insol. P <sub>2</sub> O <sub>5</sub> Total P <sub>2</sub> O <sub>5</sub> K <sub>2</sub> O	0.24 0.17 0.20 0.26 0.26
5. (28 labs.)	Solid	N Soluble P <sub>2</sub> O <sub>5</sub> Insol. P <sub>2</sub> O <sub>5</sub> Total P <sub>2</sub> O <sub>5</sub> K <sub>2</sub> O	0.16 0.24 0.20 0.21 0.47

\* Excluding obviously exceptional results and giving each Laboratory equal weight.

6. (28 labs.)	Solid	N Soluble P <sub>2</sub> O <sub>5</sub> Insol. P <sub>2</sub> O <sub>5</sub> Total P <sub>2</sub> O <sub>5</sub> K <sub>2</sub> O	0.41 0.15 0.19 0.36
7. (30 labs.)	Solid	N Omitting one lab. Soluble P <sub>2</sub> O <sub>5</sub> direct Molybdate Omitting one lab. Quinoline method Total P <sub>2</sub> O <sub>5</sub> direct Quinoline method omitting one lab.	0.22 0.16 0.16 0.17 0.09 0.16 0.16 0.12

TABLE VIII(cont.)

<u>Set</u>	<u>Nature of Sample</u>	<u>Component</u>	<u>S.D. between Labs.</u>
7. <u>continued.</u> (30 labs.)	Solid	K <sub>2</sub> O Perrins method omitting one lab. Modified perchlorate method omitting two labs.	0.22 0.35

The following are the conclusions which may be drawn from, or older truths which are emphasised by, the results of the Routine Check Analysis Scheme up to the present:

- (1) Laboratories which participate become more alert for sources of error.
- (2) More detailed and closer specification of methods produces a better agreement in the results obtained from a number of laboratories with one sample.
- (3) New methods, or modifications of old methods can be studied systematically and on a comparative basis with older methods to give an "industry" as contrasted with an individual assessment of comparative utility.
- (4) An analytical result of the type dealt with can only be regarded as the best obtainable under the conditions ruling and all are subject to probable errors.