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THE QUESTION OF FERTILISER QUALITY CONTROL

THE IMPORTANCE OF THE SAMPLING PROBLEM

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1. GENERAL OBSERVATIONS

The uncertainty bound up with the sampling procedure and with the composition of the sample is frequently under-estimated when the products of the chemical industry are under test.

In the case of relatively low-priced materials such as fertilisers, this is all the more the case because of the need to keep down the costs of quality-control.

This lack of precision results in an attitude to quality-control tolerances that is all the more vague and variable, from one country to another, because the values of such tolerances have been fixed more or less a priori, and usually in an empirical rather than a rational manner.

Most frequently, the analytical error is the only factor held responsible, although with the progress that has been made in analytical methods, this appears more and more to be negligible in comparison with the error arising from the representativeness of the sample.

It seemed imperative, therefore, to alter the attitude of mind that is usually encountered, and which results in the allocation of almost all the funds available for quality-control to the analysis itself : the distribution of funds between the two operations should be reviewed, having regard to the respective accuracies of the analysis and the sampling.

At this stage, it is necessary to take into account the nature of the product, the ultimate aim, and the magnitude of the risk incurred on both sides, as well as of their possible dissymetry.

Experience shows that fertilisers with a high content of a single compound (ammonium nitrate, ammonium phosphate, ammonium sulphate, urea...), are actually the only products for which the scatter of results from the analysis is greater than that due to sampling.

Thus, in this instance, a single sample is theoretically sufficient, and the taking of more than one sample will be more in the nature of a precautionary measure aimed at detecting the occasional mistake in labelling, rather than overcoming a problem of the representativeness of the sample.

Therefore, we shall confine ourselves today to the other cases where several components are present simultaneously and in large quantities, and also where the validity of the sample for analysis can be accepted only if it has been drawn in accordance with a well-defined procedure. In the absence of empirical statements, of similar standing to those which have served in the past as the basis for the definition of the sampling procedure used for certain ores, a satisfactory definition of the appropriate procedure to be adopted in the present instance can be provided only by the application of statistical theory.

The aim of quality-control can be very different, depending on whether one is concerned with a manufacturing process which is largely continuous, checking the quality of batches prior to despatch or as received by a customer, occasional official checks in connection with the provisions of the law relating to the "prevention of fraud", or, finally, official quality-control tests made at fairly regular intervals in the various factories.

Each of the foregoing eventualities leads to the definition of a different risk-level, since some are purely economic, and others relate to compliance with legal requirements.

Finally, the property to be monitored is not always the same ;

- Average composition of each sack (for retail sales)

- Average composition of a batch

- Median composition of a production run

- Number of sacks not within specification

- The range of variation in the composition of the material as produced and as despatched, in terms of the basic unit (sack, wagon load, batch etc.)

This raises numerous contradictory aspects which seriously complicate the choice of a correct sampling procedure owing to the multiplicity of the possible alternatives.

In particular, the nature of the sampling procedure will differ, in the light of currently accepted ideas, depending on whether one is considering quality-control during production or prior to despatch.

In the first case, the whole of the production process can be considered as a single entity over a long period, and, since the product is on the move, it is possible to envisage a procedure for drawing samples either continuously or in sequence at frequent intervals.

In the second case, the effort entailed in handling the whole of a batch, the necessity of being able to assess the scatter on the scale of a sales unit, together with the wish to obtain the maximum margin of safety at the lowest cost, lead to a "stratification" of the parcel to be sampled. The size of these "strata" can vary, according to the circumstances (railway wagon, handling-bin, sack etc.), but on account of the spirit of French legislation, is most frequently confined to the sack level.

Consequently one is led to provide for the sampling of a certain number of sacks. Since the degree of uniformity within each sack is not in question, the sampling procedure will be so defined as to ensure that the samples are perfectly representative of the sacks to which they correspond.

Thus, every sampling scheme will include a definition of :

a) the number of samples and the precise locations from which they are to be drawn.

b) the size of each sample and its subdivision up to the stage at which the analysis is carried out.

2. OPTIMISATION OF THE SAMPLE AND OF ITS ULTIMATE SUBDIVISION

Although the error associated with the first stage of sampling can be limited easily, it must be stated that this is very often far from being the case in practice.

Since liquid fertilisers pose less of a problem in this direction, we shall confine ourselves to the case of the solid products.

A correct sampling procedure should conform to two essential requirements :

- the inclusion of a sufficient number of granules
- the avoidance of any tendency to favour the drawing of one type of granule (equal probability of sampling)

A - Definition of the size of the sample

For this purpose fertilisers can be divided into two groups :

a) the first category corresponds to production processes which pass through a liquid or paste stage during manufacture, by virtue of which one can accept that there is a relative uniformity in composition.

From granule to granule there is only a continuous variation, in accordance with the Gaussian distribution law, and it is generally not far removed from the scatter on a much larger scale.

The corresponding coefficient of variation generally lies between 10 and 20%.

A systematic study of some sixty formulae involving more than twenty factories, six outside France (U.S.A. or Europe) shows that the granulometric distribution by weight also corresponds to a law of the same type (cf. Graphs I and II).

The calculation, based on the theory of the normal law, indicates that if σ' is the standard deviation corresponding to variations in the assay and ξ the desired accuracy for the sample at a probability level of 95%, the quantity of the sample to be drawn must equal closely $5.2 \; \varnothing m^3 \left(\dfrac{2 \; \sigma'}{\xi} \right)^2 \rho$, where $\varnothing m$ is the average diameter of the granules and ρ their density.

If one accepts that ρ approximately equals 2, and σ' equals 20% of the average assay, one obtains, when ξ equals 0.5% of the average assay, minimum quantities in the region of :

$$70 \text{ g. when } \varnothing m = 1mm$$
$$550 \text{ g. } " \quad " = 2mm$$
$$1850 \text{ g. } " \quad " = 3mm$$

b) the second category of fertilisers comprises dry mixtures (bulk blends and other mixtures) free from any appreciable degree of agglomeration of the components.

In these products the variation in the assay of the components is small compared with the heterogenity of the components and it is the latter which, in the ultimate, determines the size of the sample. Taking into account the fact that the density of the various components is substantially the same within about $\pm$ 20%, the use of a calculation based on the binomial theorem enables us to arrive at the formula 5.2 $\left(\frac{2}{\xi}\right)^2 \rho x \, (1-x) \varnothing m^3$, when the particle-sizes of the components are of the same order.

x represents the amount of the least abundant component, expressed as a fraction of the total.

When $\rho = 2$, $\xi = 0.5\%$ of x, $\varnothing = 1mm$ and x = 0.17, one obtains a minimum weight of 4.5 kg ; when $\varnothing = 2mm$, x = 0.17, one obtains a minimum weight of 36 kg ; when $\varnothing = 3mm$, x = 0.17, the minimum weight becomes 121 kg. When x = 0.5 the weights then become 900 g, 7 kg, and 24 kg, respectively.

If the particle-sizes are very different (a condition that should be avoided during manufacture, owing to the difficulties likely to arise from the segregation that could take place during transport), the formula becomes :

$$5.2 \left(\frac{2}{\xi}\right)^2 \rho \frac{\varnothing_1{}^6 \; \varnothing_2{}^6 \; x \, (1-x)}{(\,(1-x)\,\varnothing_1{}^3 + x \; \varnothing_2{}^3)^3}$$

When ρ and ξ have the same values as above and x = 0.2, and the average particle sizes are 1 and 2mm, the formula gives a value for m of 16.5 kg. when the predominant component is the finer, and of 800 g. if the opposite is the case.

When x = 0.5 one should allow for a weight in the region of 650 g.

It will be seen that depending on the type of material to be sampled, the necessary precautions to be taken can be widely different.

These conditions arising from the relationship between weight of sample and particle-size should be observed likewise at all stages in the preparation of both the intermediate and the final samples, up to and including the withdrawal of the aliquot to be used for the analysis.

It follows that each reduction in the amount of the sample should be accompanied by a grinding operation. For example, if in the case of the granular fertiliser referred above, the original $\varnothing m$ is 3mm and the initial sample is about 2 kg, and one wishes to reduce this to 200 g. it will

be necessary to reduce the particle-size by grinding to a $\emptyset$m in the region of 1.5mm, and at the level of an aliquot for analysis of 2 g, it will be necessary to reach a $\emptyset$m approximating to 0.2/0.3mm.

B - Choice of the sampling device

This is both important and all too often ill-considered.

Firstly, there is the instinctive reaction of many official samplers, who do not appreciate that each material may exhibit an unavoidable lack of uniformity, to make a practice of simply taking a handful from a single sack and of using this to characterise the entire batch.

The most frequently occurring errors are, however, less evident and consequently, their effects are more serious.

The convenience and the rapidity of use of sampling probes result in their widespread employment. We shall content ourselves today with drawing attention to their possible shortcomings and with insisting on the absolute necessity of avoiding devices of this type, unless a prior investigation of their reliability has been undertaken.

We shall leave aside the work on this subject undertaken in the U.S.A. and in the U.K., and we simply point out that in the course of an investigation carried out in 1965 at our laboratory, in collaboration with four other French producers, two probes specially selected for use with fertilisers (one devised by an inspector from the French organisation for the "Prevention of Fraud", and the other as proposed to the Brussels Commission of the E.E.C., to form part of a Common Market Standard Specification), when tested on a 10:8:16 compound fertiliser based on pearlurea, KCl, superphosphate and bone phosphate, gave relative discrepancies of the order of - 5%, + 2.5% and + 7% respectively for N, P_2O_5 and K_2O for one probe, and of + 4% for K_2O in the case of the second.

On the other hand, in all the investigations that have been carried out up to the present, the use of a riffled divider which can separate the material into equal parts has always given satisfactory results, providing that it has been used in the correct manner.

The use of methods involving manual quartering give adequate results only after the expenditure of a considerable amount of care and attention and end up more costly than a divider of the type described. All things considered, the latter should be used as a matter of course.

Furthermore it is possible to design similar devices to work in series thereby achieving a higher rate of reduction in a single pass. A unit of this type has been made recently by one of our factories. It embodies a series of four dividers, operating two at a time in succession, with homogenisation of the fraction retained taking place between each stage. It gives excellent results, including those from granulometric analysis.

To conclude this topic we shall quote one example of the problems that can arise when considering the subdivision of samples.

Certain fertilisers may contain sundry materials (e.g. sand), which it is practically impossible to grind in the presence of softer or somewhat tacky substances. Such particles with an average diameter in the region of 0.5mm remain unchanged in the final product.

Although the calculation indicates that under these conditions (mean $\emptyset$ for the remainder of the fertiliser is in the region of 0.25/0.3mm) the accuracy should still be of the order of 0.5% relative, for an aliquot of 1 to 2 g, experience shows that one can get errors of nearly 10%.

This can be explained by the ease with which these large particles are separated, in the sampling flask, from the rest of the product, with the result that some aliquots contain disproportionately large numbers of such particles.

The impossibility of homogenising a mixture of this type on a small scale, leads either to the use of a micro-divider to obtain the weighed quantity for the analysis, or to the modification of the method of analysis to enable it to be applied directly to the material that has been ground only to the particle-size of the sand (an aliquot of about 20 g, when $\emptyset$m equals 0.5mm approximately).

3. STATISTICAL DEFINITION OF THE SAMPLING PROCEDURE

At this stage the statistical definition of a sampling procedure will depend on the aim of the control operation and possibly on certain assumptions about variations in production.

The choices depending on these alternatives have identified the various sampling procedures that have come into being either in France or abroad, and it is, therefore, advisable to restrict the use of any particular procedure to the precise application for which it is intended.

A - Qualitative control

The assessment of the number of sacks that are inferior to a given assay.

The parcel to be examined is regarded as comprising two categories of sacks : those with an average assay above the limit, and the others whose assay is below the limit. In these circumstances, there can be no question of speaking of an average sack, nor of such units approximating more closely or less closely to the proposed limit, the distinction being only rough and ready.

The binomial theorem enables us to determine, for each level of probability, the number N of sacks to be tested in order to ascertain, with a predetermined degree of accuracy, the percentage number of sacks that fall below the specified limit.

This method of control was proposed some years ago to the E.E.C. Committee in Brussels.

It offers the advantage of avoiding any assumptions about the nature and extent of the variations in production, and of giving a useful indication (in the case of retail sales), of the number of sacks that do not conform to the guaranteed assay.

Conversely, this method of control does not give any information about the average assay of the lot as a whole that is under examination. Moreover, by not making use of all the data obtained from each analysis, it results in N, the number of samples to be tested, becoming very large. Also since this method does not permit the use of an average sample, every sack sample must be analysed separately, and the resultant volume of analytical work cannot be entertained in practice.

B - Quantitative control

For most commercial purposes, the average assay for each lot is the more interesting figure to the user.

As a general rule, the use of fertilisers does not depend on a precise spreading rate, and therefore, a slight sack-to-sack variation in the assay does not cause trouble. Moreover, this means that the fertiliser can be produced more cheaply.

Most of the work carried out on rational sampling procedures has been directed towards an average quantitative check,

especially since this, by making the maximum use of the quantitative data obtained from each analysis, allows a more effective limitation of the costs of inspection.

However, it must be borne in mind that the number of samples required to achieve a given degree of accuracy of control, will depend upon the magnitude of the variation in production.

This variation, which is unavoidable in practice, can be attributed to the large number of variables that occur during the stages of manufacture. Moreover, this is confirmed by the fact that the variation is of the same order, for products of similar type, at all plants, not only those in France, but elsewhere internationally (cf., the work carried out on this subject in 1963, by the French Fertiliser Industry and reproduced in Le Fascicule de Documentation Afnor U 42051, November 1968). (cf. Graphs III and IV).

a) The South African system of standardisation

It is possible to calculate the number N of sacks to be sampled, by making an a priori assumption as to the variation values.

This forms the basis of the regulations for the quality-control of fertilisers that was worked out in 1960 by the South African Authorities.

It takes cognizance of, and accepts the risk attendant on the variation being greater than that expected. Otherwise if the calculation were to be based on a manufacturing variation that is reasonably easy to attain in practice, no manufacturer would be inclined to see the figure increased, because the risk of his being unjustly found to be at fault would thereby increase rapidly.

Such a system is of great simplicity, since it entails only the sampling of N sacks and the analysis of a corresponding balanced sample. The figure N is given directly by the formula :

$$\xi = 2 \, \frac{\sigma}{\sqrt{N}}$$

where ξ is the absolute accuracy at a level of 95% on the average assay, and σ is the standard deviation of production.

Conversely, it is clear that if a manufacturer succeeds in substantially reducing the variations in his production, he will be able to supply, without any risk, a product that on average is consistently inferior to the guaranteed assay.

Therefore, in practice this system necessitates the authorities' carrying out occasional spot checks to assess any changes in the production variations.

b) <u>Standardisation in France - the recent Standard U 42-050</u>

These two checks can be done more or less simultaneously, by carrying out several analyses on the N samples.

The application of Student's test to a group made up of a number of samples k, enables us to define a number N/k as the number of analyses required, irrespective of the scatter of the batch under test, such that the risk of the manufacturer being unjustly found at fault, is equal to a predetermined value for a given level of probability,

$$t = \frac{\bar{y} - \mu_0}{s} \sqrt{\frac{N}{k}}$$

where $\bar{y}$ is the average of the analyses

μ_0 is the guaranteed assay

s is the estimated standard deviation for the N/k analyses.

In the same way N can be determined in such a manner that one can guarantee that, within the customary variation of production, the risk of the average assay falling below the minimum assay remains less than a well-defined <u>a priori</u> value for each level of probability.

These two requirements enable a relationship between N and $\frac{N}{k}$ to be defined, where the values of N and k are chosen so as to obtain a minimum cost for quality-control.

This theory is the basis of the recent experimental French Standard Specification NF U 42-050.

It permits the introduction of an <u>a priori</u> assumption about the standard deviation of the production only in regard to a secondary factor, the integrity of the market being absolutely assured in all circumstances by a fixed non-null risk of the manufacturer equating the median assay of his output to the guaranteed assay, and by the severity of the sanctions (law-court proceedings), incurred by such action.

Given a certain number of analyses (k) it is always possible to assess the variation within the lot and to check if this corresponds closely to production with an acceptable degree of variation.

It should be noted also that this method seems to be little-affected by variations in the normal distribution of the assays arising from the k to k grouping together of the samples.

c) Assessment by determination of the percentage of the product units inferior to a given assay L

The fact that the manufacture of fertilisers leads to normal variations in the product, also enables the percentage of defective units to be determined by measurement.

Thus, use is made of N analyses corresponding to N samples to derive the distribution law for the assays of all the units involved. From this law the required information is immediately obtainable, since it corresponds to the level of probability in the Student table for a value of :

$$t = \frac{m - L}{S}$$

This method requires that N be relatively large in order to obtain a close approximation of the average value m and of the standard deviation S.

Furthermore the manufacturers' risk is not limited if S ceases to be small.

4. ASSESSMENT IN RELATION TO THE SAMPLING PROCEDURE AND THE ANALYSIS

The setting-up of a systematic method of sampling does not enable us to formulate any appreciation whatsoever of a batch of material.

Each method of sampling used has been so in accordance with the end in view, not only from the standpoint of the nature of the test carried out, but also from a quantitative point of view : in particular the uncertainty of the sampling procedure is directly linked to the number of samples taken.

Thus the analytical results so obtained cannot be used in the absence of an exact knowledge of the sampling procedure that has been followed.

It is for this reason that every standard specification covering sampling procedures should stipulate the method of assessment that is required by the particular sampling procedure that has been chosen. This obligation is, alas, often overlooked, and serious miscalculations can occur.

It should be borne in mind that the averaging of results, or the blending of samples cannot be countenanced where the sampling procedure has been defined on the basis of qualitative theories (binomial laws).

When Student's test is applied, it is an inequality derived therefrom which must be used in the examination of the analytical results required by NF U 42050.

Finally, when the analytical error is not negligible, compared with the sampling error, this fact should be taken into account. This can sometimes pose a difficult problem, because even if the lack of analytical accuracy is recognised, it will still affect the overall inaccuracy to the relationship :

$$\zeta^2 \text{ overall } = \zeta^2 \text{ analytical } + \zeta^2 \text{ sampling}$$

Consequently, an investigation will be necessary in relation to each preferred theory.

This problem has been closely examined within the framework of NF U 42050, and the practical conditions have been so prescribed as to render it negligible.

CONCLUSIONS

A problem as extensive as this cannot be dealt with exhaustively in a paper of this type. We have simply endeavoured to show that despite the wide variety of products covered by the term fertiliser, it is possible to define and put into effect strict rules for the sampling procedure.

In spite of all the empiricism that still prevails in this field, these methods are beginning to be developed in practice. Thus, it seems high time to underline the fact that several alternative approaches are open, and the actual choice is determined by the ultimate aim.

We also emphasise that in no case can the conclusions drawn from a test be dissociated from the principle embodied in the selected sampling procedure.

Where the consumer is unable, without serious consequences, to use a material which falls outside a given assay, the appropriate percentage test should be adopted. This is not generally the case with fertilisers.

When the consequences of the risks of making an incorrect judgement in respect of both high and low assays are approximately equal (for example where the substance is used

as raw material), a sampling procedure based on a) in section 3, can be considered as being particularly suitable. A similar procedure can also be adopted for the control of production.

With regard to the commercial aspect of a finished product such as fertilisers, the consequences of the risk of incorrectly rejecting a batch, which on average is well up to the guaranteed assay, is small in comparison with that of risking by default a too large variation in the assay (at least where penal sanctions are in force).

It is, therefore, imperative to centre the sampling procedure on the constancy of the first risk, as is permissible in NF U 42-050.

If it were to be generally adopted, it would enhance the buyer's warranty, whilst at the same time prevent the manufacturer from being regularly held solely responsible for the existence of the statistical uncertainties.

This Standard Specification affords the possibility of a more rational solution than the simple a priori definition of empirical tolerances, which must of necessity be more or less variable depending on the country and the time.

From this standpoint the document is of particular interest and should facilitate international standardisation in this rather sentitive field.

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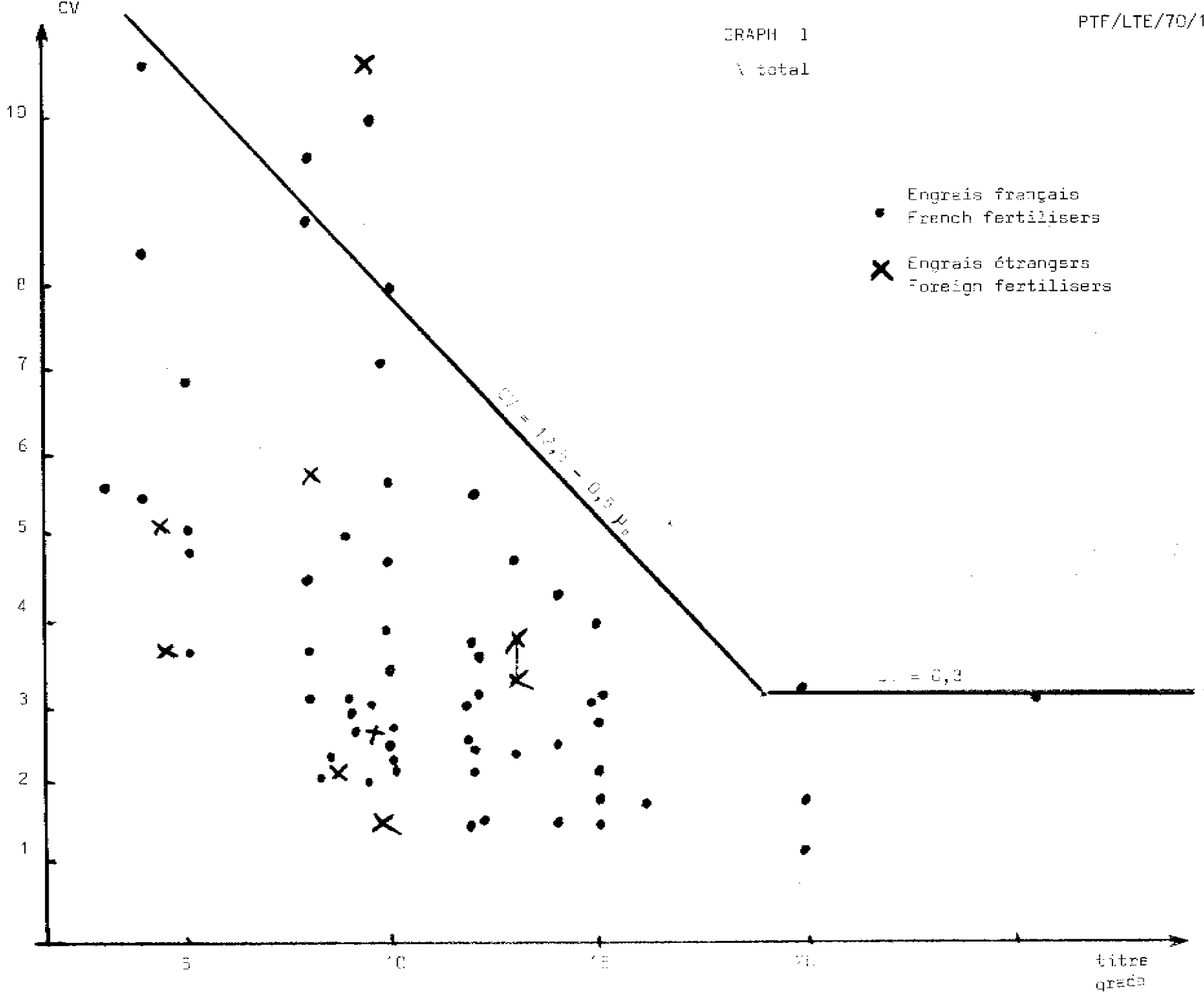   J. of A.O.A.C. 41, No. 3, 1958.

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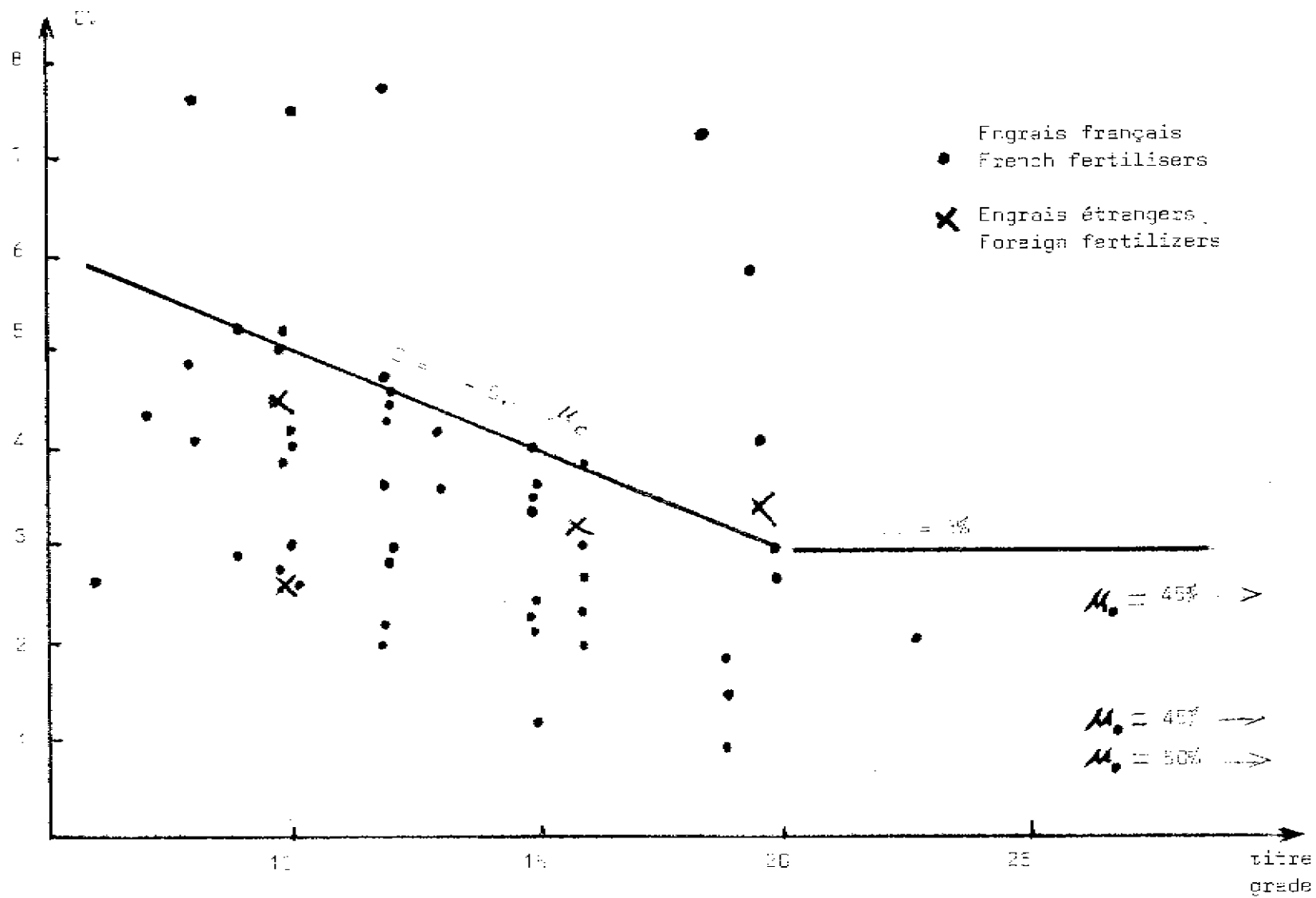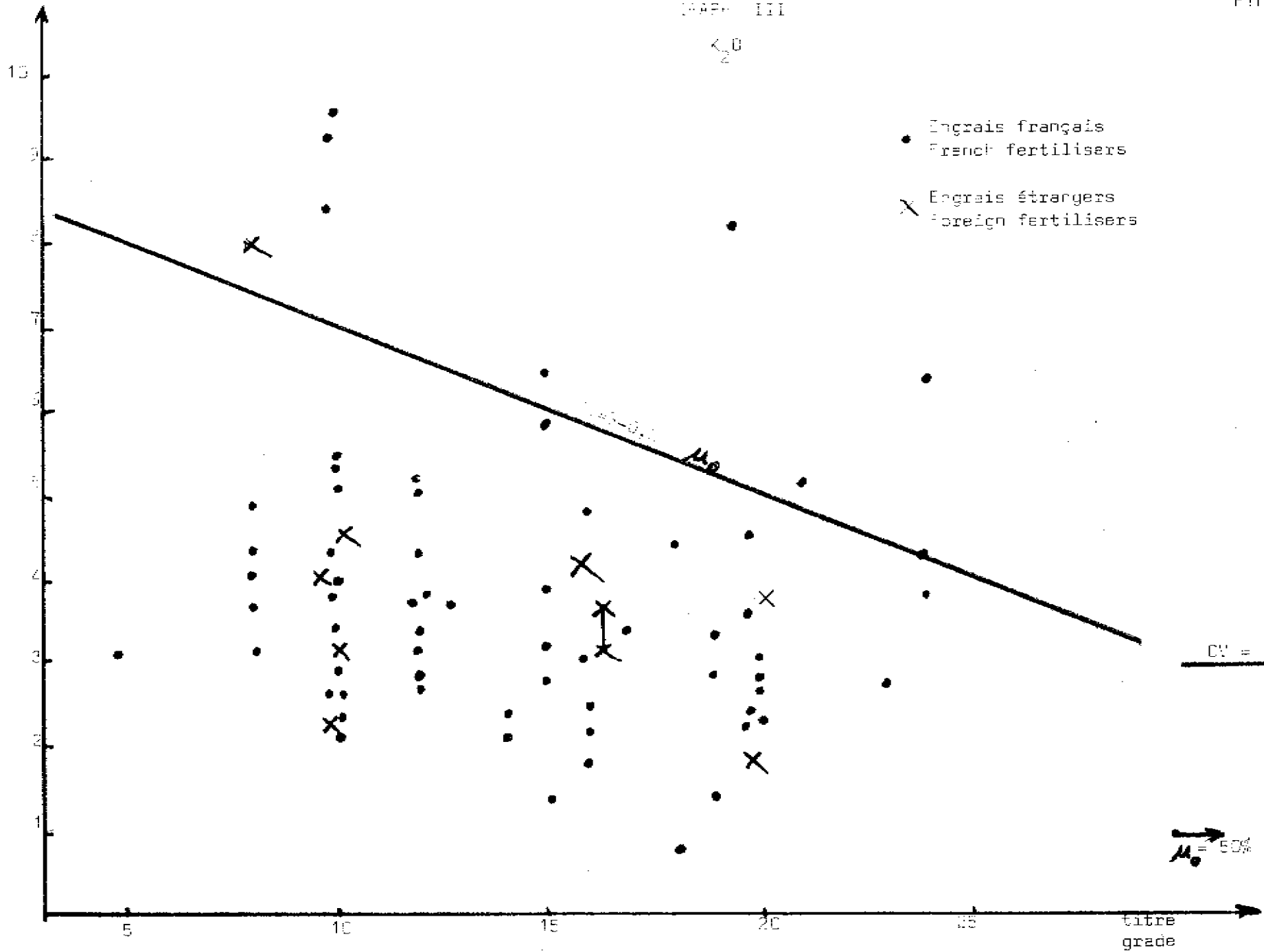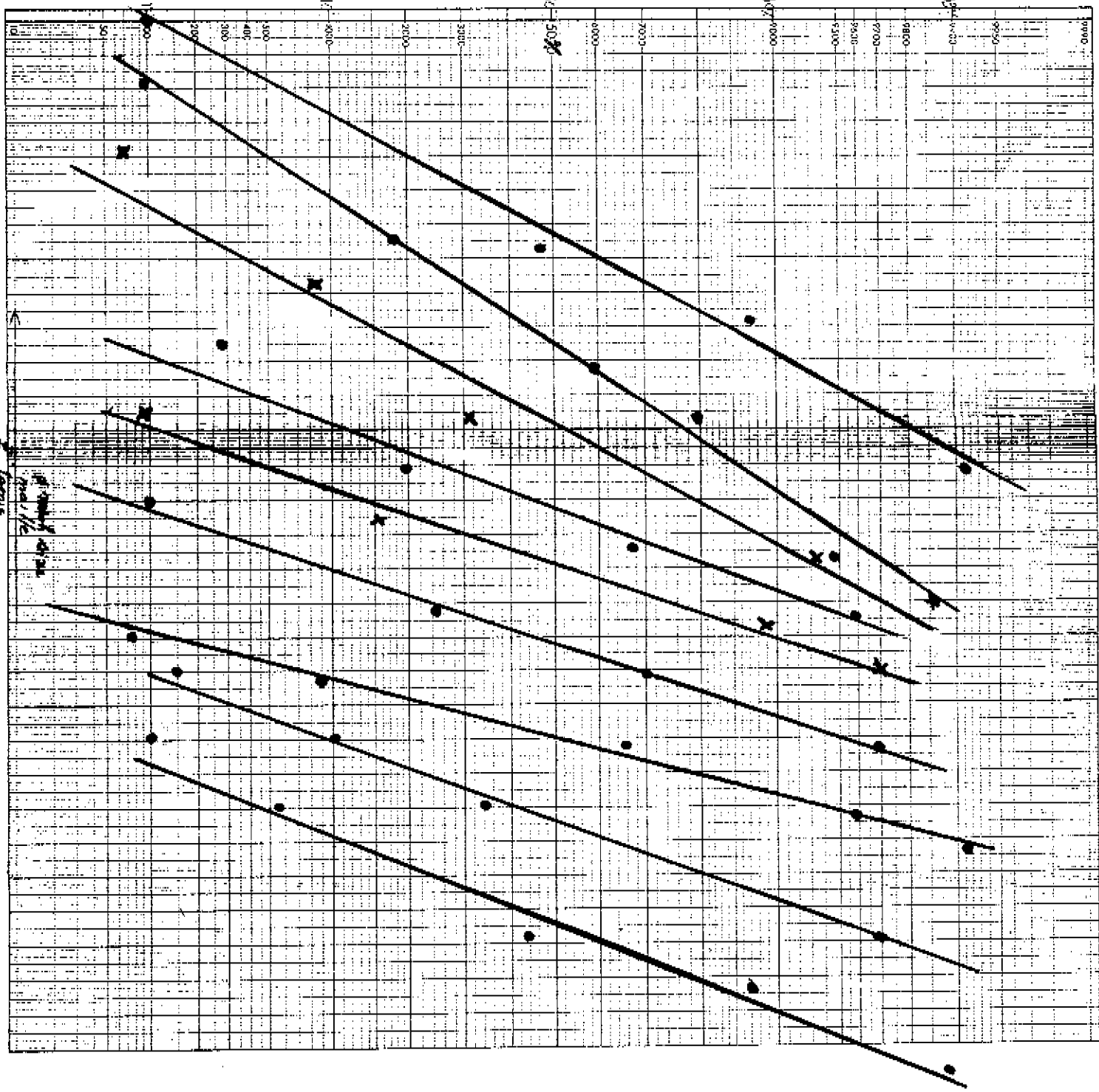   J. of A.O.A.C. 52, No. 3, 1969.

GRAPH 1

\ total

Engrais français
French fertilisers

Engrais étrangers
Foreign fertilisers

PTF/LTE/70/18

titre
grade

GRAPH II

P_2O_5 total

Engrais français
French fertilisers

Engrais étrangers
Foreign fertilizers

$\mu_\bullet = 45\%$ >

$\mu_\bullet = 45\%$ →

$\mu_\bullet = 50\%$ →

titre
grade

GRAPH III

Engrais français
French fertilisers

Engrais étrangers
Foreign fertilisers

μ_0

$CV = 3\%$

$\overrightarrow{\mu_0} = 50\%$

titre
grade

Cumulated oversize
Refus cumulé

Cumulated oversize
Refus cumulé