Quality Control in Fertilizers

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Fast pace of technological change in fertilizer manufacture dictates a new look at chemical control problems

At the National Fertilizer Association's September 1916 meeting in New York City, the Chairman of the Chemical Control Committee, Mr. C. F. Hagedorn of Armour Fertilizer Co., gave emphasis to both the difficulty and the importance of sampling and analysis. "Two experienced chemists," he pointed out, "find it difficult to take samples of the same shipment that will give concordant results; yet the analytical results of these two chemists on the same sample may be identical."

"The present state of the art of mixing fertilizers is such" Hagedorn continued, "that it is a physical impossibility to guarantee that every pound shall be identical with the calculations although the proper ingredients are combined, and it is to be hoped that the state officials will not be misled into making rulings under which it is impossible from a manufacturing standpoint to operate." That was 1916—41 years ago. But it could have with equal truth been written yesterday.

In any industry the importance of obtaining a representative sample of its product is recognized as indispensable to quality control. In the fertilizer industry it was many years before something was done in an organized manner to improve methods of sampling and of chemical analysis.

A 1916 survey by the American Chemical Society's Chemical Control Committee had revealed that eight different types of sampling tools were in vogue among state fertilizer inspectors, besides a few samplers which it was difficult to dignify as such, namely, cups and spoons. Briefly, the survey showed, among 26 states reporting, that:

- 5 used a sampler designed by the Indiana State Chemist's staff.
- 3 used a tube similar to the Indiana sampler but having its end closed.
- 14 used the so-called "butter tryer" consisting of a half-round tube tapered slightly. This tube was also used for sampling cheese and lard.
- 1 used an iron spoon.
- 1 used a cup.
- 1 used a sugar tryer, a slightly tapering tube 2 in. in diameter and 8 in. long.
- 1 used a rice sampler, a tapering tube 9 in. long.
- 1 used a tube open at bottom and side with a flange turned to act as a scraper with which to fill the tube. Wet goods tended to clog this type.

The Committee investigated the suitability of the various tubes found in practice through a project on sampling which it sponsored. The best sampling tube was that designed by the Indiana State Chemist's staff, consisting of two telescoping, slotted brass tubes which ended in a solid, pointed end. The "butter type" tryer was found unsatisfactory.

New Committee Appointed

This same ACS committee recommended that another study committee be appointed by the Association of Official Agricultural Chemists, to formulate for consideration a standard method for sampling fertilizers "so that sampling methods will be uniformly accurate throughout the country." This AOAC committee on sampling made its recommendations in 1921. The procedure on sampling bagged fertilizer was adopted as proposed, and remained unchanged for about 30 years.

Meanwhile, leaders in both AOAC and the fertilizer industry felt improvements in sampling and analytical methods could and should be made to satisfy the needs created by the new fertilizer formulations and technology. The fertilizer industry had experienced many fundamental changes in the two or three decades following World War I. The more concentrated raw materials used in processing and the new-type mixed fertilizers presented many new problems in sampling, analysis, and handling, the solution of which required improved techniques in the control laboratory.

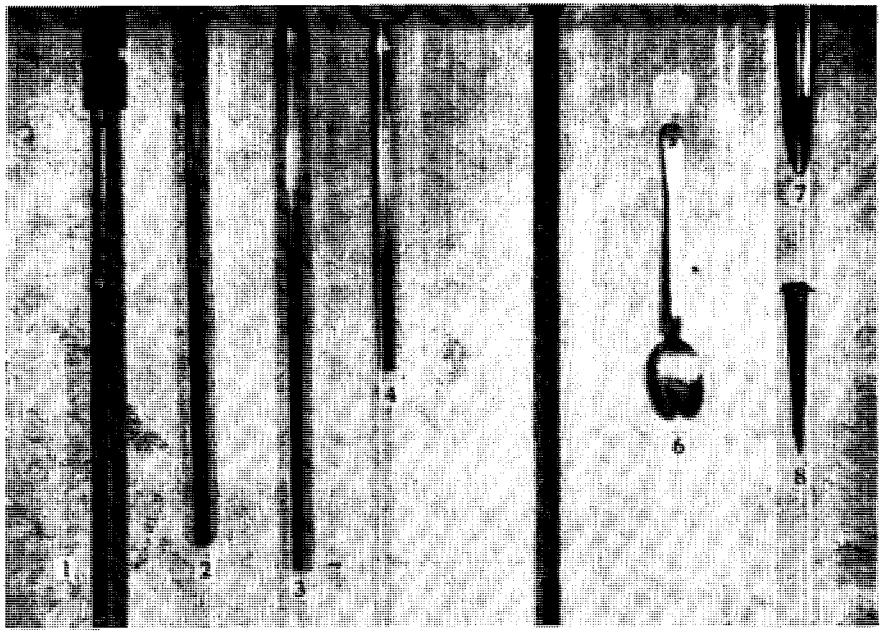
F. W. Quackenbush of Purdue University, as chairman of the AOAC committee on sampling, and his staff, feeling that the results reported at the 1921 meeting were inconclusive because of the nature of the fertilizer mixtures of that period, in 1949 undertook a new joint study on sampling in which statistical methods were used in evaluating the data. This investigation, reported in 1950, was much more comprehensive than any former study of its kind. More than 100 batches of fertilizer were sampled in seven different states. For the first time the variation was determined between sample cores from the same and different positions in the same bag and from different bags. Also, the variations existing between the chemical analyses of replicated samples in the same and different laboratories were measured.

Another series of studies was carried out at about this same time by an AOAC committee under the chairmanship of Stacy B. Randle of New Jersey. This work, also a joint project between state officials and industry laboratories, showed that the method of reducing a sample for chemical analysis is an important factor in the final result, and pointed to the use of the riffle or mechanical sample splitter as the preferred method.

These two series of studies enabled Dr. Quackenbush and his associates to calculate a set of analytical tolerances which they recommended for use by state control officials in evaluating deficiencies and in determining the intensity of sampling bagged goods.

Where We Stand Today

These studies advanced considerably the accuracy of sampling and analytical procedures, but much still remains to be done. The former studies dealt with bagged fertilizers. How properly to sample bulk fertilizer in the pile or on trucks has yet to be determined. Granulation has introduced many new difficulties that now demand correction. The problems of



Types of fertilizer samplers. 1—Indiana sampler; 2—open-end, double-tube sampler; 3, 4, and 5—butter tryer samplers; 6—spoon; 7—sugar tryer; 8—rice sampler

sampling and chemical analysis are now more acute than in the early 30's, owing primarily to the evolutionary changes in materials and manufacturing processes. As Dr. Quackenbush pointed out recently, there is no certain knowledge as to the influence of granulation on the requirements of sampling and sample-reduction; there is still a question as to whether as many, or less, or more cores of some of the new fertilizers are needed to get representativeness. The new materials are more concentrated in plant nutrients and they differ in physical qualities. It is more than likely that sampling and the pre-analytical procedures which were satisfactory for the older style fertilizers are inadequate for many of the concentrated granular fertilizers currently produced.

Overruns Are Costly

It is admitted that at present it is almost impossible to prepare a mixed fertilizer whose chemical analysis will conform exactly with the manufacturer's guarantee of plant nutrients. This is hard to believe, but it is so. Why? Because it is difficult to produce a homogeneous, nonsegregating physical mixture and avoid the errors and biases associated with sampling and subsequent chemical analysis. The manufacturer eager to avoid monetary penalties and unfavorable consumer reaction considers it necessary to add a generous quantity of each nutrient over and above the guaranteed amount, known as "overrun" or "give-away." These overruns are in the aggregate a huge annual cost. In one year (1948) this cost, based on chemical control data collected by Scholl and Wallace, was estimated at more than $6 million. In 1953, in the State of Missouri alone, fertilizer companies had overruns of some 3500 tons of potash, worth $280,000 if valued at the conservative rate of $80 per ton of K_2O. These are terrific amounts for the fertilizer industry to pay as insurance against possible deficiency penalties.

There is also the expense paid by fertilizer firms as penalties in connection with deficiencies. These, although substantial, are less important than the bad reaction generated in the consumer when he receives from the state chemist the report of a fertilizer deficiency. The average manufacturer feels strongly about this since he knows that in a great majority of cases the components of the mixture were weighed out accurately and put into the mixer honestly, and in amounts to yield the guaranteed analysis and a little more. Because the inadequacy of the sampling method must affect the analytical procedure and the determination of the plant nutrients, he feels that his reputation and that of his industry become unjustly tarnished.

While the fertilizer industry had recognized for some time that current official methods were not entirely satisfactory, Florida fertilizer manufacturers were first to do something about it. They organized a chemical control committee to outline and supervise a research project on the subject in cooperation with state control officials and the University of Florida. The purpose was to establish tolerances more realistic than those in force, especially for high-analysis N-K_2O mixtures.

In the Florida project, official samples were taken at the mixing plant and at destination. These were split by riffling, one portion going to the State Chemist, one to the University of Florida department of soils and one to Thornton Laboratories, Tampa, Fla. Statistically evaluated, the chemical data on the complete fertilizer gave a positive bias for nitrogen of the same magnitude as the average excess added, a small negative bias for potash, and a positive bias for available P_2O_5.

The standard errors were found to be caused chiefly in the analyses of the materials used in the formulation. Differences between laboratories, segregation, and sample splittings made small contributions to the sample error.

Samples drawn from the mixer discharge by a scoop gave data similar to those obtained by using the official sampling tube. Samples taken with a scoop at the mixture discharge gave about half the bias but had standard errors not much less than those encountered with bagged or bulk goods.

In the case of the no-phosphate bulk-mixtures negative biases for total nitrogen and nitrate averaged 1.0 and 0.593 percentage points respectively, and potash was positively biased by 0.791. Corresponding standard errors were 0.571, 0.396, and 0.716. The main variation was in the sample splitting stage. Segregation, differences between laboratories, and differences between duplicates contributed no appreciable variation. Bagged goods showed higher biases and higher standard errors than did bulk goods.

Sieve analyses showed that particles larger than 20-mesh were not getting into the sampler in sufficient numbers, and there was an overabundance of particles in the 20–100 mesh range. These circumstances led to underestimation of the nitrogen in the fertilizer, and over-estimation of potash.

Both sieve and chemical results showed that a representative sample was not being drawn even though the number of cores was sufficient to give negligible differences between samples.

Official directions in the "AOAC Methods of Analysis" book are "to use slotted single tube, slotted double tube, or slotted tube and rod, all with pointed ends." The open end Florida tube studied in 1956 gives less bias on dry mixtures than the official and other tubes tried, but on wet mixtures all tubes studied showed about a 2% bias (G. M. Volk and J. M. Myers, Mimeo. report 57-1, 1956). Use of a different sampling procedure by the State Chemist's inspectors has reduced the number of deficient or out-of-tolerance samples by about 40% (J. J. Taylor, memo. 5/7/57). However, the number of samples reported out of tolerance is still disproportionately high for the X-O-X type fertilizers.

None of the sampling devices tested to date has completely eliminated bias for all types of fertilizer mixtures. The need continues for further study of the physical causes of bias and the

possible further improvement in sampling devices.

Surveys Point the Way

In the fall of 1954 the National Plant Food Institute's chemical control committee decided to appraise current sampling and analytical procedures by means of a questionnaire on bagged fertilizer. This was sent to approximately 200 fertilizer manufacturing companies, and to each of the 48 state chemical control officials. The replies from both groups showed extensive variations in sampling techniques. For example, to the question: What instrument is used in taking the sample of bagged fertilizer?, the industry replies were these: 18 used a tube; 9, a butter tryer; 13, a spoon; 6, a shovel; 1, a trowel; 2, a can; 3, an auger; 2, their hands; 2, various unnamed tools; 1, an automatic sampler.

To the same question, the state chemists replied: 15 used a slotted double tube; 24 used a slotted single tube; and 1 used a butter tryer.

These answers differed but little from those of the 1916 survey! They brought out emphatically that many chemists were not following the official AOAC prescribed methods. To give an individual interpretation to the official method seemed to be a prerogative jealously guarded and exercised by most chemists. Why? one may ask, since any method is arbitrary and needs to be followed closely to get reproducible results.

Seeking ways to solve this and other current problems of sampling and chemical analysis of new types of fertilizers, the Soils, Water, and Fertilizer Advisory Committee to the U. S. Department of Agriculture at its annual meeting in January 1956 recommended that consideration be given to the improvement of methods for fertilizer quality control.

On March 23, 1956, the chemical control committee of NPFI met jointly with representatives of AOAC and the American Association of Fertilizer Control Officials to discuss the recommendation made by the advisory committee. The group discussed the need for statistical quality control in analytical procedures, and the development and use of new techniques including electronic equipment in the future sampling and analysis of fertilizers. As a result of this group's recommendations, a task force was appointed by NPFI to supervise the design of a comprehensive research project on chemical control.

The NPFI task force in the fall of 1956 approved a design of experiments as submitted by the counsellor statisticians. Briefly, the experiments comprising the first phase are designed to: detect and measure differences resulting from the use of three representative sampling instruments; estimate the variation in composition within a bag of fertilizer and from bag to bag; and estimate the precision of the participating laboratories.

State control chemists in New Jersey, Virginia, and South Carolina have volunteered to provide their laboratory facilities for the analytical work. The fertilizer grades selected will be sampled at one fertilizer plant located in Baltimore, Md. Official inspectors from each of the state laboratories will take the sample cores. About 476 chemical analyses and 144 sieve analyses will be made by each laboratory.

The four fertilizers selected for the tests are: nongranulated 5-10-10, 0-20-20; and granulated 10-10-10, 8-16-16.

The three sampling instruments to be used are a single tube as customarily used by most states; a single tube but with larger bore and wider slot than the usual single tube; and a double tube.

Samples will be selected at random from 24 bags of each fertilizer grade. The bags will be taken from production over an interval of time, that is, not all from one day's run. Each sampler will remove a sample core from the same bag and same place in the bag, disturbing the contents as little as possible.

This project will in time be integrated with comparable work at state control laboratories and will be conducted in close association with AOAC and USDA through the NPFI task force. All funds needed for the project are being furnished by the NPFI, while the government agencies provide their laboratory facilities and make the statistical computations. This, then, is a joint research project in which government and private industry are collaborating to make it comprehensive and authoritative.

In the past, the agronomy factor has perhaps been ignored or subordinated in planning chemical control research. The fertilizer control laws were enacted primarily for the benefit of consumers and indirectly for the protection of honest manufacturers. All too often farmers have been caused to doubt the ethics of fertilizer manufacturers on the basis solely of the control chemist's adverse report. They have given no consideration to the important fact that the fertilizer to be purchased could be entirely satisfactory for making the crop and was an honest value despite the reported deficiency in the chemical analysis. For example, such doubt as to the ethics of the manufacturer could be dissipated if the farmer could be shown that a guaranteed analysis of 5-10-10, for instance, which the chemist reports as 4.9-10.6-9.5, may be accepted as an honest value from the agronomic viewpoint since the two analyses would be equally effective for making his crop. Some agronomists and control chemists wonder if segregation, as sometimes occurs and is reflected in the chemist's report, has not been unduly stressed as to its influence on the final crop yield. That unfavorable consumer reaction does exist is true, and it might be desirable in time, therefore, to have official representation of major farm groups on the task force either at the state or national level.

One of the aims of the task force project is to reduce the toll industry pays in overruns and penalties for deficiencies, *without sacrificing quality of product and service to the farmer.*

Summary

This is a period of rapid change in all phases of our economy. Nearly every day brings changes in fertilizer manufacturing processes and raw materials, or new developments in soils, crops, plant nutrition, agricultural engineering and new farm equipment of all kinds. It seems unreasonable to expect, under these dynamic conditions, that AOAC and AAFCO can carry out all the research currently needed in chemical control methods. Despite many handicaps these official organizations have done a wonderful job of developing procedures and techniques. The work of their members, however, is on a voluntary basis. They have no funds of their own to expend on the study and development of new methods and instrumentation. Because of critical man-power shortages in their laboratories, caused to a large extent by losses to better paying jobs in industry, and insufficient funds, individuals among these groups have been able to engage only sporadically in the investigation of chemical control problems. NPFI has felt that with the right approach AOAC groups would welcome a bona fide, comprehensive research program designed to get factual information and develop new techniques and instruments which could aid them also to keep their methods and techniques timely.

The problems to be solved are complicated and difficult. The success achieved by the Florida group, however, offers hope that understanding on the part of the fertilizer industry and friendly cooperation on the part of state control officials will lead to success.

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