three fumigants in Table III can be brought out in the relationship of residue to fumigant concentration. Table IV shows the halide equivalent residue of the three compounds in white flour. If equal concentration of fumigants had been used, these residues would have assumed different proportions relative to one another. We define these values as relative specific residues.

Methanesulfonyl fluoride is more reactive than the other two compounds relative to those reactions leading to permanent residues. The relative specific residue, then, would appear to be a good indicator of chemical reactivity in these residue-forming reactions. This relationship appears to be well supported by the data from Kenaga (*7*) in which confused flour beetles were placed under columns of white flour at varying depths and then fumigated for 16 hours with each of the three compounds at the rate of 0.5 pound per 1000 cubic feet. The penetrating properties were measured; sulfuryl fluoride gave 100% control through 9 inches of flour, methyl bromide through 5 inches, and methanesulfonyl fluoride only in the first inch.

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PESTICIDE ANALYSIS METHODOLOGY

An Automatic Sampling Device for Improved Reproducibility in Testing Granular Materials

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Physical testing of granulated insecticide formulations has been hampered by inadequate reproducibility, particularly in determination of dust content. The variation is due in large measure to the difficulty of maintaining a thorough dispersal of the dust in the stock sample. The turntable sampler described here is a practical means of effecting a pronounced improvement of reproducibility in analytical testing of granular materials for dust content and related qualities. The apparatus is easily constructed.

A DRY-SIEVE TEST of an essentially macroscopic granular material is likely to be regarded as a simple operation. In granulometric analysis, however, even as in chemical analysis, each type of formulation presents its own peculiar problems.

Since the essential advantages of the granulated form for pesticides depend on its free-flowing quality in the dry state without the hazards and inconvenience of dustiness, it follows that to ensure good physical quality one must first be able to specify a reasonable maximum tolerance for dust content, and then be able to test accurately for compliance with the stated requirement. The dust particles, constituting a minor component of the total composition, and being of a lower order of size than the granules, are free to shift around in the intergranular spaces in the most haphazard manner, making it virtually impossible for the analyst to maintain a uniform distribution of the dust while withdrawing a sample for test. For some years, it was considered sufficient merely to tumble the stock sample thoroughly just before withdrawing the test sample, but this has proved to be not enough.

In a series of collaborative tests sponsored by the Association of Official Agricultural Chemists (*2*), in which the material passing the 250-micron sieve by dry shaking was considered to be the dust fraction, the interlaboratory mean deviations were 1 to 2% of the sample weight. This amount represents an embarrassing uncertainty of determination in relation to the frequently specified tolerance of 5% for the dust fraction. The mean deviation among replicate runs by a single observer is usually smaller, but still serious. In replicate observations made by the author on each of four samples (at least three and usually four runs per sample) according to the standardized procedure of Interim Federal Specifications for granulated insecticides (*3*), the average results for the respective samples in terms of per cent dust, or per cent under 250 microns, were 0.8, 1.2, 2.5, and 4.5. The mean deviations were 0.1, 0.5, 0.6, and 0.7, respectively; that is, from one eighth to nearly half of the dust fraction.

Accumulated experiences such as the foregoing show that one cannot assume the attainment of a representative test sample by taking a few grabs at random, even when the stock sample has been tumbled. For statistical safety, the ideal plan would be to traverse the whole stock sample in a narrow swath, taking little bites of uniform size at frequent regular intervals from beginning to end. In effect, that is just what is accomplished by the new apparatus described here.

The principle is familiar and well established, being used in gross sampling of coal during loading or unloading of freight cars (*1*), and in sampling of truck loads of bulk-handled peanuts (*4*). The new device, called a turntable sampler, is a convenient means of applying the same principle to the small-scale operation of drawing 20 grams or so from the few ounces of material usually available

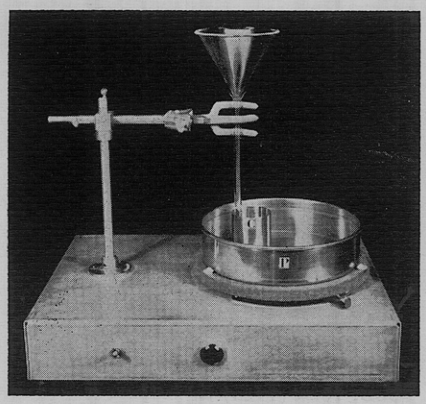

Figure 1. Turntable sampler

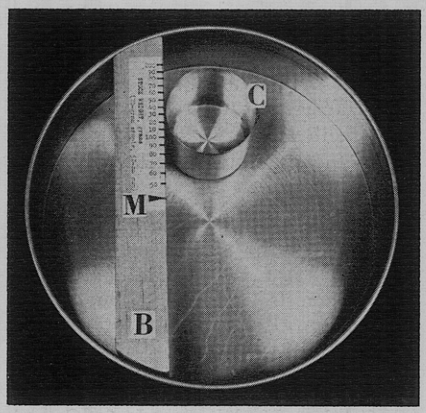

Figure 2. Setting block and cup in pan

Table I. Observations of Dust Content[a] with and without Turntable Sampling

Sample	Without Turntable		With Turntable	
	Average	Mean deviation	Average	Mean deviation
Heptachlor, 10% (in attapulgite)	1.3	0.7	1.7	0.1
Attapulgite, clean	1.2	0.4	1.1	0.2
Attapulgite, dusty	7.3	0.8	6.6	0.2
Vermiculite	2.0	0.7	2.1	0.4
Wyoming bentonite	14.2	7.6	16.6	1.1

[a] Per cent under 250 microns.

in routine acceptance testing of granulated pesticides. All of these applications are based on the accepted view (*1*, *4*) that where adequate blending cannot be effected, the most dependable way of getting a representative sample is by taking many uniformly distributed cross sections from a stream.

Design

The general structure of the sampler is shown in Figure 1. A sieve receiver pan *P*, 20.32 cm. (8 inches) in diameter, 5 cm. (2 inches) deep, is secured in a centered position on a phonograph turntable. A sheet-metal cup *C*, approximately 5 cm. in diameter, is placed within the pan. A 60° glass funnel is adjusted on a support so that the outlet tip just clears the top of the cup, and the funnel and cup are set off-center with respect to the turntable by such an amount that the arc projected by the funnel tip across the cup in rotation of the table will bear the same ratio to the complete circle as the weight of the desired sieve sample bears to the weight of the whole stock sample. The bore diameter of the funnel stem should be just sufficient to provide free flow for the granular material. With the turntable rotating at 45 r.p.m., the entire pretumbled stock sample is poured through the funnel so as to be delivered continuously in a steady stream. If clogging or bridging occurs, normal flow is restored (the table still turning) by probing with a stout wire flattened as a spatula on the lower end. The portion for testing falls in the cup, while the remainder falls in the pan outside the cup. The cup is removed, any dust clinging to its outside surface is brushed back into the pan, and the cup with its load is weighed for determination of the test-sample weight; the remainder in the pan is returned to the stock jar.

The proper setting of cup and funnel to give the specified size of test sample may be found in a variety of ways. Much of the early work was done by a system that avoids the necessity for precise centering of the pan. A setting block was placed on the bare turntable without the pan. A guide attached to the under side of the block was allowed to engage the truncated spindle of the turntable, and the funnel was then positioned over a scale on the top surface of the block. The block was then removed, and the pan and cup were put in place for operation. The cup was of an elongated rectangular shape, long enough to extend from the center of the pan to its wall, so that placement of the cup required no adjustment.

This external setting-block system underwent several experimental modifications, some of which were quite successful, but eventually it became apparent that if care were taken to center the pan accurately by means of its adjustable retainers, the extra pains could be well repaid with a more convenient setting-block arrangement. One of the simplest plans is illustrated in Figure 2. Here the pan is viewed from above. The setting block *B* is laid in the pan with its ends against the wall. The labeled graduations of the scale on the top edge of the block designate weights of stock sample in grams. The cylindrical cup *C* is set against the block opposite the point on the scale that corresponds to the previously determined weight of the stock sample. The funnel is positioned with the bottom of its stem centered over the edge of the cup at the point where the cup touches the scale. The block is removed without disturbance to the cup, and the adjustments are now complete. After the several dozens of revolutions required to run the whole stock sample through the funnel, the accumulation of material caught in the cup will be adequately close to the sample size for which the scale has been calibrated.

The outline of method for calibrating the setting-block scale may be introduced by a more detailed description of the block itself. The block has the same height as that of the cup, which should be practically the same as the inside depth of the pan, or not greater. The width is not critical; the stock lumber thickness of 2.86 cm. (1.125 inches) is suitable. The block is somewhat shorter than the diameter of the pan, and the ends are rounded asymmetrically to fit against the pan wall. When both ends are in contact with the wall, the perpendicular distance between the center of the pan and the near face of the block equals the outside radius of the cup. Along the upper edge of this near face, the scale is plotted, by calculation of displacements from the midpoint *M* of the edge, which is exactly opposite the center of the pan. For laying off the length and the end curves of the block, a template may be made in the following manner: Using the skirt of a testing sieve as a marking gage, draw a circle 20.32 cm. (8 inches) in diameter on a sheet of cardboard or other suitable material, and on this circle draw a chord so placed as to miss the center by an amount just equal to the outside radius of the cup. The segment bounded by the chord and its minor arc will, when cut out, form the desired template; the straight side corresponds to the long side of the setting block, regardless of the width of the block material.

Under the foregoing conditions it can be shown that for delivery of a 20-gram sample from a stock of any given weight, *S* grams, into a cup with inside radius *R*, the displacement of the funnel is given by the formula,

$$D = R \cot(3600/S)^\circ$$

This is the formula by which the scale on the block shown (Figure 2) was plotted. Provision for other sizes of sample may be made by obvious manipu-

lation, either in plotting or in actual operation with the same scale.

The apparatus has been so designed that it can be constructed easily in the ordinary laboratory from commonly available parts, with no significant amount of labor other than simple trimming, fitting, assembly, and calibration. A list of suitable components has been prepared, specifying aluminum and stainless steel as dominant materials; a sturdy preformed sheet-metal base; and adequate controls, including panel-mounted switch and pilot lamp (Figure 1). The total cost of parts is approximately $40.

Performance

A good illustration of performance is the record of the first three series of replicate sieve runs made with the sampler. The materials were granulated heptachlor formulations, one each of low, medium, and high dust content. All samples were repeated to exhaustion, the first yielding 16 runs and the others seven each. The mean values for dust content (fraction under 250 microns) were 1.5, 4.6, and 8.6%; the mean deviations were 0.1, 0.2, and 0.3%, respectively, of the sample weight. Thus the mean deviations were roughly proportional to the dust content; and near the critical dust content of 5%, the mean deviation was only 0.2% of the sample weight.

The original tests by the designer have been supplemented with large numbers of analyses by another observer, on formulations of various insecticides with attapulgite and on several other types of carriers without toxicants. The improvement in reproducibility effected by the turntable was generally about threefold, and the mean deviation with materials of normal quality was seldom more than 0.2% of the sample weight.

In many instances, the same sample was subjected to two nearly simultaneous series of analyses, one with turntable and one without. Examples for direct comparison of the two methods are an analytical series on five samples, each of which was divided into two portions, one for testing with turntable and one without; the observations were repeated until the material was exhausted, each portion yielding either seven or eight runs. The results are summarized in Table I.

The advantages of this sampling procedure, in addition to their direct relationship to dust determination, have an important bearing on other kinds of tests, especially where dust content may be a factor. The possibilities in grain-breakdown determination as prescribed in Interim Federal Specifications for granulated insecticides (*3*) have been investigated, and it has been found that there is often a worthwhile improvement in reproducibility when the turntable is used. The first five pairs of comparative test series comprised a total of 98 observations divided approximately equally between use and omission of turntable with the same samples. For the four samples (out of five) for which the mean deviations by the usual procedure were as much as 0.5% of the sample weight, the mean deviations were from one third to two thirds as great with turntable as without.

Possible Extensions

The sampling apparatus and procedure as described are intended specifically for use in taking the ultimate test sample from the laboratory stock sample of moderate size as ordinarily received for analysis. Beyond the scope of the analyst's operation, but equally important, is the drawing of the laboratory sample in such a way that it will be truly representative of the lot from which it is taken. The same principle may be followed, with any necessary modification in dimensions of equipment, for sampling on a larger scale, as in drawing a laboratory stock sample from a 50-pound bag, or for dividing an original sample into subsamples. Two or more test samples may be taken simultaneously from the stock sample by using a separate cup for each test sample.

Acknowledgment

Test runs to confirm the effectiveness of the sampler were made by James R. G. Jones, Entomology Research Division, U. S. Department of Agriculture.

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FUNGICIDE RESIDUES

Extraction and Determination of 2,6-Dichloro-4-nitroaniline in Processed Fruits

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Interest in the use of 2,6-dichloro-4-nitroaniline (dicloran) (Botran, The Upjohn Co.) in California as a control for postharvest fungus rots on stone fruits has created a need for a suitable method of analysis and residue studies in processed fruits. For effective control of the diseases, fruits are treated with the chemical after harvesting, but before storing for ripening (*5*). Once ripened, they are processed as usual for canning (*4*). Postharvest application places this fungicide in the category with food additives, making it imperative that residue data be obtained with the canned products.

The existing method for the determination of dicloran residues is based on the reduction of the parent structure to the corresponding phenylenediamine by zinc and acid (*1*, *2*). Although useful for some crops (*2*), this procedure was not sensitive enough nor readily adapted for our purposes.

In the present study, a procedure is described for the extraction and colorimetric determination of dicloran residues in processed fruits and their sirups. The colorimetric procedure is based on the development of an intense yellow color characteristic of some mononitro aromatic compounds in the presence of strong alkali and acetone. It is a modification of the method previously described by Porter (*6*) for aromatic nitro compounds, and employs the Janovsky reaction (*3*).

Treatment of Fruit

The peaches (Vivian, clingstone; Fay Elberta, freestone) and apricots (Royal) were dipped for 2 minutes in suspensions containing 250, 500, 750, and 1000 p.p.m. of dicloran and stored for 24 hours at 72° F., 80% relative humidity. After storing, the fruits were canned as halves by the Department of Food