sium oxide using platinum crucibles followed by either gravimetric or flame photometric measurements are in good agreement with the bureau's values. However, the sodium oxide values, with the exception of those for No. 70, feldspar, are consistently low. Many tests were made, as shown in Table III, using various modifications of the methods in an effort to duplicate the bureau's values more closely, but without success. Believing that the use of the regular platinum crucibles may have been a source of error, the tests were repeated with nickel crucibles similar to those used by the Bureau of Mines (11), or standard J. Lawrence Smith platinum crucibles. The sodium oxide results, as shown in Table III, were still low for four out of five of the samples, although the J. L. S. crucibles gave somewhat closer values than either of the other kinds of crucibles.

The reasons for the discrepancies are not entirely clear. The errors due to the presence of sodium oxide in the calcium carbonate used in sintering the samples were over and above the compensating errors caused by the calcium (and traces of sodium) introduced in equal amounts into both the standard (calibration) solutions and solutions under test. In the case of gravimetric analyses, however, there is no compensation for impurities in the calcium carbonate. Hence, all the author's reported values were corrected for blank tests. However, if these corrections were not applied, the values would be much closer to the values reported by the National Bureau of Standards and by other investigators who have analyzed some of the same standard samples by flame photometric methods. For example, the values shown in Table III for sample 1a, argillaceous limestone, uncorrected for blanks, would range from 0.36 to 0.39% sodium oxide, in close agreement with the certified value of 0.39%. With sample 1a, an examination of the Bureau of Standards' certificate of analysis showed that the material was analyzed over 20 years ago and that the values used in computing the certified average range from 0.31 to 0.45% sodium oxide.

The J. L. S. crucibles, having shown somewhat higher sodium oxide values than other types of crucibles on the tests of the standard samples, were used for repeat tests of the raw mix and kiln dust samples (columns 6 and 11 of Table I). The differences,

however, as shown in columns 7 and 12, were neither significant nor consistently in the same direction. Therefore, considering all the data in Table I it appears that the results obtained by the proposed flame photometric method, using either regular platinum or J. L. S. crucibles, are in good agreement with the longer gravimetric procedure.

TIME REQUIREMENTS

The time required for alkali analysis by the proposed method was less than half of that required for gravimetric analysis of acid-insoluble silicates. One of the primary objects of this study has been to get an accurate as well as a rapid method. It is possible that for less accurate routine work the method would require one third or less of the time of the gravimetric method.

ACKNOWLEDGMENT

The author wishes to acknowledge the contributions of Helen E. McMillen and William G. Hime in connection with certain phases of the analytical and literature research portions of this study.

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RECEIVED for review February 23, 1954. Accepted July 14, 1954.

Determination of 2,4-Dichlorophenoxyacetic Acid. 2.4.5-Trichlorophenoxyacetic Acid, 2-Methyl-4-Chlorophenoxyacetic Acid, and 4-Chlorophenoxyacetic Acid

In Technical Mixtures by Isotope Dilution Analysis

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Methods for the specific determination of 2,4-D, 2,4,5-T, and MCP are proposed. Mixtures of 2,4-D and 2,4,5-T are frequently used and on that account methods for the determination of each of the compounds in such mixtures have been elaborated. 4-Chlorophenoxyacetic acid may find use as a weed killer in the future and is therefore included in the investigations.

THE active compounds in weed killers of the hormone type commonly used are 2,4-dichlorophenoxyacetic acid (2,4-D), 2,4,5-trichlorophenoxyacetic acid (2,4,5-T), and 2-methyl-4chlorophenoxyacetic acid (MCP). Because of the methods of preparation (3, 4, 7, 14, 17, 21) technical 2,4-D, 2,4,5-T, and MCP may contain varying amounts of other chlorine substituted phenoxyacetic acids with little or no activity. Furthermore, the technical products may contain chlorophenols and glycolic acid.

The method adopted by the Association of Official Agricultural Chemists for the determination of 2,4-D acid is that used by Rooney (18), in which the total amount of phenoxyacetic acids is determined. Ketelaar, Gersmann, and Beck (15) have since pointed out that the presence of chlorophenols interferes with the determination and have modified Roonev's method.

A specific method for the determination of 2,4-D, reported by Stroud (23), is based on separation of the acids by partition chromatography. Gordon and Beroza (8) also used partition chromatography in the separation of 2,4-D from 2.4,5-T. The influence of homologs has not been reported.

Hill (13) and Grabe (9) have published methods for the determination of MCP by ultraviolet spectrophotometric measurements. Sjöberg (20) was able to determine MCP and the presence of homologs by the use of infrared spectrophotometry. Freeman and Gardner (5) have separated MCP from homologs by partition chromatography. A method published by the author (22) is reproduced in this paper, with some slight modifications.

This investigation was carried out with the following mixtures:

2,4-D and homologs—i.e., 2-chlorophenoxyacetic acid, 4-chlorophenoxyacetic acid, 2,6-dichlorophenoxyacetic acid, and 2,4,6-trichlorophenoxyacetic acid.

2,4,5-T and homlogs—i.e., 2,5-dichlorophenoxyacetic acid, 2,3,6-trichlorophenoxyacetic acid, and 2,3,4,6-tetrachlorophen-

phenoxyacetic acid.

4-Chlorophenoxyacetic acid and homologs—i.e., phenoxyacetic acid, 2-chlorophenoxyacetic acid, and 2,4-D.

METHOD OF ANALYSIS

The isotope dilution principle is generally known. As applied to the present investigation, it was used as follows.

Radioactive X (where X may be 2,4-D, 2,4,5-T, MCP, or 4-chlorophenoxyacetic acid) is synthesized from radioactive chlorine_(chlorine-36). A solution is then prepared containing ymg. of X per mg. of solution. A standard sample is prepared from a mg. of active solution and b mg. of inactive X. The pure X, or derivative thereof, that is isolated from the mixture will have a specific activity, c.

When the same experiment is carried out with A mg. of active solution and an unknown amount, B mg. of X, the final specific activity is C, and we obtain the relationship,

$$r = \frac{C}{c} = \frac{A}{a} \times \frac{b+ay}{B+Ay}$$
 or $B = \frac{1}{r} \times \frac{A}{a} \times b + Ay \times \frac{1-r}{r}$

In the above expression B is the only unknown quantity and ris the ratio of specific activity of the final sample to the standard sample. When X is isolated, as X or as an X derivative, with a known purity, P%, the expression may be written,

$$B = \left(\frac{1}{r} \times \frac{A}{a} \times b + Ay \times \frac{1-r}{r}\right) \times \frac{P}{100}$$

With this modification a high purity of radioactive X is not necessary. Contamination with other radioactive substances may give rise to errors, but this source of error is eliminated by preparing the active solution with an acceptably high content of these substances in inactive form. When the X derivative is isolated by the analytical procedure, radioactive contaminants are removed together with their inactive counterparts. In other words, further purification of the product must change the specific activity only to a degree corresponding to the change in purity.

Preliminary work indicated that the acid desired could not be easily isolated from the constituents listed above. After testing various derivatives it was found that the anilides had practically ideal properties for the purpose. They are easily prepared and easy to obtain in a nearly pure state by recrystallization, and the purity can be determined accurately by their melting points.

PREPARATION OF MATERIALS

Phenoxyacetic Acids. All the above-mentioned substituted phenoxyacetic acids are known, with the exception of 2,3,4,6tetrachlorophenoxyacetic acid. Methods of preparation are described by Leaper and Bishop (16) and by Sjöberg (20). The phenoxyacetic acids used in this investigation were prepared by similar methods.

2,3,4,6-Tetra-2,3,4,6-TETRACHLOROPHENOXYACETIC ACID. 2,3,4,6-Tetra-chlorophenol with a melting point of 67-69° C. was obtained by recrystallization from acetic acid of a technical product (Dowicide

6, from the Dow Chemical Co.). By condensation with monochloroacetic acid 2,3,4,6-tetrachlorophenoxyacetic acid was obtained. The crude product was first crystallized twice from monochlorobenzene and finally from benzene. _____2,4-D, 2,4,5-T, MCP, AND 4-CHLOROPHENOXYACETIC ACID.

These may be purified from technical products. They are converted to the anilide by the method described below, and are then recrystallized from ethanol until the correct melting point is

attained. The pure anilide is saponified by solium hydroxide and the acid is obtained by crystallizing twice from benzene. **Phenoxyacetanilides.** The anilides were prepared according to the method of Fritzsche (\mathcal{C}), by refluxing the acid with 2 to 3 times as much aniline for 1 hour, precipitating with an excess of budgeobleic acid. Elicence methods were prepared according in the second hydrochloric acid, filtering, washing with water, and crystallizing from ethanol, methanol, or 61% ethanol.

Most of the anilides have been reported previously (6, 12, 16). Table I gives melting points for the compounds prepared and analyses for the new compounds.

Table I.	Melting	Points of	Compounds	Used
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	Acid, ° C.	Anilide, ° C.
Phenoxyacetic acid 2-Chlorophenoxyacetic acid 4-Chlorophenoxyacetic acid 2.4-Dichlorophenoxyacetic acid 2.5-Dichlorophenoxyacetic acid 2.6-Dichlorophenoxyacetic acid 2.4,5-Trichlorophenoxyacetic acid 2.4,5-Trichlorophenoxyacetic acid 2.3,4,6-Tetrachlorophenoxyacetic acid 2.Methyl-henoxyacetic acid 2-Methyl-4-chlorophenoxyacetic acid 2-Methyl-4,6-dichlorophenoxyacetic acid 2-Methyl-4,6-dichlorophenoxyacetic acid	$\begin{array}{c} 99.5{-}100.5\\ 147.0{-}148.0\\ 158.0{-}159.0\\ 140.0{-}140.5\\ 148.0{-}149.0\\ 136.0{-}137.0\\ 147.0{-}148.0\\ 156.0{-}137.0\\ 184.0{-}185.0\\ 176.5{-}177.5^a\\ 155.0{-}155.5\\ 119.5{-}120.0\\ 109.0{-}109.5\\ 187.5{-}188.0\\ \end{array}$	$\begin{array}{c} 100.3-100.7\\ 123.2-123.4\\ 128.8-129.1\\ 111.0-111.1\\ 145.5-145.8\\ 84.6-85.0\\ 87.5-88.0\\ 178.0-178.2\\ 110.5-110.8\\ 117.6-118.0b\\ 108.2-108.4\\ 129.8-130.0c\\ 78.0-78.3d\\ 100.8-101.1e\end{array}$
^a Anal. Calcd. for C ₈ H ₄ O ₃ ClCl ₄ : C, 3: C, 33.4; H, 1.7; Cl, 48.8. ^b Anal. Calcd for Cl ₃ H ₉ O ₂ NCl ₄ : C, 46 Found: C, 46.2; H, 2.7; Cl, 38.7; N, 3.8. ^c Anal. Calcd for Cl ₃ H ₁₅ O ₃ NCl: C, 65 Found: C, 65.7; H, 4.9; Cl, 12.9; N, 5.3. ^d Anal. Calcd for Cl ₃ H ₁₅ O ₃ NCl: C, 65 Found: C, 65.5; H, 5.0; Cl, 12.9; N, 5.0. ^e Anal. Calcd for Cl ₃ H ₁₅ O ₃ NCl: C, 58 Found: C, 58.1; H, 4.2; Cl, 22.9; N, 4.4.	3.1; H, 1.39; C .1; H, 2.49; Cl .4; H, 5.12; Cl .4; H, 5.12; Cl .4; H, 4.23; Cl	 Cl, 48.9; Found: 38.8; N, 3.84; 12.9; N, 5.08. 12.9; N, 5.08; 22.9; N, 4.52;

Radioactive Compounds. These were prepared according to a method proposed by Haskelberg (10), by chlorination of the starting material with radioactive chlorine. The source of radioactive chlorine was a solution of hydrochloric acid with an activity of about 5 microcuries per milliequivalent, obtained from the U. S. Atomic Energy Commission, Oak Ridge, Tenn. By dilution with 1N hydrochloric acid an activity of about 1 micro-curie per milliequivalent was obtained. The chloride was pre-

curie per milliequivalent was obtained. The chloride was pre-cipitated as silver chloride, which was washed with water, abso-lute ethanol, and petroleum ether, and dried at 40°. Elementary chlorine was obtained by oxidation of the silver chloride with potassium dichromate in sulfuric acid, a method used by Baubigny and Chavanne (2). About 1.2 grams of active silver chloride was added to 3 grams of potassium dichromate in a 50-ml. round-bottomed flask, with a side arm for the evolution of blosine. A cheat when the was attrached to the side arm to chlorine. A short rubber tube was attached to the side arm to Twentyserve as a flexible connection to the chlorination vessel. five milliliters of concentrated sulfuric acid was added in one portion and the flask was gently shaken by a mechanical arrange-ment in an oil bath. The bath was kept at room temperature for the first hour, and then heated to 200° during the next 3 hours. At this elevated temperature oxygen is also evolved and helps re-move chlorine from the flask. The last traces of chlorine were removed by blowing air through the flask (by suction).

Cold runs showed that 95 to 98% of the theoretical amount of chlorine could be recovered by absorption in sodium hydroxide solution.

RADIOACTIVE 2,4-D. This was prepared by chlorination of 2-chlorophenoxyacetic acid (a less pure 2,4-D was obtained when 4-chlorophenoxyacetic acid was used as the starting material). The 2-chlorophenoxyacetic acid (0.925 gram) was dissolved in acetic acid (10 ml.) at 100°, and chlorinated with the chlorine produced from radioactive silver chloride (1.35 grams). The chlorinated solution was diluted 10 times with water, heated to a clear solution, and crystallized by cooling to 0°. Crystals of active 2,4-D were filtered off, washed with water, and dried. Yield, 0.84 gram; melting point 136–138°. Pure 2,4-D (4.50

grams) was added to this crude, active preparation and the mixture was recrystallized twice from 40 ml. of benzene. 4.80 grams; melting point 140-140.5°. Yield.

The hydrochloric acid, together with small amounts (2 to 39 of unreacted chlorine, was absorbed in water containing 1% sodium hydrogen sulfite and precipitated again as silver chloride. The filtrate from the crude, active 2,4-D was reduced with Raney nickel-aluminum alloy as described by Schwenk, Papa, and Ginsberg (19), and the liberated chloride was precipitated as silver chloride. The yield of crude 2,4-D was about 80% with respect to the amount of chlorine consumed. RADIOACTIVE 2,4,5-T. Chlorination of 0.999 gram of 2,5-

dichlorophenoxyacetic acid was accomplished with the chlorine derived from 1.30 grams of active silver chloride. Yield, 1.15 grams; melting point 150–152°; estimated purity, 90%. RADIOACTIVE MCP. Chlorination of 0.868 gram of 2-methyl-

henoxyacetic acid was performed with the chlorine produced from 1.45 grams of active silver chloride. Yield, 0.85 gram; melting point 115–117°; estimated purity, 95%. RADIOACTIVE 4-CHLOROPHENOXYACETIC ACID. Phenoxyacetic

acid, 0.676 gram, was chlorinated with the chlorine derived from 1.22 grams of active silver chloride. Yield, 0.55 gram; melting Pure 4-chlorophenoxyacetic acid, 3.40 grams, point 154-157 point 154–157°. Pure 4-chlorophenoxyacetic acid, 3.40 grams, was added and the mixture was recrystallized twice from 100 ml. Yield, 3.75 grams; melting point 158-159° of benzene.

APPARATUS AND MEASUREMENTS

Purity of Anilides. The purity of an anilide may be found by a melting point determination, using a capillary method in a Hershberg apparatus (11). The temperature at which a meniscus forms in the capillary is taken as the melting point. The difference in the melting points of two samples is determined by placing the two capillaries in the Hershberg apparatus at the same time. The difference in melting points is determined with an accuracy of $\pm 0.1^{\circ}$.



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Figures 1 to 4 show the depressions of the melting points of 2,4-D anilide, 2,4,5-T anilide, MCP anilide, and 4-chlorophenoxyacetanilide by different contents of anilides of the homologous acids. The different curves will give practically the same corrections for purities above 99%. Figure 5 shows the melting points of mixtures of anilides of 2,4-D and 2,4,5-T.

Radioactivity Determination. Radioactivity of a sample is measured with a conventional end-window Geiger-Müller counter [Madsen tube, window thickness 3 mg. per sq. cm., background about 12 counts per minute (1)].

About 50 mg. of the fine crystalline sample is placed in an aluminum dish and weighed. The number of counts per minute measured is corrected for background and self-absorption. Curves of self-absorption may be determined by each investigator for his own technique.

The accuracy of the activity determination is limited by the statistical counting error. The samples used in these experiments (about 1000 counts per minute) are counted for about 20 minutes and the standard deviation of the number of counts is about 0.7%—i.e., the ratio, r, of the specific activities of the two samples is determined with a standard deviation of about 1%. In comparison to this uncertainty, the uncertainties due to corrections for background, self-absorption, weighing, and transfer to the aluminum dish are very small and may be disregarded.



To transfer the sample to the aluminum dish in such a way as to form a uniform layer, the powder is placed in the dish and suspended in a few drops of methanol or acetone. During the evaporation of the methanol or acetone the sample is smoothly applied to the dish with the aid of a nickel spatula. It is then dried under an infrared lamp and weighed again.

ANALYTICAL PROCEDURES

The methods first described deal with determinations of the compounds in the form of acids or salts. Later, methods of determining esters or other saponifiable compounds are proposed.

The common reagents used are: 4N sodium hy-Reagents. droxide; 4N hydrochloric acid; aniline, reagent grade; absolute ethanol, reagent grade 99.5–99.9%; methanol, reagent grade; 61% ethanol, 2 volumes of absolute ethanol plus 1 volume of water.

SPECIAL REAGENTS. Radioactive 2,4-D, 1% solution, consists of 1.00 gram of recrystallized radioactive 2,4-D (about 0.7 microcurie), 0.25 gram of 2,6-dichlorophenoxyacetic acid, 0.25 gram of 2,4,6-trichlorophenoxyacetic acid, 10 ml. of 1N sodium hydroxide,

40 ml. of ethanol, and water to make 100 grams. Radioactive 2,4,5-T, 0.5% solution, consists of 0.19 gram of radioactive 2,4,5-T (about 0.7 microcurie), 0.33 gram of 2,4,5-T, 0.25 gram of 2,3,6-trichlorophenoxyacetic acid, 0.25 gram of 2,3,4,6-tetrachlorophenoxyacetic acid, 5 ml. of 1N sodium hy-

2, 5, 5, 0-tenaemorophenoxyacetic acid, 5 ml. of 1/V sodium hy-droxide, 40 ml. of ethanol, and water to make 100 grams. Radioactive MCP, 1% solution, consists of 0.15 gram of radio-active MCP (about 0.7 microcurie), 0.86 gram of MCP, 0.50 gram of 2-methyl-fe-phoreneouscetic acid, 0.50 gram of 2-methyl-6-chlorophenoxyacetic acid, 0.50 gram of 2-methyl-4,6-dichlorophenoxyacetic acid, 10 ml. of 1N sodium hydroxide, 40 ml. of ethanol, and water to make 100 grams.

Radioactive 4-chlorophenoxyacetic acid, 1% solution, consists of 1.00 gram of recrystallized radioactive 4-chlorophenoxyacetic acid (about 0.7 microcurie), 0.25 gram of 2-chlorophenoxyacetic acid, 0.25 gram of 2,4-D, 10 ml. of 1N sodium hydroxide, 40 ml. of ethanol, and water to make 100 grams.

The phenoxyacetic acids used for preparing these solutions do not need to be of high purity

Because of the lower solubility of the 2,4,5-T sodium salt, only a 0.5% solution can be prepared. Pure 2,4-D, 2,4,5-T, MCP, and 4-chlorophenoxyacetic acid.

Pure 2,4-D anilide.

Procedures. A1. DETERMINATION OF 2,4-D WITHOUT 2,4,5-T. Weigh a quantity of the product to be analyzed which is estimated to contain about 250 mg. of 2,4-D. Add 1.5 ml. of active 2,4-D solution and determine this amount (A mg.) accurately by another weighing. Dissolve in sodium hydroxide and Filter off and dry at 80° to 100°. Add 1.5 ml. of aniline and reflux for 1 hourin a test tube provided with a cold finger. After cooling, add 10 ml. of 4N hydrochloric acid, boil for a moment, and cool again. Filter off the anilide and wash with water. Crystallize the wet, crude anilide first from 2.5 ml. of absolute ethanol, and then three or more times from 5 ml. of 61% ethanol, until the melting point differs from that of the standard sample by less than 0.5° —i.e., until it has a purity greater than 99%. Measure the specific activity as a ratio (=r) of the standard sample [prepared in the same way, but from a known amount (b

mg) of pure 2.4-D]. From the melting point determine the purity (P%). Calculate the amount (B mg.) of 2.4-D in the original sample by the formula given earlier.



Figure 3. Melting Point Depression of MCP Anilide

- 2-Methylphenoxyacetanilide 2-Methyl-6-chlorophenoxyacetanilide 2-Methyl-4,6-dichlorophenoxyacetanilide ö

A2. DETERMINATION OF 2,4-D TOGETHER WITH 2,4,5-T. Prepare an amount of crude anilide from a sample estimated to contain about 500 mg. of 2,4-D as described above. Boil the crude, wet anilde in 50 ml. of methanol. After cooling, filter off the crystals and discard. Dilute the filtrate with 50 ml. of water, filter off the crystals which precipitate, and recrystallize. first from 5 ml. of absolute ethanol and then three times from 10 ml. of 61% ethanol (the amount of 61% ethanol used will not dissolve all the crystals, and at the last crystallization the hot solution is decanted from the undissolved crystals of 2,4,5-T Now dissolve the crystals in 10 ml. of hot methanol. anilide). Seed the solution with 2,4,5-T anilide, allow it to crystallize by standing, filter off, and discard the crystals. To the filtrate add standing, filter off, and discard the crystals. 5 ml. of methanol and 7.5 ml. of water. Heat to a clear solution, allow it to crystallize by standing, then filter off the crystals and dry at 80° to 90°.

Measure the specific activity as a ratio of

the standard sample (Procedure A1). The purity of these crystals will be about 90 to 95%, and is determined by mixing about 1 part of the sample with 2 parts of pure 2,4-D anilide. To ensure complete mixing, dissolve accurately weighed amounts in acetone and evaporate to dryness. Determine the melting point of the mixture as described above. Repeat this determina-tion 2 to 3 times. The purity of the original sample is easily calculated.

B. DETERMINATION OF 2,4,5-T. The procedure is essentially as described in A1. The anilide is crystallized twice from 10 ml. of absolute ethanol and then from 10 ml. of methanol.

C. DETERMINATION OF MCP. This procedure is also essentially as described in A1. The anilide is crystallized from 5 ml. of absolute ethanol and two or more times from 10 ml. of 61% ethanol.

D. DETERMINATION OF 4-CHLOROPHEN-OXYACETIC ACID. The procedure is the same as in A1.

MODIFICATIONS OF METHODS. The isotope dilution analysis of technical samples or preparations may be slightly modified from one sample to another, but a number of cold runs will usually suffice to indicate a convenient method for isolating the anilide

As an example, MCP preparations may contain tarry subsubstances. If, before the preparation of the anilide, the acid is dissolved in about 50 ml. of boiling water and filtered, the acid which crystallizes on cooling will yield a pure anilide without difficulty when Procedure C is followed.

In the analysis of butoxyethanol esters of 2,4-D and 2,4,5-T the sample to be analyzed is weighed, radioactive solution is added, and the mixture is saponified with an excess of alcoholic 1N potassium hydroxide at room temperature. The potassium salts of the acids precipitate, and are filtered off and washed free from oily substances with benzene. The potassium salts are dissolved in water and filtered, and the acids precipitated with hydrochloric acid. Procedure A or B is then followed.

2,4,5-T butyl ester is analyzed by the same procedure, except that the saponification is carried out at refluxing temperature.

DETERMINATION OF TOTAL AMOUNT OF PHENOXYACETIC ACIDS. Weigh an amount estimated to contain about 0.4 gram of phenoxyacetic acids. Dissolve in about 100 ml. of water and pour the solution into a Kutcher-Steudel extractor (24). Add a small excess of hydrochloric acid. Extract the phenoxyacetic acids liberated continuously with benzene for 1 to 1.5 hours. It is important that a large amount of benzene passes through the solution to be extracted. For this reason the benzene must be heated on a vapor bath and the whole system kept under a reduced pressure of about 0.33 atmosphere, the pressure being maintained with the aid of a manostat. The benzene will ex-



4-Chlorophenoxyacetanilide Phenoxyacetanilide 2-Chlorophenoxyace 2-Chlorophenoxyacetanilide 2,4-D anilide





Figure 5. Melting Points of Mixtures of 2,4,5-T Anilide and 2,4-D Anilide

Vertical lines indicate interval from settling point to total melting. Points through which curve is drawn are meniscus points

tract the phenoxyacetic acids and the phenols. After extraction, add the same volume of ethanol and 10 drops of bromothymol blue solution (0.1%) to the benzene solution. Titrate with 0.1Nsodium hydroxide. During the titration two phases will appear. The end point of the titration is a green color in the aqueous phase.

Experiments have shown that glycolic acid is not extracted by benzene and that phenols are not titrated in the procedure suggested.

Technical samples of phenoxyacetic acids may be titrated as such without preceding extraction. The presence of glycolic acid, however, may give a value that is too high.

RESULTS

Analysis of Known Mixtures. The procedures were tested on a series of known mixtures. The results are given in Table II.

Analysis of Technical Products. Table III gives analytical data for different technical samples. Table IV gives the data for different agricultural preparations. Each of the samples of the same type originates from a different manufacturer.

ACCURACY OF METHODS

From an estimation of the accuracy of the methods it is obvious that all other sources of error may be disregarded in comparison with the uncertainty of the radioactive measurement, r, and of the purity determination, P.

Tabl	e II. Analyses of K	nown	Mixtures	
Compound Analyzed, Mg.	Other Compounds Add Mg.	led ^a ,	Found. Mg.	Deviation,
2,4-D 202.0 251.8 301.4	2,4-D homolog mixt.	40 40 40	$204 \\ 250 \\ 303$	$+1.0 \\ -0.7 \\ +0.5$
503.2	2,4,5-T	500	503	0
505.0	2,4-D homolog mixt. 2,4,5-T 2,4,5-T homolog mixt.	80 500 60	498	1 . 4
2,4,5-T 225.8 301.4	2,4,5-T homolog mixt.	30 30	$225 \\ 299$	-0.3 - 0.8
222.2	2,4-D	200	221	-0.5
221.6	2,4,5-T homolog mixt. 2,4-D 2,4-D homolog mixt.	$30 \\ 200 \\ 40$	222	+0.2
MCP 400.7 292.4 256.2	MCP homolog mixt.	200 200 100	$398 \\ 294 \\ 256$	$ \begin{array}{r} -0.7 \\ +0.5 \\ -0.5 \end{array} $
4-Chlorophenoxy- acetic acid				
204.4 253.2 303.0	4-chlorophenoxyacetic acid homolog mixt.	30 30 30	206 254 307	$^{+0.8}_{+0.3}_{+1.3}$
4 2 4 D homolo	mixture Equal amount	s of 2-c	hloropheno	vacetic acid

^a 2,4-D homolog mixture. Equal amounts of 2-chlorophenoxyacetic acid, 4-chlorophenoxyacetic acid, 2,6-dichlorophenoxyacetic acid, and 2,4,6 trichlorophenoxyacetic acid. 2,4,5-T homolog mixture. Equal amounts of 2,5-dichlorophenoxyacetic acid, 2,3,6-trichlorophenoxyacetic acid, and 2,3,4,6-tetrachlorophenoxyacetic acid.

acid. MCP homolog mixture. 20% 2-methylphenoxyacetic acid, 60% 2-methyl-6-chlorophenoxyacetic acid, and 20% 2-methyl-4,6-dichlorophenoxy-acetic acid. 4-Chlorophenoxyacetic acid homolog mixture. Equal amounts of phenoxyacetic acid, 2-chlorophenoxyacetic acid, and 2,4-D.

Table III. Analyses of Technical Samples

	Total Phenoxyacetic Acids,	Active Phenoxyacetic		
Product	%	Acid, %		
2,4-D acid	<u>99.7</u>	99.0		
2,4-D sodium salt	98.5 80.0 84.1 81.3	97.0 73.7 80.3 79.0		
2,4,5-T acid	99.0 99.4 99.0	96.0 90.2 93.8		
2,4,5-T butyl ester	$\begin{array}{c}100.0\\82.8^a\end{array}$	$\begin{array}{c} 96.5 \\ 75.0 \end{array}$		
MCP acid	94.4 96.0 100.0	87.5 88.5 78.5		
^a Titrated after saponification.				

Table IV. Analyses of Agricultural Preparations (Duplicate determinations)

Composition Stated by Manufactures	Total Phen- oxyacetic	Active Phenoxyacetic Acid, %
Composition stated by Manufacturer	Acias, %	2, 1 2, 1, 1-1
Butoxyethanol esters of 2,4-D and and 2,4,5-T: 15.8% 2,4-D, 7.8% 2,4,5-T		
		2.4.5 - T
Butoxyethanol ester of $2,4,5$ -T, 42.4% $2,4,5$ -T		$\begin{pmatrix} 39.3\\ 39.5 \end{pmatrix}$
		MCP
MCP sodium salt		
21.7% MCP ^a	27.0	
$21.0^{c_{r_0}}_{-0}$ MCP ^a	34.0	$\binom{21.3}{21.2}$
21.3% MCP ^a	27.1	${19.9 \\ 19.9}$
a Original declaration in weight-vol from specific gravity.	ume units.	Indicated value calculated

When P is above 99%, the uncertainty of this quantity may also be disregarded.

The accuracy of the determination of the purity, P, of 2,4-D in the presence of 2,4,5-T is within about $\pm 1\%$; the standard deviation of the final result will be about 2%.

In the other cases, where only the uncertainty of r determines the uncertainty of the final result, the standard deviation will be about 1%--i.e., the value determined has a 90% probability of being within $\pm 1.64\%$ of the real value.

ACKNOWLEDGMENT

The author wishes to thank Köge Chemical Works, Ltd., for permission to publish this article. The assistance of Jytte Jørn Jensen in performing the radioactive measurements and of Ernst Boss in performing the elementary analyses is gratefully acknowledged.

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RECEIVED for review December 30, 1953. Accepted July 27, 1954.