# Kelthane Decontamination Studies on Almond Hulls

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Decontamination of Kelthane residues on almond hull meal was studied by exploitation of such physical or chemical properties of the pesticide as volatility, instability to hydrolysis, and other treatments. Excess moisture was essential for best removal of the pesticide from the hulls by warm air. Water washing was inefficient for decontamination. Vapor treatment of the hulls with benzene removed 91% of the Kelthane and 75% of the total residue due to the formation of 4,4′-dichlorobenzophenone (4,4′-D), water removed 80% of the Kelthane and 68% of the total residue, and 15% ammonia in water removed 57% of the Kelthane but no significant amount of the total residue due to 4,4′-D formation. A hot chemical alkaline wash with various reagents removed 80 to 100% of the Kelthane contaminant and 41 to 96% of the total residue due to the formation of 4,4′-D. Feed ingredient analyses were performed on the treated hulls.

Pesticides have become essential to the economical production of most animal feedstuffs, including also the by-products of other agricultural industries, for example: almond hulls, seed screenings, fruit pomaces, and other materials. The treatment which results in contamination may be intentional such as acaricide applications to almond hulls, or incidental such as drift onto alfalfa fields; but an increasing proportion of feed samples contains unacceptable levels of pesticide residues.

Commercial feed may be defined as including all substances which are used as feed or for mixing in feed for animals with a few exceptions. In California, although under Federal law there is no tolerance for Kelthane on almond hulls as a feed, the permitted tolerance for Kelthane or dicofol [1,1-bis(*p*-chlorophenyl)-2,2,2-trichloroethanol] is 10 p.p.m. in or on any ingredient to be used in the manufacture of a complete, commercial feed ration, provided the complete, commercial feed ration contains not more than 1.5 p.p.m. and is sold only for use as a feed for ruminant meat animals. The permissible Kelthane tolerance for dairy animal and poultry feeds is 0 p.p.m.

Chlorinated hydrocarbon insecticides have been predominantly responsible for feed contamination. Removal of these residues may be accomplished by exploitation of some characteristic physical or chemical property such as volatility, instability to hydrolysis, or other treatments (Archer, 1968b; Archer and Crosby, 1968).

The purpose of the present work was to find means by which Kelthane residues on dry almond hull meal might intentionally be removed or detoxified. Decontamination methods would improve both the value of the feed as a marketable commodity and the potential marketability of animal products containing residues derived from the feed source; they would be of particular value in instances of accidental over-application or drift contamination. Observations that DDT is relatively volatile, especially in the presence of water (Bowman *et al.*, 1959) and remains near the plant surfaces in alfalfa (Archer and Crosby, 1967) might also provide the basis for effective practical removal of Kelthane residues from animal feedstuff.

## MATERIALS AND METHODS

**Sample Preparation.** A previously analyzed, dry, ground almond hull meal (14% moisture) sample was well mixed. The sample was selected to be as free as possible from pesticide contamination so that a known quality and amount of Kelthane could be impregnated on the hulls. Weighed, mixed hulls were covered with redistilled acetone containing a known amount of analytical grade Kelthane to result in a theoretical residue deposit of 15,000 p.p.b. The solvent was evaporated from the sample at 50° to 60°C. with the aid of an air stream until completely dry. The plant material was mixed in the solvent concentrating jar and stored for analysis. By triplicate analyses, the hulls contained 10,200 p.p.b. of Kelthane on a dry weight basis. Some contaminant was lost by volatilization and nondeterminant factors during the coating operation as might be expected. However, all decontamination losses are based on the residue found on the plant material after coating.

**Extraction and Cleanup.** Extraction of the plant samples (15 grams per 250 ml. of solvent) was accomplished by three $^1/_2$-hour refluxes with benzene; the solvent was pooled, concentrated, and analyzed (Archer and Crosby, 1967). The solvent extracts were cleaned up on Florisil (activated at 270° C. for 3 hours). Kelthane and 4,4′-dichlorobenzophenone were eluted from the Florisil with 390 ml. of 30% diethyl ether and 70% pentane (Archer, 1968a) and recoveries were in excess of 90%, as checked by standards and fortified samples through the analytical procedures.

**Methods for the Detection and Determination of the Pesticide.** Gas-liquid chromatography (GLC) and thin-layer chromatography (TLC) procedures were employed routinely, either separately or in combination. All chemicals used in these studies were reagent grade. The pesticides were analytical standards; the reagent grade solvents were redistilled shortly before use. The gas chromatograph was the Varian Aerograph (Model 1200) equipped with an electron-capture detector and a Leeds and Northrup Speedomax W 1-mv. recorder with a chart speed of $^1/_2$-inch per minute. Areas under the peaks were measured with a polar planimeter. The chromatographic column, made with an 8-foot × $^1/_8$-inch stainless steel tube packed with 60- to 80-mesh silylated Chromosorb W, acid washed, was coated with 5% Dow 710 silicone fluid and 5% SE-30 silicone gum rubber. Nitrogen carrier gas (50 p.s.i., 20 ml. per minute) and a column temperature of 220° C. gave the best results and were used in these experiments. A practical method sensitivity was established at 0.01 p.p.m. All residue data were expressed on a dry weight basis and represent at least duplicate analyses unless otherwise stated. The GLC response was relative to an aliquot of Kelthane standard which was applied to the hulls. The standard

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Kelthane was also compared and extracted from TLC plates as was the plant material for analyses in combination with GLC. These responses were reproducible under the stated conditions.

TLC was employed for screening and in combination with GLC, as an analytical tool. Silica gel H (0.5-mm. layer thickness) absorbent, developing solvent (5% isopropanol and 95% pentane), and the silver nitrate–2-phenoxyethanol color test (Mitchell, 1958) as a dip solution were employed. For quantitative work chromatogram areas containing the unknowns were extracted from the silica gel with 5% isopropanol and 95% pentane after comparing $R_f$ values (Kelthane, 0.50; 4,4′-dichlorobenzophenone, 0.67) with those of parallel standard pesticide tracers, and the extracts were analyzed by GLC. Recoveries were in excess of 90% as determined by standards and fortified plant material.

**Vapor Treatment.** The vapor treatment of the hulls was in the apparatus (over-all dimensions, 2.1 meters) as shown in Figure 1. The solvent vapors were generated in the 3-liter boiler and passed from the spreader through the sample packed in the vapor column (1 meter). The entire apparatus with the exception of the Liebig condenser was insulated with glass wool and aluminum foil to maintain the solvents in vapor form. Sufficient solvent vapors were passed through the sample (200 grams dry, ground almond hull meal) to result in four 500-ml. condensate fractions, and the treated hulls and solvent condensates were stored for analysis. The water fractions were mixed with an equal volume of benzene by a 10-minute shake following a 30-minute reflux for a total of three extractions per condensate. The benzene extracts were pooled, concentrated, and analyzed.

**Water Washing.** The vigorous water washing experiments were performed by placing a weighed amount of hulls (100 grams) in a large Erlenmeyer flask with 30 volumes of either cold (25° C.) or hot (90° to 100° C.) distilled water and agitating vigorously for 15 minutes on a laboratory shaker at room temperature. The wash water was centrifuged from the plant material, and the washing was repeated three times. Each wash water was subdivided into three aliquots, extracted three times in a separatory funnel at room temperature with an equal volume of redistilled pentane. The solvent aliquots were pooled, concentrated, and analyzed. The treated hulls and wash waters were stored for analysis.

**Warm Air Treatment.** A warm air convection-type oven controlled at 100° C. + 5° C. was used for the oven heating experiments. The dry heating experimental treatment (50 grams) was for 12 hours. The wet heating experimental treatment involved saturating 50 grams of mixed hulls with 250 ml. of water, adding water in excess to cover the sample, heating to dryness, and additional heating for a total of 12 hours' treatment. Five replicate subsamples were treated by dry and wet heating. The 50 grams of almond hull meal were distributed over 314 cm.$^2$ during the treatment to heat.

**Feed Ingredient Analysis.** The almond hull meal samples were analyzed for per cent of crude protein, fat, fiber, ash, and Vitamin A activity units from carotene per pound as recommended by the "Official Methods of Analysis," of the Association of Official Agricultural Chemists (1960). The samples (Table VI) were those described under sample preparation or after the decontamination treatments as explained within the text.

**Hot Chemical Alkaline Wash.** Separate subsamples of the composited hull meal (45 grams per 150 ml. of solution) were washed with agitation for 15 minutes at a temperature of 60° to 70° C. After treatment, the plant materials were cooled in ice baths and centrifuged from the wash solutions. The plant materials were washed twice with 150 ml. of water, and the liquid was separated by centrifugation and pooled with the treatment solutions. The treatment solutions and the hulls, after air drying, were stored for the analysis. The treatment solutions were 100% water, 100% ethanol, 2% sodium ethoxide in water, and 2% sodium ethoxide, 2% sodium methoxide, and 2% potassium hydroxide in ethanol. Hull samples were also refluxed for 1 hour in 20% potassium hydroxide in ethanol and 15% ammonia in water followed by a water rinse of the treated plant material until the pH of the water wash was 7 to 8 with universal indicator paper.

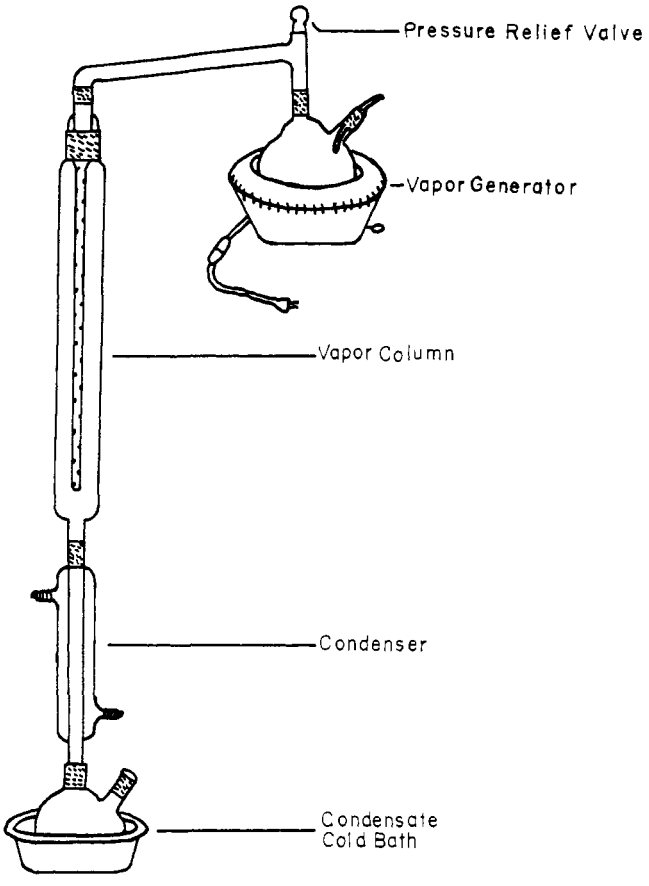


**Figure 1. Apparatus for vapor washing almond hull meal with aqueous and organic solvents**

## RESULTS AND DISCUSSION

Vigorous water washing of the plant material was performed to determine whether the pesticide contaminant was loosely distributed on the plant surfaces as an easily removed thin film. The data in Table I show the nature of the distribution of the residues on the hulls. After three vigorous washes with either hot or cold water, very little residue was removed from the plant material. This indicates that the contaminants were not loosely distributed on the plant surface as an easily removed deposit. No residues could be detected in the water washes, but 36% of the Kelthane was removed from the hulls by the cold water wash and 53% by the hot water wash. If the 4,4′-D(4,4′-dichlorobenzophenone) residues found on the hulls after treatment were converted to equivalent Kelthane and summed with the Kelthane found after treatment, 19% of the original Kelthane was removed by the cold water and 35% by the hot water.

If the total residue found after treatment was calculated as

**Table I. Vigorous Water Wash to Determine if Pesticide Residues on Almond Hulls Were Loose Surface Deposit[a]**

| Sample | Kelthane, P.P.B. | | 4,4′-D, P.P.B.[b] | |
|---|---|---|---|---|
| | Cold water[c] treatment | Hot water[d] treatment | Cold water treatment | Hot water treatment |
| Residue before treatment[e] | 10,200 | 10,200 | N.D.[f] | N.D. |
| Residue after treatment | 6,500 | 4,800 | 1300 | 1300 |
| Residue in combined water washes | N.D. | N.D. | N.D. | N.D. |
| Kelthane residue loss due to treatment, % | 36 | 53 | — | — |
| Total residue loss due to treatment calculated as Kelthane, % | 19 | 35 | — | — |
| Total residue recovered calculated as Kelthane | 81 | 65 | — | — |

[a] Washed three times for 15 minutes with vigorous agitation.
[b] 4,4′-D signifies 4,4′-dichlorobenzophenone.
[c] Cold water temperature 25° C.
[d] Hot water temperature 90° to 100° C.
[e] All residues calculated on a dry weight basis.
[f] N.D. signifies nondetectable.

**Table II. Effect of Dry and Wet Oven Heat on Kelthane Residue Removal from Almond Hulls[a,b]**

| Sample Treatment | Kelthane, P.P.B. | 4,4′-D, P.P.B.[c] |
|---|---|---|
| No water saturation | | |
| No oven heat | 10,200 | N.D.[d] |
| No water saturation | | |
| Dry oven heat | 3,500 | 2700 |
| Kelthane residue loss due to treatment, % | 66 | — |
| Total residue loss due to treatment calculated as Kelthane, % | 32 | — |
| Water saturated | | |
| Wet oven heat | 2,300 | 1400 |
| Kelthane residue loss due to treatment, % | 77 | — |
| Total residue loss due to treatment calculated as Kelthane, % | 59 | — |

[a] Oven heated 12 hours at 100° C.
[b] All residues calculated on a dry weight basis.
[c] 4,4′-D signifies 4,4′-dichlorobenzophenone.
[d] N.D. signifies nondetectable.

Kelthane, 81% of the original residue was recovered for the cold water wash and 65% for the hot water wash. The higher loss of residue with the hot water treatment may possibly be explained by the volatility of the pesticide with water vapors. Others (Acree *et al.*, 1963) have observed that DDT was lost from various media as a result of the DDT-water codistillation phenomenon.

The effect of dry- and wet-oven heating on Kelthane removal from the almond hull meal is shown in Table II. Dry heat removed approximately 66% of the Kelthane, but some 4,4′-D was found on the hulls which was derived from the Kelthane. If the 4,4′-D was calculated as Kelthane and added to the Kelthane found after treatment, 32% of the original Kelthane was removed. The water-saturated hulls after treatment had a 77% loss of Kelthane but again some 4,4′-D was derived from Kelthane. If the 4,4′-D residue was converted to Kelthane and added to the Kelthane residue found, 59% of the original Kelthane was removed by the oven heating in the presence of excess moisture. The presence of excess moisture in the samples was essential for the effective removal of the pesticide contaminant. After the first treatment with excess water, two similar succeeding treatments did not further reduce the residue levels in the sample.

The dependence of Kelthane losses on the presence of an excess of water vapor suggested that some practical form of "steam distillation" with water or even organic solvents might facilitate removal.

The removal of Kelthane residues from the almond hull meal by solvent vapor treatment is shown in Table III. Ben-

**Table III. Removal of Kelthane Residues from Almond Hulls by Solvent Vapor Washes[a]**

| Sample | Benzene | | Water | | 15% $NH_3$ in Water | |
|---|---|---|---|---|---|---|
| | Kelthane | 4,4′-D[b] | Kelthane | 4,4′-D | Kelthane | 4,4′-D |
| | P.P.B. | | | | | |
| Almond hulls | | | | | | |
| Before treatment | 10,200 | N.D.[c] | 10,200 | N.D. | 10,200 | N.D. |
| Vapor washed | 900 | 1200 | 2,000 | 900 | 4,400 | 4600 |
| Loss of Kelthane residue, % | 91 | — | 80 | — | 57 | — |
| Loss of total residue calculated as Kelthane, % | 75 | — | 68 | — | ±[d] | — |
| Residue recovered in four vapor condensates | 3,000 | 1700 | N.D. | 550 | N.D. | 190 |
| Total residue recovered | 4,800 | 2900 | 2,000 | 1450 | 4,400 | 4700 |
| Total residue recovered calculated as Kelthane | 8,810 | — | 4,000 | — | 11,010 | — |
| Recovery of original residue calculated as Kelthane, % | 86 | — | 39 | — | 108 | — |

[a] All residues calculated on a dry weight basis.
[b] 4,4′-D signifies 4,4′-dichlorobenzophenone.
[c] N.D. signifies nondetectable.
[d] ± signifies no significant loss of total residue due to the formation of 4,4′-D.

Table IV. Chemical Treatment of Kelthane Contaminated Almond Hulls for Residue Removal[a]

| Sample Treatment[b] | Before Treatment | | After Treatment | | Residue Removed as Kelthane, % | Total Residue Removed as Kelthane, % |
|---|---|---|---|---|---|---|
| | Kelthane | 4,4′-D[c] | Kelthane | 4,4′-D | | |
| | P.P.B. | | | | | |
| 100% water | 10,200 | N.D.[d] | 3800 | 1600 | 65 | 41 |
| 100% ethanol | 10,200 | N.D. | 300 | 100 | 97 | 96 |
| 2% sodium ethoxide and 98% water | 10,200 | N.D. | 1900 | 2700 | 81 | 45 |
| 2% sodium ethoxide and 98% ethanol | 10,200 | N.D. | N.D. | 900 | 100 | 88 |
| 2% sodium methoxide and 98% ethanol | 10,200 | N.D. | N.D. | 700 | 100 | 91 |
| 2% potassium hydroxide and 98% ethanol | 10,200 | N.D. | N.D. | 1000 | 100 | 87 |

[a] All residues calculated on a dry weight basis.
[b] Heated 15 minutes at 60° to 70° C. with agitation, cooled, centrifuged, washed with 150 ml. of water.
[c] 4,4′-D signifies 4,4′-dichlorobenzophenone.
[d] N.D. signifies nondetectable.

zene removed 91%, water removed 80%, and 15% ammonia in water removed 57% of the Kelthane residues during vapor treatment. Some loss of residue from the treated plant material could have occurred during air drying at room temperature; however, as shown in Table II, heating at 100° C. was very inefficient for contaminant removal. The total residue loss due to vapor treatment followed by air drying is important since the treated plant material must be dried to prevent spoilage. In all treated samples, a 4,4′-D residue was derived from the Kelthane present. When the 4,4′-D residues were converted to Kelthane and added to the Kelthane detected after treatment, benzene removed 75%, water removed 68%, but 15% ammonia in water did not show any significant loss of the original Kelthane on the hulls. If all residues found after treatment including those in the vapor wash condensates were totaled, 86% of the original Kelthane residues were recovered for the benzene vapor treatment, 39% for the water vapor, and 108% for the 15% ammonia in water vapor. Again the low recovery of Kelthane residues from the water vapor treatment was the result of the volatility and codistillation characteristics of the pesticide in the water vapors as previously shown for DDT (Archer and Crosby, 1968; Bowman *et al.*, 1959). The collection efficiency of the contaminant in a solvent is related to the vapor pressure, boiling point, and polarity of the solvent. Difficulties in collection efficiencies can occur with high boiling polar solvents. Some nondetectable degradation products could also have been produced.

The effect of a hot chemical alkaline wash on the removal of Kelthane from the almond hull meal is shown in Table IV, and the data represent the averages of duplicate results. When the treatment solutions consisted of 100% water, 65% of the Kelthane residue was removed; 100% ethanol, 97% was removed; 2% sodium ethoxide in water, 81% was removed; 2% sodium ethoxide, 2% sodium methoxide, and 2% potassium hydroxide in ethanol, 100% of the Kelthane was removed. In all cases, 4,4′-D residues were detected on the treated plant material. When the 4,4′-D residues were converted to Kelthane and added to the Kelthane residue detected after treatment, total residues removed from the plant material by the treatment were 41, 96, 45, 88, 91, and 87%, respectively, as discussed.

Table V. Effect of Alkaline Reflux on Removal of Kelthane Residues from Almond Hulls[a,b]

| Sample Treatment | Kelthane, P.P.B. | 4,4′-D, P.P.B.[c] |
|---|---|---|
| No treatment | 10,200 | N.D.[d] |
| 20% potassium hydroxide and 80% ethanol | N.D. | N.D. |
| Residue removal, % | 100 | 100 |
| 15% ammonia in water | N.D. | 4900 |
| Residue removal calculated as Kelthane, % | 100 | — |
| Residue removal total calculated as Kelthane, % | 47 | — |

[a] Refluxed 1 hour, alkali washed free with water to pH 7 to 8.
[b] All residues calculated on a dry weight basis.
[c] 4,4′-D signifies 4,4′-dichlorobenzophenone.
[d] N.D. signifies nondetectable.

Although sodium ethoxide could have been extensively hydrolyzed by the water because the acidity of water and alcohol is nearly the same ($C_2H_5ONa + H_2O \rightleftharpoons C_2H_5OH + NaOH$), it was not completely hydrolyzed since differences did exist between this sample and those containing alkaline ethanol. The alkaline aqueous solution partially degraded the Kelthane present but the water was inefficient in removing the contaminant. The alcohol solvent was more efficient in removing the degradation products as well as any Kelthane present. The 100% water and ethanol samples, while not alkaline, were included in the experiments as control comparisons. All alcohol solutions were effective in removing the contaminants; but since Kelthane is alkali degradable, the presence of alkali is desirable to ensure the possibility of degrading Kelthane to potentially less toxic products.

The effect of strong alkaline reflux on the removal of Kelthane from the almond hull meal is shown in Table V. When the hulls were refluxed for 1 hour in the presence of 20% potassium hydroxide in ethanol, no residues of Kelthane or 4,4′-D were detected in the treated hulls. When the hulls were refluxed in 15% ammonia in water for 1 hour, no Kel-

Table VI. Feed Ingredient Analyses for Almond Hull Meal[a]

| Uncoated | Kelthane Coated | Sample Treatment | Crude Protein, % | Crude Fat, % | Crude Fiber, % | Ash, % | Vitamin A Activity Units from Carotene/lb. |
|---|---|---|---|---|---|---|---|
| + | − | None | 5.4 | 2.5 | 13.4 | 7.3 | N.D.[b] |
| − | + | None | 5.5 | 2.7 | 14.6 | 7.1 | N.D. |
| − | + | Refluxed in benzene 1 1/2 hrs. | 5.5 | 1.4 | 13.2 | 6.7 | N.D. |
| + | − | Refluxed in benzene 1 1/2 hrs. | 5.5 | 1.4 | 13.6 | 8.4 | N.D. |
| − | + | Refluxed 1 hr. in 15% $NH_3$ in water | 10.2[c] | 2.2 | 30.6 | 5.4 | 3332 |
| − | + | Refluxed 1 hr. in 20% KOH in ethanol | 2.8 | 0.5 | 42.7 | 11.0 | 1666 |
| − | + | Agitated in 2% KOH and 98% ethanol[d] | 5.3 | 1.5 | 15.7 | 10.3 | — |
| − | + | Agitated in 2% sodium ethoxide and 98% ethanol[d] | 5.4 | 1.8 | 16.3 | 7.8 | — |
| − | + | Agitated in 2% sodium methoxide and 98% ethanol[d] | 4.7 | 1.3 | 15.5 | 8.8 | — |
| − | + | Agitated in 2% sodium ethoxide and 98% water[d] | 5.0 | 2.0 | 20.7 | 10.9 | — |
| − | + | Agitated in 100% water[d] | 5.5 | 1.7 | 16.2 | 6.0 | — |
| − | + | Agitated in 100% ethanol[d] | 5.3 | 2.6 | 17.5 | 6.4 | — |
| − | + | Benzene vapor treated | 5.7 | 1.9 | 13.0 | 7.5 | 1666 |
| − | + | Steam vapor treated | 6.4 | 1.5 | 23.1 | 6.8 | 1666 |
| − | + | Ammonia vapor treated | 17.1[c] | 2.3 | 26.7 | 3.7 | 1666 |
| − | + | Three 15-minute washes in cold water (25° C.) | 6.3 | 3.1 | 21.2 | 6.5 | — |
| − | + | Three 15-minute washes in hot water (90° to 100° C.) | 5.8 | 2.7 | 23.6 | 4.7 | — |
| − | + | Dry oven heat at 100° C. for 12 hrs. | 5.6 | 2.2 | 17.0 | 7.2 | — |
| − | + | Water saturated and heated in oven at 100° C. for 12 hrs. | 5.8 | 3.3 | 16.1 | 7.8 | — |

[a] Composited samples pre- and post-treatment.
[b] N.D. signifies nondetectable.
[c] High per cent of protein probably due to residual ammonia.
[d] Stirred for 15 minutes at 60° to 70° C.

thane could be detected in the treated hulls, but 4900 p.p.b. of 4,4′-D was detected. If the 4,4′-D was calculated as equivalent Kelthane, 41% of the original Kelthane was removed by ammonia reflux.

To determine whether detrimental effects occurred during sample decontamination treatments, standard feed ingredient analyses of per cent of crude protein, crude fat, crude fiber, and ash, and Vitamin A activity units produced from carotene content per pound were determined on the samples (AOAC, 1960). Table VI contains data for the feed ingredient analyses on the almond hull meal samples. No significant differences were observed between the samples except in the refluxed sample in 20% potassium hydroxide in ethanol. The protein value was low and the sample was badly hydrolyzed. The high protein values in the ammonia treated samples were probably due to residual ammonia in the samples. Any reported Vitamin A activity in the samples is probably doubtful but was expressed as apparent activity.

The above studies may provide basic information for future practical applications for residue decontamination procedures for animal feedstuff.

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