

were quite pronounced. The first dilution almost eliminated decomposition and produced a corrected CS₂ reading of 244 units, approximately the reading which would be expected from 25.3 mg. of CS₂ per liter when inhibition is complete (Figure 4). The first dilution of "Fire inhibited" 80:20, which contained 1% *n*-pentane, completely eliminated decomposition and produced a corrected CS₂ reading of 245 units. The joint inhibitory effects of CCl₄ and pentane apparently raised the lower limit of the critical CS₂ concentration range above that for CS₂ in 80:20 without pentane.

FUMIGANT RESIDUES

Determination of 1,2-Dibromo-Ethane in Air and as Residue in Fruits

Since low dosages of 1,2-dibromo-ethane are effective as a fumigant, an accurate, simple, and rapid method was needed for its determination in air or as residue. The method presented is based on conversion to bromide followed by coulometric titration. The conversion to bromide from mixtures with air and extraction and conversion from fruits was achieved by the Kennett method. The accuracy of the method was determined using standards of 1,2-dibromo-ethane-air mixtures in the range selected from 0.75 mg. to 30 mg. Recovery was 101 to 99.6% in the above range. Examples from practical application are given for residual 1,2-dibromo-ethane and bromide.

THE FUMIGANT 1,2-dibromo-ethane (ethylene dibromide) is especially toxic to certain dipterous insects in fruits. It is also used in grain fumigation, alone (3) or in mixture with other fumigants (7). It is effective in small amounts but desorbs slowly from fumigated foodstuffs because of comparatively low vapor pressure.

1,2-Dibromo-ethane can be analyzed by several methods using monoethanolamine and Volhard titration (8), amperometric titration (7), or iodometric titration (5, 6), and the residual fumigant, by extraction and iodometric titration (4). Since low dosages of the fumigant are effective, an accurate, simple, and rapid method for the determination of small amounts was needed. In previous work for methyl bromide analysis (2), the coulometric method was found to satisfy the above requirements, and was used for the determination of this compound in air and as residue from small samples, after extraction and conversion to bromide (4).

Apparatus

The apparatus used was the Fisher Coulomatic Titrator with modifications (2).

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Procedure

A special flask (2) was used for sampling of the 1,2-dibromo-ethane-air mixtures. The flask was evacuated to 0.2 mm. of Hg and the sample drawn in. Methanolic sodium hydroxide reagent was introduced for absorption and conversion, and the contents boiled under reflux for 15 minutes on a steam bath. This was sufficient time for complete conversion of one bromide from 1,2-dibromo-ethane (4) using 1 ml. of 0.5*N* sodium hydroxide. However, 1*N* was used to ensure complete reaction.

The flask was then cooled to about 25° C., and nitric acid was added to neutralize the excess sodium hydroxide. The resulting sodium bromide was determined by coulometric titration (2).

The residual 1,2-dibromo-ethane in apples was determined by extracting, absorbing, and converting to inorganic bromide by the Kennett method (4), and the resulting bromide determined by coulometric titration.

The total bromide residue was determined by treating the sample with alcoholic sodium hydroxide, followed by ashing as described by Neufeld (7). The procedure was modified to reduce the number of ignitions from five to

three by using a larger amount of sodium hydroxide for the first ignition and progressively less for the following two—for the first ignition 1 ml., for the second 0.5 ml., and 0.05 ml. of 10*N* NaOH for the third. The fourth filtrate was titrated by the coulometric method, and no halide was found.

Since chloride content was higher than bromide in the ash, the latter was determined by oxidation to bromate and subsequent iodometric titration based on the method of van der Meulen (6), as modified by Kolthoff and Yutzky (5).

Known amounts of 1,2 - dibromo-ethane were used as standards to determine the accuracy and range of the method for 100% conversion. Thin-wall capillaries of small diameter and 20 to 30 mm. in length were used, depending on the amount required. The capillaries were filled by immersing one end in 1,2-dibromo-ethane. The liquid was then moved to the center of the capillary by tilting. The relatively high vapor pressure and the very short time between weighing and introduction into the flask made the sealing of capillaries unnecessary.

The amount of 1,2-dibromo-ethane was found by weighing the capillary before and after filling. The capillary

Table I. 1,2-Dibromo-Ethane^a and Total Bromide Residue from Fumigated Apples

Time after Fumigation, Hours	1,2-Dibromo-Ethane Remaining, ^b Mg./Kg.
1	33.0
2	19.2
24	1.71
Days	Total Bromide ^c
1	1.23
8	0.53
10	0.47
Nonfumigated	0.40

^a Ethylene dibromide, 4 mg./liter, 2 hours fumigation at 15.6° C. ^b Av. of two determinations on Winesap apples. ^c Av. of two determinations on McIntosh apples.

from the weighing balance was transferred into a flask and broken by a glass rod introduced through the condenser. After vaporization of the liquid 1,2-dibromo-ethane, the reagent used for absorption and conversion was introduced through the condenser rinsing the glass rod as it was removed. The conversion and coulometric determination were the same as described above.

Results and Discussion

Standard samples of 1,2-dibromo-ethane were used to determine the per cent conversion. In this way, the accuracy of the method was found for the selected range of 0.75 mg. to 30 mg. of 1,2 - dibromo - ethane. In the above range, the recovery was 99.6 to 101%, and for the range 0.75 mg. to 19 mg. of 1,2-dibromo-ethane, the recovery was 99.9 to 101%.

For the determination of 1,2-dibromo-ethane and bromide residue, two varieties of apples were used, Winesap for 1,2-dibromo-ethane disappearance and McIntosh for bromide residue because Winesap variety was not available at the time of the experiment for residue determination.

Each sample of apple consisted of three segments from three different apples, with total weight of about 60 grams. After fumigation, apples were stored at 15.6° C. The rate of 1,2-dibromo-ethane disappearance after fumigation is shown in Table I. After 24 hours at 15.6° C., the remaining 1,2-dibromo-ethane was 1.71 mg. per kg. The increase of inorganic bromide residue due to fumigation after 10 days was very low (0.07 mg. in 1000 grams of apples). By extraction, no volatile halide was found

in nonfumigated apples, but 0.40 mg. of bromide residue was present.

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INSECTICIDE RESIDUES

Method for the Detection of Microgram Quantities of O,O-Dimethyl-S-(N-methyl-carbamoylmethyl) Phosphorodithioate (Dimethoate) in Milk

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A specific semiquantitative method for the estimation of dimethoate in milk has been developed. It is based on a paper chromatographic separation and is sensitive to 0.01 p.p.m. Dimethoate is extracted from milk by using a diethyl ether-hexane mixture. After removal of the ether, the hexane is extracted with acetonitrile. Residual pigments and lipides are removed by adsorption on a Florisil column. Dimethoate is further separated from interfering extractives by paper chromatography, and detected as a red spot after spraying the dried chromatogram with a solution of 2,6-dibromo-N-chloro-p-quinoneimine.

AEROSOL and spray formulations containing O,O-dimethyl-S-(N-methyl-carbamoylmethyl) phosphorodithioate (dimethoate) are effective in the control of biting flies on dairy cattle (1, 2). A method for detection of this insecticide in milk has been developed to determine whether these formulations could be used on lactating cows without subsequent contamination of the milk. Chilwell and

Beecham (3) have summarized the methods available for the determination of dimethoate residues. These have been investigated and found to lack the desired sensitivity of at least 0.01 p.p.m. A specific method with such a high sensitivity would be most useful in studies of residues in milk.

Dimethoate can be extracted from milk by using either chloroform (4) or a diethyl ether-hexane mixture (5). The latter is more convenient to use because fewer emulsions are encountered and

there is no need to evaporate to dryness before partitioning with acetonitrile. The ether is removed by vacuum distillation, and the insecticide is extracted from the hexane with acetonitrile (6). The extract is evaporated and the residue dissolved in chloroform. Following adsorption on a Florisil column (8), the column is developed, and the effluent is concentrated and spotted on Whatman No. 1 filter paper impregnated with Carbowax 4000 (10). The chromatogram is developed with a hexane-

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