

Table VII. Attractiveness Ratings of Aliphatic Methyl Ketones as Melon Fly Lures

Compound No.	R	Olfactometer Rating	Compound No.	Olfactometer Rating
105	$-\text{C}_3\text{H}_7$	1	115	0.4
106	$-\text{C}_2\text{H}_4\text{C}=\text{CH}_2$	3	116 ^a	6
107	$-\text{C}_2\text{H}_4\text{C}(\text{OC}_3\text{H}_7)$	1	117	4
108	$-\text{C}_2\text{H}_4\text{C}(\text{OCH}(\text{CH}_3)_2)$	2	118	0
109	$-\text{C}_2\text{H}_4\text{C}(\text{OCH}_2\text{CH}(\text{CH}_3)_2)$	2	119	0.1
110	$-\text{C}_2\text{H}_4\text{C}=\text{CHCH}_2\text{Cl}$	4		
111	$-\text{C}(\text{CH}_2\text{C}=\text{CCl})\text{C}(\text{OC}_2\text{H}_5)$	3		
112	$-\text{C}(\text{CH}_2\text{C}=\text{CCl})\text{C}(\text{OC}_2\text{H}_5)$	2		
113	$-\text{CH}_2$ (piperidine ring)	0		
114	$-\text{CH}_2$ (cyclohexane ring)	1		

^a A wick test was run only on compound 116. It attracted less than 5% as many flies as *p*-hydroxyphenyl-2-butanone (compound 2).

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Table VIII. Field Test Comparisons of Anisylacetone with the Most Attractive 4-Phenyl-2-butanones

Compound No.	R	Total Number of Melon Flies Caught in 14 Days in Steiner Plastic Traps
3	CH_3 —(anisylacetone)	700
4	$\text{CH}_3\text{C}(\text{O})$ —(cue-lure)	16,000
5	$\text{CH}_3\text{CH}_2\text{C}(\text{O})$ —	10,000
2	H	8,000
6	$\text{CH}_3\text{CH}_2\text{CH}_2\text{C}(\text{O})$ —	6,000
7	$(\text{CH}_3)_2\text{C}(\text{H})\text{C}(\text{O})$ —	3,000

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FUMIGANT MEASUREMENT

The Coulometric Determination of Methyl Bromide

METHYL BROMIDE has been used extensively for fumigation of plants and plant products in railroad cars, warehouses, under tarpaulins, and in the holds of cargo ships. Under these conditions, large samples are available

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for methyl bromide determination, so that the concentration of the fumigant can be measured in the field by hot wire detectors (2) or by drawing samples into flasks containing monoethanolamine (5) and completing the analysis by volumetric or amperometric titration (1). Micro amounts of methyl bromide, however, found in the equipment used

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for fumigation research in these laboratories (4) require especially sensitive methods. In investigations of the penetration of methyl bromide into jute bales, an analytical method was required which was sensitive at the microgram level, rapid, and relatively simple. A large number of samples having methyl bromide concentrations

Methyl bromide was determined from air mixtures by coulometric titration using 35-ml. samples. The vapor was absorbed and converted to inorganic bromide by a caustic-alcohol solution and the bromide determined coulometrically. Samples containing 17 to 350 μg . were readily analyzed in less than 1 hour. By a modification of the instrument, the limit of detection was lowered to 3 μg . per sample.

ranging from 1 to 100 mg. per liter and a volume not exceeding 30 to 35 ml. were to be analyzed.

A survey of the literature did not reveal a method which fulfilled all of the above requirements. Recent improvements in instrumentation for coulometric titration suggested that after suitable chemical conversion the resulting inorganic bromide could be titrated directly.

Experimental

Apparatus. The coulometric Titrimer (Fisher Scientific Co.) used consisted of an indicating unit which stops the titration at the preset end point potential and a generating unit which supplies a constant current of 5, 10, or 20 ma. and measures the time of current flow to 0.1 second. Potential measurements are made through the indicating electrode system of either a silver-calomel pair with a bridge of saturated potassium nitrate connecting the solution with the calomel, or a silver-glass pair. The latter was used for routine determinations because of its greater ease of handling. This equipment as supplied by the manufacturer was modified in two ways: The sensitivity of the instrument was increased by the addition of 1-ma. generating-current range λ . The modification was made by the Fisher Scientific Co. at the request of the authors.

When perchloric acid was used as a ground solution, the electrode connection above the solution corroded, giving poor electrical contact. Construction of electrodes with long leads permits connections to be made at some distances from the supporting electrolyte vapors.

A recorder (Brown) and pH meter (Beckman Model, No. 2) were used to obtain continuous potentiometric curves (Figure 1) from which the half-wave potential was determined.

For collecting samples of methyl bromide-air mixtures from fumigation chambers, 30-ml. flasks with standard taper joints (Figure 2) were used. These were supported by wooden holders which also secured the top, preventing the loss of methyl bromide when temperatures between 25° and 60° C. were used during the conversion step.

Reagents. Nitric acid, 0.5*N* in 80% ethanol, as supporting electrolyte.

Perchloric acid, 0.5*N* in 80% ethanol, as supporting electrolyte.

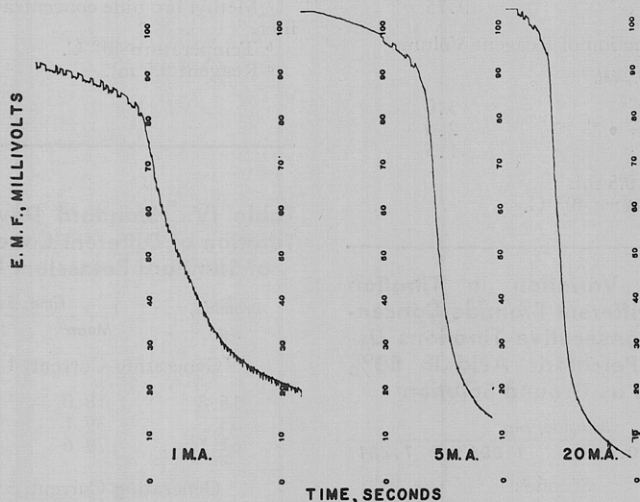


Figure 1. Potentiometric curves obtained with a recorder

Potassium hydroxide, 1*N* in methanol. Methyl bromide, liquid in cylinders or ampoules.

Procedure. Samples of the methyl bromide-air mixtures were drawn from the fumigation chamber (4) into the 30- to 35-ml. calibrated flasks (Figure 2). These flasks, which had been evacuated to a pressure of 0.1 mm. of Hg, were connected to the sampling ports on the chambers containing the material under test. The sampling lines were flushed to eliminate the air by using an evacuated smaller flask. The volume of air in the sampling tube is less than 2 cc. After sampling, the reagent for absorption and conversion was drawn into the flask (cooling if necessary to reduce the pressure) and the flasks were set aside to allow the reaction to occur.

Monoethanolamine is used by many workers as the reagent for absorption and conversion of methyl bromide to inorganic bromide, but in this work it was found to interfere with end point detection during coulometric titration, and consequently could not be used. Sodium or potassium hydroxide in methanol or ethanol was then investigated and found to be satisfactory for this purpose. By using 0.5 ml. of 1*N* potassium hydroxide in methanol at 24° C., 7 hours were needed for complete conversion. At 60° C., however, only 45 minutes were required.

Before titrating the sample, the electrodes and the electrolyte were con-

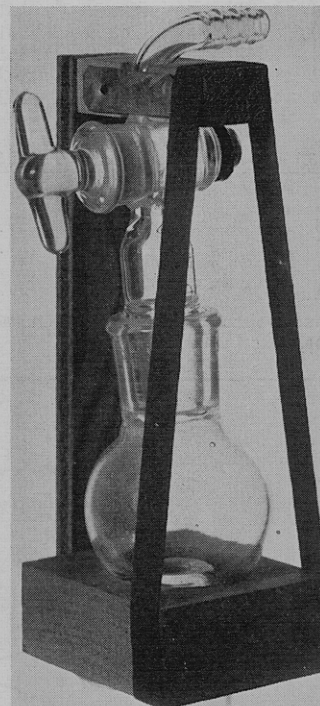


Figure 2. Sampling flask with holder

ditioned and the impurities in 100 ml. of 0.5*N* perchloric acid in 80% ethanol as supporting electrolyte were removed by titration of a standard bromide sample.

The excess potassium hydroxide in the unknown sample was then neutralized with 1*N* nitric acid and transferred

Table I. Conversion Time as a Function of Temperature and Reagent Volume

Temp., ° C.	100% Conversion, Hours
As a Function of Temperature ^a	
24	7.0
30	6.0
40	3.0
50	1.25
60	0.75
As a Function of Reagent Volume ^b	
Reagent Vol., ml.	
0.5	3.0
0.75	2.0
1	1.5

^a Reagent 0.5 ml.
^b Temperature 40° C.

Table III. Variation in Titration Time for Different Bromide Concentrations, Consecutive Titrations Using 0.5N Perchloric Acid in 80% Ethanol as Ground Solution^a

Bromide, Mg.			
0.336	0.672	1.008	1.431
Seconds			
85.3	170.4	249.0	358.3
83.9	168.0	247.7	361.6
85.3	170.5	248.2	355.6
85.2	170.0	251.0	355.6
83.4	168.8	251.0	359.7
83.6	170.3	251.4	361.8
85.0	168.8	248.9	361.1
83.4	170.1	250.0	361.3
84.2	169.2	249.8	362.4
84.9	168.3	247.8	362.2
Bromide, Mg.			
0.00336	0.00672	0.0134	0.0336
Seconds			
3.8	4.9	13.2	39.3
3.2	4.0	14.3	39.2
2.4	5.8	11.5	41.0
2.4	5.0	13.4	39.4

^a First 10 titrations used 5 ma. generating current, next 4 used 1 ma.

Table II. Optimum Potassium Hydroxide Concentration in Methanol, for Methyl Bromide^a Conversion^b

Potassium Hydroxide ^c Concn., N	100% Conversion, Hours
1	3.0
1.5	2.0
2	1.5

^a Methyl bromide concentration 40 mg./liter.
^b Temperature 40° C.
^c Reagent 0.5 ml.

Table IV. Standard Deviation for Titration of Different Concentrations of Standard Potassium Bromide

Bromide, µg.	Time, Seconds	
	Mean ^a	Std. dev.
Generating Current, 1 Ma.		
16.8	18.0	1.70
33.5	39.1	0.86
67.1	79.6	0.72
Generating Current, 5 Ma.		
67.1	15.9	0.34
168	41.6	0.33
355	84.0	0.80

^a Ten determinations at each concentration.

Table V. Recoveries of Methyl Bromide

Methyl Bromide in Ampoules, Mg.	Amount Found, Mg.	Recovery, %
902.95	875.1	97.0
30.157	30.10	99.6
21.268	21.20	99.7

to the titration beaker, using the conditioned supporting electrolyte to rinse the flask, and titrated coulometrically with the half-wave potential as an end point.

Concentrated perchloric acid is a fire and explosion hazard in the presence of some organic substances (3), but at a concentration of only 0.5N as used here no difficulties were encountered. Care should be taken, however, to make certain all reagents and the distilled water used are very pure and the resulting solution should be clear and stored in a brown bottle with a tightly fitting cap.

To determine the per cent recovery, ampoules containing a known amount of methyl bromide were prepared as follows: Weighed glass ampoules were placed in a desiccator containing a drying agent and dry ice, and covered with a glass plate. Methyl bromide was introduced through a small-bore polyethylene tube which passed through a hole in the glass plate and into the ampoules. These were then sealed and reweighed. This filling method prevented condensation of moisture on the cold ampoules.

Results and Discussion

With potassium hydroxide in methanol as the conversion agent, the time required to reach 100% conversion of a known amount of methyl bromide at different temperatures was measured and reported (Table I). From these data, the temperature necessary to effect complete conversion can be determined. Thus, if the samples may be conveniently left overnight, no heating is required, while for shorter periods the flasks must be heated to the appropriate temperature.

The results of the determination of the effect of volume and concentration of conversion reagent are shown in Tables I and II. Complete conversion was obtained in 1.5 hours at 40° C. with 0.5 ml. of 2N methanolic potassium hydroxide or with 1 ml. of 1N methanolic potassium hydroxide. When a large number of samples were to be determined in the same supporting electrolyte, it was essential that the reagent volume be kept as low as possible to avoid the effect of dilution, so that the electrodes would not have to be reconditioned too often. If a volume of 0.5 ml. of 1N potassium hydroxide in methanol was used, the time required for complete conversion was determined by temperature.

From a combination of temperature and volume of reagent, the total time required for the analysis of one sample, including sampling, was 15 minutes when the conversion temperature was 60° C., and 1 ml. of 2N methanolic potassium hydroxide was employed.

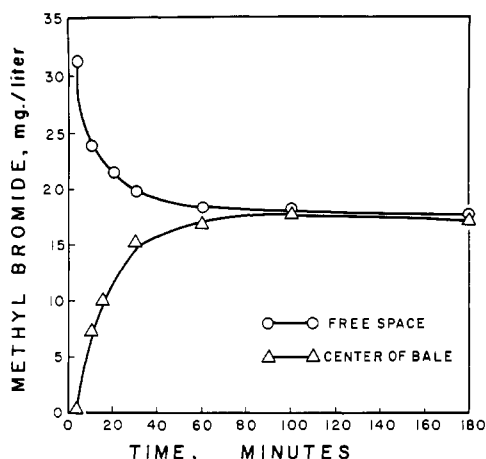


Figure 3. Change in concentration of methyl bromide as a function of time at different points in a fumigation chamber

The number of consecutive titrations possible with the same supporting electrolyte depends upon the rate at which the electrodes became contaminated.

Table III indicates the amount of variation obtained from consecutive titrations of standard potassium bromide solution using 0.5*N* perchloric acid in 80% ethanol as supporting electrolyte. With a ground solution of 0.5*N* nitric acid in 60% ethanol, the electrodes became contaminated more quickly, but this more convenient supporting electrolyte may be used if only a few titrations are to be carried out.

Different concentrations of standard potassium bromide were titrated to determine the standard deviation for the 1- and 5-ma. generating current ranges (Table IV). Concentrations of bromide below those given in Table IV may be

determined by using the 1-ma. generating range, but the deviation increases until a sensitivity limit of about 3 μg . is reached. Recoveries of methyl bromide (Table V) range from 97 to 99.7%, depending upon the amount taken.

Figure 3 illustrates the change in concentration of methyl bromide as a function of time at various points in a fumigation chamber. The chambers were packed with jute bales and sampling ports were arranged so that methyl bromide-air mixtures could be drawn from the center of the bales and the free space around them.

Acknowledgment

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HERBICIDE RESIDUES

Separation and Colorimetric Determination of Monuron and Diuron Residues

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Diuron residues are determined by minor modifications of a colorimetric method for determining monuron residues. Monuron and diuron residues are determined simultaneously in the presence of each other by an extension of the liquid chromatographic technique. The method is sensitive to 2 μg . of either compound and will recover both compounds quantitatively in the presence of a wide variety of plant tissue and soil. If only one of the two compounds is present, the procedure will identify it.

WEEED KILLERS based on 3-*p*-chlorophenyl-1,1-dimethylurea (monuron and 3-(3,4-dichlorophenyl)-1,1-dimethylurea (diuron) are useful on both agricultural and nonagricultural sites for control of a wide range of annual and perennial weed species. When applied to the soil at low rates, they selectively control germinating annual weeds in certain crops. They are used at higher rates where residual control of all vegetation is desired.

The two chemicals may be used alternately for selective weed control in an increasing number of crops. Thus, a sensitive residue method is needed to determine which chemical is present or to determine each compound if both are present in the same plant tissue.

A method for the determination of microgram quantities of monuron in a wide variety of plant tissues (2) has been modified for the determination of diuron residues. It involves the quantitative hydrolysis of the urea herbicide, under reflux conditions in a strongly alkaline

medium, to the corresponding aromatic amine with simultaneous partitioning of the amine into an organic solvent. The amine is then extracted into dilute acid and determined colorimetrically after diazotization and coupling reactions.

Many plant tissues contain small amounts of naturally occurring materials, such as tryptophan, which will also respond to this procedure. This interference can be eliminated by chromatographically separating the azo dye derived from *o*-aminoacetophenone (hydrolysis product of tryptophan) from that formed from *p*-chloroaniline (7) or 3,4-dichloroaniline.

The chromatographic technique has now been extended to separate the azo dye derived from *p*-chloroaniline from that derived from 3,4-dichloroaniline. This paper describes the latter technique and the modified colorimetric procedure which makes possible essentially simultaneous determination of monuron and diuron. Recovery data are presented for various plant tissues

to which known quantities of both urea herbicides were added (Table I).

This method is complementary to one discussed by Kirkland (3).

Reagents and Apparatus

p-Chloroaniline, recrystallized from 70% aqueous ethanol.

3,4-Dichloroaniline, recrystallized from 70% aqueous ethanol.

Sodium hydroxide solution, 20% aqueous, prepared from reagent grade chemical.

Hydrochloric acid, 1*N* solution.

Dow Corning Antifoam A, emulsion.

n-Hexane, washed twice with $\frac{1}{10}$ its volume of 2*N* hydrochloric acid.

Sodium nitrite, 2% aqueous solution, prepared fresh daily.

Sulfamic acid, 10% aqueous solution, prepared fresh daily.

N-(1-Naphthyl)ethylenediamine dihydrochloride, Fisher Scientific Co. (N-21), 2% aqueous solution, prepared fresh daily.

Hydrochloric-acetic acid mixture, equal volumes of 1*N* hydrochloric acid and glacial acetic acid.