

FUMIGANT ANALYSIS

Determination of Ethylene Dibromide and Ethylene Chlorobromide in Air

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Ethylene dibromide or ethylene chlorobromide is absorbed in ethyl alcohol and decomposed with sodium hydroxide, and the liberated halogen is estimated by the Volhard thiocyanate method.

IN FUMIGATING VARIOUS FRUITS for the destruction of the larva and eggs of the fruit fly, rapid and simple methods for determining organic halogen compounds in air are required. The most convenient published method for ethylene dibromide and ethylene chlorobromide is that of Sinclair and Crandall (2, 3), in which monoethanolamine is used for removing all the halogen from these compounds. A sample of air is drawn into an evacuated 1-liter bulb containing 3 ml. of monoethanolamine, and the bulb is heated in an oven for 30 minutes at 90° C. in the determination of ethylene dibromide and 60 minutes at 100° C. in the determination of ethylene chlorobromide. After cooling, the contents are rinsed into a beaker and titrated by the Volhard thiocyanate method.

The method here described is simpler and more rapid, and avoids heating the sampling bulb in an oven. It is based upon the fact that in alcoholic sodium hydroxide ethylene dibromide and ethylene chlorobromide readily lose one atom of bromine, forming vinyl bromide and vinyl chloride, respectively. Further dehalogenation occurs very slowly in alcoholic solution. The author has found that exactly one equivalent of inorganic bromide is removed from both compounds by boiling in 0.067*N* ethanolic sodium hydroxide for 10 to 60 minutes. Both the dibromide and the chlorobromide can be readily absorbed from air by shaking with ethyl alcohol. Hence they can be determined by absorbing in ethyl alcohol, boiling with sodium hydroxide, and titrating by the Volhard method.

Procedure

A 2-liter spherical bulb fitted with a one-way stopcock of 8-mm. bore is

evacuated and the sample of air drawn in. The stopcock is opened while 50 ml. of ethyl alcohol are introduced from a pipet. The bulb is shaken for about 15 seconds and the contents are transferred to a 250-ml. conical flask with standard ground-glass joint. The bulb is rinsed with a further 20 ml. of ethyl alcohol which are added to the conical flask.

After 5 ml. of 1*N* sodium hydroxide are added to the conical flask, the contents are boiled under reflux for 15 min-

utes. The flask is then cooled to a temperature not higher than 25° C. (4), and 5 ml. of 5*N* nitric acid is added, followed by a measured volume (10 to 20 ml.) of 0.01*N* silver nitrate. After 1 ml. of ferric indicator is added, the excess silver is titrated with 0.01*N* potassium thiocyanate. This titer is subtracted from a blank titer obtained with all the ingredients except the halogen compound. The ferric indicator is prepared by dissolving 20 grams of ferric sulfate

Table I. Recovery of Ethylene Dibromide

| Added, Mg. | Recovered, Mg. | Recovery, % | Added, Mg. | Recovered, Mg. | Recovery, % |
|------------|----------------|-------------|------------|----------------|-------------|
| 1.44 | 1.49 | 103.5 | 11.35 | 11.31 | 99.7 |
| 1.76 | 1.71 | 97.2 | 12.90 | 12.70 | 98.5 |
| 2.39 | 2.35 | 98.3 | 13.44 | 13.24 | 98.5 |
| 2.75 | 2.77 | 100.7 | 13.49 | 13.45 | 99.7 |
| 2.78 | 2.77 | 99.6 | 14.21 | 14.09 | 99.2 |
| 2.85 | 2.88 | 101.1 | 15.81 | 15.80 | 99.9 |
| 3.43 | 3.42 | 99.7 | 16.20 | 15.80 | 97.5 |
| 3.72 | 3.74 | 100.5 | 16.94 | 16.65 | 98.3 |
| 4.98 | 4.91 | 98.6 | 19.05 | 19.00 | 99.7 |
| 6.11 | 6.19 | 101.3 | 19.97 | 19.86 | 99.5 |
| 9.86 | 9.82 | 99.6 | 22.04 | 21.99 | 99.8 |
| 10.05 | 10.04 | 99.9 | 29.62 | 29.04 | 98.0 |

Table II. Recovery of Ethylene Chlorobromide

| Added, Mg. | Recovered, Mg. | Recovery, % | Added, Mg. | Recovered, Mg. | Recovery, % |
|------------|----------------|-------------|------------|----------------|-------------|
| 1.67 | 1.63 | 97.6 | 8.63 | 8.64 | 100.1 |
| 1.75 | 1.79 | 102.3 | 9.33 | 9.29 | 99.6 |
| 1.91 | 1.96 | 102.6 | 10.37 | 10.26 | 98.9 |
| 2.88 | 2.77 | 96.2 | 11.60 | 11.41 | 98.4 |
| 3.30 | 3.26 | 98.8 | 12.48 | 12.22 | 97.9 |
| 4.97 | 4.81 | 96.8 | 13.30 | 13.37 | 100.5 |
| 5.21 | 5.22 | 100.2 | 13.31 | 13.20 | 99.2 |
| 6.11 | 6.11 | 100.0 | 13.56 | 13.53 | 99.8 |
| 6.33 | 6.19 | 97.8 | 13.77 | 13.85 | 100.6 |
| 7.10 | 7.17 | 101.0 | 20.21 | 20.20 | 100.0 |
| 8.15 | 8.15 | 100.0 | 22.01 | 21.84 | 99.2 |
| 8.30 | 8.31 | 100.1 | 24.43 | 23.80 | 97.4 |

and 10 ml. of 5*N* nitric acid in hot water and diluting to 100 ml.

The bromide equivalent of the potassium thiocyanate solution is obtained by standardizing with 5 ml. of 0.0100*N* potassium bromide. Boiling under reflux has been found unnecessary in the blank and standardization. Then

$$\text{Mg. of ethylene dibromide} = 1.879 \times 5 \times \frac{T_B - T_D}{T_B - T_S}$$

and

$$\text{Mg. of ethylene chlorobromide} = 1.434 \times 5 \times \frac{T_B - T_D}{T_B - T_S}$$

where T_B , T_D , and T_S are the respective titers obtained in the blank, determination, and standardization.

Recovery Tests

Purified ethylene dibromide, boiling at 131.1–131.2° C., was obtained by fractional distillation through a spinning band column. Ethylene chlorobromide, boiling at 106–108° C., was prepared by the method of Calingaert *et al.* (7) and separated by distillation through a packed column of 10 theoretical plates.

The weighed sample was sealed in a thin-walled capillary tube which was introduced into the sampling bulb and broken by shaking. The bulb was warmed in the vicinity of the broken tube to ensure complete vaporization and subsequently cooled before introduction of the ethyl alcohol.

The mean per cent recovery was 99.5 ± 1.3 for ethylene dibromide and 99.4 ± 1.6 for ethylene chlorobromide. The results are given in Tables I and II.

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COTTONSEED CONTENTS VARIATION

Influence of Variety and Environment on Oil Content of Cottonseed Kernels

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The oil contents of moisture-free cottonseed kernels from the seed of 8 commercial varieties of cotton grown at 13 locations during 3 years ranged from 26.8 to 43.4%. Analysis of variance indicated that both variety and environment have a highly significant influence on the oil content. Correlations on a basis of years in locations between oil content of the kernels and temperature for six periods of boll and seed development showed that the highest correlation was obtained for mean maximum temperature during the maturation period. Similarly, the highest correlation between oil content and rainfall for rain-grown cottons was obtained for the same period. Rainfall had a significant influence on oil content even when temperature was held constant, and maximum temperature significantly influenced oil content when rainfall was held constant. Maximum temperature and rainfall appeared to be of nearly equal importance in influencing oil content under the conditions of the investigation. A considerable part of the environmental variation in oil content is due to other factors. There was no statistically significant difference in the response of any of the varieties to variations in temperature and rainfall.

AS COTTONSEED OIL is next to lint in economic importance among the products of the cotton plant, information on the factors influencing the oil content of the kernels is of both interest and value to oil mill operators, geneticists, agronomists, and others associated with the cottonseed industry. The present communication reports findings regarding the influence of variety of cotton and environment during seed development

on the oil content of cottonseed kernels, which are a portion of the results of a symmetrically planned investigation of the factors influencing the composition of cottonseed.

Though numerous reports pertaining to the oil content of cottonseed have appeared in the literature, only a few are cited here. Most of these have dealt with analyses of commercial samples from a limited geographic area (2, 8, 9)

or investigations at various experiment stations, where most of the samples of seed were from cottons grown in individual states (4, 6, 7, 15). Although such investigations allow certain trends to be observed, such as the increase in oil content when cotton receives an unusual amount of rain during the growing period, the data are difficult to interpret satisfactorily, because they are limited in geographic scope or