The Dow Chemical Company
Midland, Michigan 48667

ANALYTICAL METHOD

September 25, 1985

Method No. TC-AM-85-21
Q.A. Number 2438

Free Acid in Allyl Chloride and Similar Halogenated Organic Compounds

1. Scope

This method is suitable for the titrimetric determination of free acid, as HCl, in allyl chloride. Data is also presented that shows this method is comparable to ASTM D 2989-74, "Acidity-Alkalinity of Halogenated Organic Solvents and Their Admixtures" and is capable of determining free acid, as HCl, over a concentration range from less than 5 ppm to greater than several hundred ppm. The method is applicable for 2,3-dichloropropene and similar halogenated organic compounds that contain no acid scavengers that readily react with the basic titrant.

2. Safety Precautions

2.1 Allyl chloride is a colorless liquid with a pungent odor and is capable of causing burns to the eyes and skin. It is also readily absorbed through the skin in toxic amounts. The vapors are irritating to the eyes and nose as well as being highly toxic. Handle with care. Prevent skin and eye contact. Minimize contact with vapors by handling samples in a well-ventilated hood.

2.2 Other halogenated organic compounds of similar structure will have toxic properties similar to allyl chloride and should be handled with like caution.

2.3 The isopropyl alcohol-water mixture is toxic. The 0.05N KOH in methanol is toxic and corrosive. Wear side shield safety glasses when using the previously mentioned reagents. If contact occurs wash the affected area with copious amounts of water. If eye contact occurs wash with water for a minimum of fifteen minutes and secure medical attention.

2.4 Each analyst should be acquainted with potential hazards of the reagents, products, and solvents before commencing laboratory work. SOURCES OF INFORMATION INCLUDE: MATERIAL SAFETY DATA SHEETS, LITERATURE, AND OTHER RELATED DATA. Safety information on non-Dow products should be requested from the supplier. Disposal of reagents, reactants, and solvents must be in compliance with local, state, and federal laws and regulations.

3. Principle

The sample is solubilized in a 90% isopropyl alcohol/10% water mixture (v/v) that has been previously neutralized to the basic side of the phenol red end point with 0.05N KOH in methanol. The sample is added to the 90% isopropyl alcohol mixture, which again is titrated to the phenol red endpoint with 0.05N KOH in methanol to determine free acid in the sample.

4. Apparatus

Ordinary laboratory glassware available from most laboratory supply companies.

5. Reagents

5.1 Isopropyl alcohol, ACS reagent grade (See 5.7).

5.2 90% (v/v) Isopropyl alcohol solution. Add 100 mL of distilled water with a graduated cylinder to 700 mL of isopropyl alcohol in a 1000 mL volumetric flask. Make the addition slowly with stirring. Dilute to the mark with isopropyl alcohol.

5.3 Methanol, ACS reagent grade (See 5.7).

5.4 Potassium hydroxide pellets, ACS reagent grade (See 5.7).

5.5 Potassium hydroxide, methanolic, 0.05N. Add 2.81 grams of ACS reagent grade potassium hydroxide pellets to 500 mL of methanol in a 1000 mL volumetric flask. Dilute to the mark with methanol. Standardize with 0.1N hydrochloric acid.

5.6 Phenol red indicator solution. Add 0.10 g of phenolsulfonphthalein (phenol red) (See 5.7) to a 100 mL volumetric flask and dilute to the mark with ethanol.

5.7 Available from most chemical supply companies.

6. Procedure

6.1 Add 50 mL of 90% (v/v) isopropyl alcohol mixture, using a graduated cylinder, to a 250 mL Erlenmeyer flask.

6.2 Add several drops of phenol red indicating solution and place the Erlenmeyer flask containing the isopropyl alcohol mixture on a magnetic stirrer.

6.3 Titrate with 0.05N methanolic potassium hydroxide from a 25 mL buret to the pink phenol red endpoint.

6.4 Add 50 mL of sample, using a graduated cylinder, to the 250 mL Erlenmeyer flask.

6.5 Titrate with 0.05N methanolic potassium hydroxide to the same pink phenol red endpoint obtained in step 6.2.

6.6 Record the volume of 0.05N methanolic potassium hydroxide used in titration step 6.5.

7. Calculation

$$\% \text{ Acid as HCl} = \frac{V_b \times N_b \times E_w \times 100}{S_v \times S_g}$$

where: V_b = mL 0.05N methanolic KOH (See 6.5)

N_b = normality of methanolic potassium hydroxide (0.05N)

E_w = meq weight of hydrochloric acid (0.0365)

S_v = sample volume (mL)

S_g = density of sample (g/mL) .932

8. Precision

Data obtained by this method indicate a relative standard deviation of 2.69% at the 40 wt ppm level. The values obtained may be expected to vary from the average by no more than ±5.38% relative at the 95% confidence level.

The data listed compares this method to the ASTM D 2989-74 method. Results indicate that the two methods are comparable. An allyl chloride sample was analyzed for its acid content by both methods. Then the original sample was spiked with hydrochloric acid to give an acid increase of 30 ppm.

METHOD	DOW	ASTM D 2989-74
Original ppm acid, as HCl	11	12
Spiked with 30 ppm HCl		
Total Acid Content	41	42
First Day Results, ppm HCl		
Test #1	42	43
Test #2	42	42
Test #3	42	41
Test #4	42	42
Test #5	39	39
Second Day Results, ppm HCl		
Test #1	41	39
Test #2	40	39
Test #3	40	40
Test #4	41	40
Test #5	40	40
Mean	40.9	40.5
Relative Standard Deviation	2.69%	3.53%
Relative Precision at the 95% Confidence Level	±5.38%	±7.06%
Average Percent Recovery of HCl Spike	99.7%	95%

A sample of TELONE* II soil fumigant was also analyzed for its acid content by both methods. The original sample was once again spiked with hydrochloric acid to give an acid increase of 30 ppm.

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September 25, 1985 4 of 4 pages Method No. TC-AM-85-21

Method	DOW	ASTM D 2989-74
Original ppm acid, as HCl	10	10
Spiked with 30 ppm HCl, Total Acid Content	40	40
First Day Results, ppm HCl		
Test #1	27	23
Test #2	30	21
Test #3	27	23
Test #4	30	22
Test #5	30	22
Second Day Results, ppm HCl		
Test #1	30	31
Test #2	30	29
Test #3	30	31
Test #4	30	26
Test #5	30	24
Mean	29.4	25.2
Relative Standard Deviation	4.30%	15.1%
Relative Precision at the 95% Confidence Level	±8.6%	±30.2%
Average Percent Recovery of HCl Spike	64.7%	50.7%

The analysis results of the acid content in TELONE II soil fumigant show that both methods are once again comparable. However, recovery of the spiked acid was low in both methods. The acid scavenger added to TELONE II soil fumigant is probably largely responsible for the poor recovery.

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This method was updated to the current format on July 10, 2019.