

## Analytical Method for 2,2-DPA (Agricultural Products)

### 1. Analytes

2,2-DPA (Dalapon, 2,2-Dichloropropionic acid)  
Dalapon-sodium

### 2. Instrument

Gas chromatograph-electron capture detector (GC-ECD)  
Gas chromatograph-mass spectrometer (GC-MS)

### 3. Reagents

Use the reagents listed in Section 3 of the General Rules, except the following.

Reference standard of 2,2-DPA: Contains not less than 99% of 2,2-DPA.

### 4. Procedure

#### 1) Extraction and Clean-up

Weigh 10.0 g of sample, add 70 mL of 2% sodium borate solution saturated with sodium chloride to the sample, shake for 30 min, and filter by suction through glass fiber filter paper. Add 30 mL of the solution to the residue on the filter paper, treat as described above, and combine the filtrates. Add 100 mL of ether to the filtrates, shake vigorously for 5 min, let stand, and discard the ether layer. Add 6 mol/L hydrochloric acid to the aqueous layer, adjust pH to 1.0, and extract with shaking twice using 50 mL each of ether. Combine the resulting extracts, and then extract with shaking twice using 30 mL each of 1% sodium hydrogen carbonate solution. Combine the extracts, add 6 mol/L hydrochloric acid to adjust the pH to 1.0 while stirring, and then extract twice using 40 mL each of ether. Combine the extracts, filter using phase-separator filter paper, concentrate under reduced pressure to about 2 mL at below 30°C, and remove the solvent in a nitrogen gas stream.

#### 2) Esterification

Add 1 mL of butanol and 3 drops of sulfuric acid to the residue, install a reflux condenser, and heat to reflux for 30 min on a boiling water bath. After cooling, wash the inner wall of the condenser with a small amount of water, remove the condenser, and extract the reaction solution twice using 10 mL each of *n*-hexane. Filter the extracts using phase-separator filter paper, add *n*-hexane to make exactly 25 mL, and use this solution as the test solution.

### 5. Calibration curve

Prepare a 20 mg/L 2,2-DPA standard solution (acetone), and take a 1 mL aliquot of the solution, remove the solvent in a nitrogen gas stream at room temperature, and perform the same operation as in 4. 2). Dilute the solution with *n*-hexane, prepare 0.02–1 mg/L 2,2-DPA standard solutions of several concentrations, inject 2 µL each of the solution into GC, and make a calibration curve by

peak-height or peak-area methods.

## 6. Quantification

Inject 2 µL of the test solution into GC, and calculate the concentration of 2,2-DPA from the calibration curve made in 5.

## 7. Confirmation

Confirm using GC-MS

## 8. Measurement conditions

GC

Detector: ECD

Column: 50% phenyl-methyl silicone, 0.25 mm inside diameter, 25 m in length, and 0.1 µm in film thickness

Column temperature: 40°C

Inlet temperature: 250°C

Detector temperature: 250–300°C

Carrier gas: Helium

Expected retention time: 5 min

## 9. Limit of quantification

0.05 mg/kg

## 10 Explanatory note

### 1) Outline of analytical method

The method consists of extraction of 2,2-DPA from the sample using 2% sodium borate solution saturated with sodium chloride, washing the extract with ether, adjusting to acidic (pH 1), extraction with ether, then extraction of 2,2-DPA from the ether extract using 1% sodium hydrogen carbonate solution, adjusting the extract to acidic (pH 1), extraction again using ether, removing the solvent, adding butanol and sulfuric acid, heating to reflux for 30 min, extraction of the esterified form of 2,2-DPA from the reaction solution using *n*-hexane, measurement using GC-ECD, and confirmation using GC-MS.

### 2) Notes

- i) Since 2,2-DPA is lost in the concentration operation, set the bath temperature low and remove the solvent in a nitrogen gas stream. A keeper may be used.
- ii) Esterified 2,2-DPA products are highly volatile and have large losses due to concentration. Therefore, use the solution as a test solution by fixing the volume as it is without concentrating it.
- iii) LC-MS may also be applied. In this case, omit the esterification step and dissolve the final residue obtained in 1)-Extraction in 8 mL of 0.1% acetic acid.

LC-MS measurement conditions

Column: Octadecylsilanized silica gel (5 µm in particle diameter), 2.0 mm inside diameter, and 150 mm in length

Mobile phase: 1% formic acid/methanol solution (4:1, v/v), flow rate: 0.2 mL/min

Column temperature: 40°C

Ionization mode: ESI (+)

Major monitoring ion ( $m/z$ ): 141

Expected retention time: 7 min

## 11. Reference

- 1) Cotterill, E.G., Determination of residues of dalapon in soil by gas chromatography of the 1-butyl ester. *J. Chromatogr.*, 106, 409–411, 1975
- 2) Zweig, G. & Sherma, J. ed., Analytical Method for Pesticides, Plant Growth Regulators, and Food Additives. vol.VI p.621–624, Academic Press (1972)

## 12. Type

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