

1-Methylcyclopropene Impurities

GC method

CIPAC Collaborative Trial
according to
CIPAC Information Sheet Number 282

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April 2009

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OUTLINE OF METHOD

1-chloro-2-methylpropene (1-CMP) and 3-chloro-2-methylpropene (3-CMP) are impurities in the active ingredient 1-methylcyclopropene (1-MCP). 1-MCP is a gas at room temperature and is stabilized for commercial use by encapsulation in SmartFresh™ 3.3% Technology. 1-MCP, 1-CMP and 3-CMP are released for analysis by dissolving a formulation sample in water in an airtight container. The container headspace is sampled and analyzed by capillary gas chromatography with flame ionization detection and external standard calibration. 1-CMP and 3-CMP content is reported as percent relative to 1-MCP concentration which is determined by a separate method [1].

REAGENTS

Water purified to remove traces of heavy metals

1-chloro-2-methylpropene (1-CMP) purity 98.0% minimum

3-chloro-2-methylpropene (3-CMP) purity 98.0% minimum

1-CMP and 3-CMP Stock solution. Measure the 1-CMP (10 μ L) into a 10 μ L syringe, inject the 1-CMP into a 1 liter glass bottle equipped with a VICI gas tight valve. Repeat this procedure to introduce 3-CMP into the same bottle. Shake the bottle vigorously on a mechanical shaker for at least 60 minutes. Calculate the concentration (mg/mL) of the 1-CMP ($c_{s\ 1-CMP}$) and 3-CMP ($c_{s\ 3-CMP}$) (Note 1).

1-CMP and 3-CMP Calibration solution. Measure the stock solution (200 μ L) into a 250 μ L gas tight syringe, inject the contents of the syringe into a 250 mL glass bottle equipped with a VICI gas tight valve. Shake the bottle vigorously on a mechanical shaker for at least 60 minutes. Calculate the concentration (mg/mL) of 1-CMP ($c_{c\ 1-CMP}$) and 3-CMP ($c_{c\ 3-CMP}$) based on volumetric dilution of the stock solution. Prepare duplicate calibration solutions (solutions C_A and C_B) (Note 1).

APPARATUS

Gas chromatograph equipped with split/splitless inlet and a flame ionization detector

Capillary column DB-624: 30 m x 0.25 mm (i.d.) and 1.4 μ m film thickness (Agilent, Inc.)

Electronic integrator or data system

Analytical balance with 0.1 mg sensitivity

Mechanical shaker rotary or reciprocating type

Mininert gas tight valves with 24 mm cap size for 250 mL bottles; with 1/8 inch NPT thread for 1 L bottles (Preceision Sampling , Inc.)

Gas tight glass syringes 0.25 mL and 0.50 mL, equipped with ~5 cm side port needles (Note 2)

Liquid syringe 10 μ L

Glass or plastic syringe to measure 3 mL, equipped with a 22 to 25 gauge needle

Glass bottles 250 mL (nominal) Boston Round, 24 mm threaded neck; 1 liter (nominal) glass Media/solution bottle with polypropylene plug seal cap and pouring ring (Note 3)

PROCEDURE

(a) *Gas chromatographic conditions* (typical):

Column DB-624 30 m length x 0.25 mm i.d. x 1.4 μ m film thickness (Note 4)

Injection system

Injector mode split injection

Injector insert 4 mm i.d., straight through glass (no glass wool) (Note 5)

Injection volume 0.50 mL

Split flow 20 mL/min

Detector flame ionization

Temperatures

Injection port 75 °C

Detector 185 °C

Oven program temp 1 40 °C, hold 0 min, ramp rate 25 °C/min

temp 2 165 °C, hold 0 min

Gas flow rates

Carrier:

Helium 2 mL/min; approximately 40 cm/sec (run at constant flow)

Detector:

Air 400 mL/min

Hydrogen 45 mL/min

Nitrogen (make up) carrier flow + make up flow = 30 mL/min

Retention times

1-CMP 2.6 min to 2.8 min

3-CMP 2.7 min to 2.9 min

(b) *System equilibration.* Inject 0.5 mL aliquots of the calibration solution C_A until the response factors obtained for two consecutive injections differ by less than 5%. Then inject 0.5 mL aliquots of calibration solution C_B . The response factor for solution C_B should not deviate by more than 5% from that of solution C_A , otherwise prepare new calibration solutions (Note 6). If the peak retention times are not within the listed time windows, adjust the carrier flow rate accordingly.

(c) *Linearity check.* Check the linearity of the method by injecting 0.50 mL aliquots of solutions with 1-CMP and 3-CMP concentrations of 0.5, 1 and 2 times that of the calibration solution before conducting analyses.

(d) *Sample preparation.* Prepare sample solutions in duplicate (solutions S_A and S_B). Weigh (to the nearest 0.1 mg) 90 mg to 110 mg (*w* mg) of SmartFresh™ 3.3% Technology into a 250 mL glass bottle. Cap the bottle with a gas tight valve immediately. Inject water (3 mL) through the valve into the bottle. Close the valve. Place the bottle on a mechanical shaker and mix vigorously for a minimum of 60 minutes (Note 7).

(e) *Determination.* Inject in duplicate 0.50 mL aliquots from the headspace of each sample solution bracketing them by injections of the calibration solutions as follows: calibration solution C_A, sample solution S_A, sample solution S_A, calibration solution C_B, sample solution S_B, sample solution S_B, calibration solution C_A, and so on. Measure the relevant peak areas.

(e) *Calculations.*

Calculate the concentration (mg/mL) of 1-CMP and 3-CMP in the stock solution.

$$c_{s\ 1-CMP} = \frac{d_{1-CMP} \times V_{1-CMP} \times P_{1-CMP}}{V_{sb}} \quad c_{s\ 3-CMP} = \frac{d_{3-CMP} \times V_{3-CMP} \times P_{3-CMP}}{V_{sb}}$$

where:

$c_{s\ 1-CMP}$ = concentration of the 1-CMP stock solution (mg/mL)

$c_{s\ 3-CMP}$ = concentration of the 3-CMP stock solution (mg/mL)

d_{1-CMP} = density 1-CMP (mg/mL)

d_{3-CMP} = density of 3-CMP (mg/mL)

P_{1-CMP} = purity of 1-CMP expressed as a decimal fraction

P_{3-CMP} = purity of 3-CMP expressed as a decimal fraction

V_{1-CMP} = volume of the 1-CMP standard material (mL)

V_{3-CMP} = volume of the 3-CMP standard material (mL)

V_{sb} = volume of the stock solution preparation bottle (mL)

Calculate the concentration of 1-CMP and 3-CMP in the calibration solution.

$$c_{c\ 1-CMP} = \frac{c_{s\ 1-CMP} \times V_s}{V_{cb}} \quad c_{c\ 3-CMP} = \frac{c_{s\ 3-CMP} \times V_s}{V_{cb}}$$

where:

$c_{c\ 1-CMP}$ = concentration of the 1-CMP in the calibration solution (mg/mL)

$c_{c\ 3-CMP}$ = concentration of the 3-CMP in the calibration solution (mg/mL)

V_s = volume of the stock solution aliquot diluted (mL)

V_{cb} = volume of the calibration standard preparation bottle (mL)

Calculate the response factors for 1-CMP and 3-CMP.

$$f_{i1\text{-CMP}} = \frac{c_{c1\text{-CMP}}}{H_{s1\text{-CMP}}} \quad f_{i3\text{-CMP}} = \frac{c_{c3\text{-CMP}}}{H_{s3\text{-CMP}}}$$

where:

$f_{i1\text{-CMP}}$ = individual 1-CMP response factor

$f_{i3\text{-CMP}}$ = individual 3-CMP response factor

$c_{c1\text{-CMP}}$ = concentration of the 1-CMP in the calibration solution (mg/mL)

$c_{c3\text{-CMP}}$ = concentration of the 3-CMP in the calibration solution (mg/mL)

$H_{s1\text{-CMP}}$ = peak area of 1-CMP in the calibration solution

$H_{s3\text{-CMP}}$ = peak area of 3-CMP in the calibration solution

Calculate the mean value of each pair of response factors bracketing the two injections of a sample and use this value for calculating the 1-CMP and 3-CMP contents of the bracketed sample injections.

$$1\text{-CMP content} = \frac{f_{1\text{-CMP}} \times H_{w1\text{-CMP}} \times HS \times 1000}{w} \text{ g/kg}$$

$$3\text{-CMP content} = \frac{f_{3\text{-CMP}} \times H_{w3\text{-CMP}} \times HS \times 1000}{w} \text{ g/kg}$$

where:

$f_{1\text{-CMP}}$ = mean 1-CMP response factor

$f_{3\text{-CMP}}$ = mean 3-CMP response factor

$H_{w1\text{-CMP}}$ = peak area of 1-CMP in the sample preparation

$H_{w3\text{-CMP}}$ = peak area of 3-CMP in the sample preparation

HS = volume of the headspace in the sample preparation bottle (mL)
(= bottle volume – water volume)

w = mass of sample taken (mg)

1-CMP and 3-CMP specifications are based on the percent relative concentration versus 1-MCP. 1-MCP content must be determined by a separate method [1]

$$\% \text{ Relative content 1-CMP} = \frac{1\text{-CMP content g/kg}}{1\text{-MCP content g/kg}} \times 100$$

$$\% \text{ Relative content 3-CMP} = \frac{3\text{-CMP content g/kg}}{1\text{-MCP content g/kg}} \times 100$$

REFERENCES

- [1] 767. 1-Methylcyclopropene, GC Method

- Note 1* Segregate the syringe used to prepare the CMP calibration solution; do not use for injection of sample preparations.
- Note 2* Side port needles are required; standard taper needles will partially plug and cause irreproducible injection volumes.
- Note 3* Accurately measure the total volume of each type of bottle using water i.e. vendor volume specifications are approximate and usually do not include the volume in the neck of the bottle. The plastic cap of the media bottle must be taped to make a hole with threads to accommodate a gas tight valve with a male 1/8 inch NPT thread.
- Note 4* DB-624 is manufactured by J&W and distributed by Agilent. It is a proprietary phase; the performance of similar phases from other suppliers is uncertain. Condition the column before use at 225 °C following the manufactures instructions.
- Note 5* An insert with an internal volume of approximately 1 mL is necessary to completely contain the large sample volume injected.
- Note 6* Peak areas will vary with injection speed. During standard and sample injection depress the syringe plunger with a constant and consistent speed. Fast injection speeds can be reproduced most easily.
- Note 7* Insure that all of the sample powder drops onto the bottom of the bottle and that none adheres to the iside wall. The sample must be in contact with the water during mixing. Wrist action shakers are not recommended. Static charge on the glass bottle can compromise weighing accuracy and precision, if static is a problem weigh the sample onto a piece of weighing paper and transfer into the bottle.

Representative Chromatogram SmartFresh™ 3.3 % Technology

