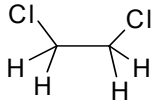
Determination of 1,2-dichloroethane in aqueous solutions of chlormequat chloride

Chemical structure



Empirical Formula $C_2H_4Cl_2$
RMM 98.97

Sampling

Take at least 250 ml.

Identity test

Use the GC method below. The retention times of 1,2-dichloroethane in the sample solution and from the added calibration solution should be identical.

Outline of method

Chlormequat chloride technical concentrate or formulation is dissolved in water/dimethylacetamide and analyzed by headspace gas chromatography, using a fused silica capillary coated with polyethylene glycol. Alternatively, the chromatography can be carried out using a polydimethylsiloxane-coated capillary column. Detection is by flame ionization detector and quantification is by standard addition. Calibration by standard addition can provide excellent accuracy in headspace analysis but the quantities of sample, water and dimethylacetamide must be consistent between the sample and calibration determinations.

Reagents

Water, drinking water.

N,N-dimethyl acetamide (DMAA). purity 99.99% (w/w).

1,2-dichloroethane, at least 99.8 area % (GC) purity. Prepare a stock standard solution of 1,2-dichloroethane by weighing approximately 1 g (to the nearest 0.1 mg) into a 20 ml volumetric flask, making to volume with DMAA and mixing thoroughly. The stock standard contains 500 µg 1,2-dichloroethane per 10 µl. Aliquots should be diluted to form working standard solutions, required for the preparation of calibration solutions, to give the appropriate numbers of µg per 10 µl. If tightly stoppered, the stock and working standards may be stored in a refrigerator for up to one month, before replacing them. Stored solutions must be brought to room temperature and mixed before use.

Calibration solutions. Calibration solutions are prepared from aliquots of the sample to be analyzed and are therefore intended to calibrate only that sample. Prepare two calibration solutions, each containing different concentrations of 1,2-dichloroethane. Weigh approximately 1 g (to the nearest 0.1 mg) of the TK or SL sample into a headspace vial, add 1 ml water and exactly 10 µl of an appropriate working standard of 1,2-dichloroethane in DMAA (see preceding and following paragraphs). Immediately seal the vial with a gas tight septum.

The quantity of 1,2-dichloroethane added to the sample to form a calibration solution should be adjusted according to the concentration of chlormequat chloride in the

sample and the consequent concentration of 1,2-dichloroethane represented by the specification limit. A reasonable indication of impurity concentration may be obtained when the two levels of addition are within approximately 0.2 to 5 times the level originally present in the sample and, for checking compliance, it should be assumed that the sample contains impurity at the limit. For example, if an SL contains chlormequat chloride at 500 g/kg, the limit for 1,2-dichloroethane corresponds to 50 µg in a 1 g sample. The two calibration standards are therefore prepared by: (i) by diluting 1ml stock standard to 50 ml with DMAA (= 10 µg/10 µl); and (ii) by diluting 5ml stock standard to 10 ml with DMAA (= 250 µg/10 µl). If better accuracy is required, three calibration standards should be prepared by addition of 1,2-dichloroethane at approximately 0.5, 1 and 2 times the measured level in the sample.

Apparatus

Capillary gas chromatograph, with flame ionisation detector (FID), automatic headspace sample dispenser system, data system for signal capture and integration.

Chromatography column, fused silica. Either 50 m x 0.32 mm with 1.2 µm film thickness of polyethylene glycol (method A), or 30 m x 0.25 mm with 1.0 µm film thickness of polydimethylsiloxane (method B).

Headspace vials, 22 ml volume.

Procedure

(a) Preparation of sample solution. Weigh (to the nearest 0.1 mg) in duplicate 1 g sample solution into a headspace vial, immediately add 1ml water and 10 µl *N,N*-dimethyl acetamide (DMAA) and seal the vial with a gas tight septum.

(b) Chromatographic conditions (typical)
Method A (polyethylene glycol stationary phase)

Headspace parameters:	
Thermal equilibrium time:	45 min
Temperature during equilibrium:	70°C
Temperature of transfer line:	150°C
Pressure build-up time:	60 s
Headspace pressure:	0.9 bar
Injection time:	6 s
Dwell time:	12 s
GC conditions:	
Detector temperature:	250°C
Column oven:	50°C, 5 min isothermal 50°C to 200°C at 5°C/min 200°C, 15 min isothermal
Carrier gas:	He
Column head pressure:	0.9 bar
Split:	7ml/min
Combustion gases for FID:	hydrogen and synthetic air adjusted to the equipment manufacturer's specification.

Method B (polydimethylsiloxane stationary phase)

Headspace parameters:	
Thermal equilibrium time:	45 min
Temperature during equilibrium:	70°C
Temperature of transfer line:	150°C
Pressure build-up time:	60 s
Headspace pressure:	0.7 bar
Injection time:	12 s
Dwell time:	12 s
GC conditions:	
Detector temperature:	250°C
Column oven:	40°C, 5 min isothermal 40°C to 230°C , 5°C/min 230°C, 10 min isothermal
Carrier gas:	He
Column head pressure:	0.7 bar
Split:	11 ml/min
Combustion gases for FID:	hydrogen and synthetic air adjusted to the equipment manufacturer's specification.

(c) Repeatability and linearity checks. Inject headspace from each calibration solution at least twice and determine the mean peak area to mass ratios. The single values should differ by less than 0.5% from the mean value for each calibration solution, otherwise repeat the calibration.

If an acceptable response is obtained from the low level calibration and the mean peak area to mass ratio obtained from the highest level calibration solution is less than 99% that of the lowest level calibration solution, the quantity injected has probably exceeded the linear range of the detector. The weighings and/or dilutions must be adjusted to ensure that concentrations are within the linear range.

(d) Determination. Inject headspace from each sample solution in duplicate and "bracket" duplicate sample headspace injections by duplicate injections of the headspace from calibration solutions as follows: calibration solution 1 (two injections), sample solution 1 (two injections), calibration solution 2 (two injections).

If required, a series of four injections, representing two samples, may be made between the bracketing calibration injections but, in this case, the two samples must be of a similar product. Where dissimilar products are to be analyzed, they must be calibrated separately and injected as separate sequences.

Measure areas of the peaks obtained from 1,2-dichloroethane.

(e) Calculations

Calculate the average headspace response factor (f^{hs}) for each calibration solution as follows.

$$f^{hs} = \frac{B - A}{C}$$

where: A = average peak area of 1,2-dichloroethane in the sample without addition of dichloromethane;
B = average peak area of 1,2-dichloroethane in the calibration solution with addition of dichloromethane;
C = mass of 1,2-dichloroethane added to 1 g of sample (µg).

Calculate the overall average headspace response factor ($f^{hs)}$ obtained from the two (or three) standards used to calibrate the bracketed sample injections and use this value to calculate the 1,2-dichloroethane content of the sample(s) as follows.

$$\text{1,2-dichloroethane content (µg/g)} = \frac{A}{f^{hs}}$$

where: A = average peak area of 1,2-dichloroethane in the sample without addition of dichloromethane;
f^{hs} = overall average headspace response factor for 1,2-dichloroethane.

Calculate the concentration of 1,2-dichloroethane relative to chlormequat chloride content as follows.

$$\text{1,2-dichloroethane (g/kg of chlormequat chloride)} = \frac{\text{1,2-dichloroethane content (µg/g)}}{\text{chlormequat content (g/kg)}}$$

Repeatability, r (from manufacturer's data)

Method A, r = 0.058 mg/kg at 2.77 mg/kg 1,2-dichloroethane;
Method B, r = 0.059 mg/kg at 3.68 mg/kg 1,2-dichlorethane.

Limit of quantification (1, 2-dichloroethane in 1 g sample)

Methods A and B, 0.2 µg/g.