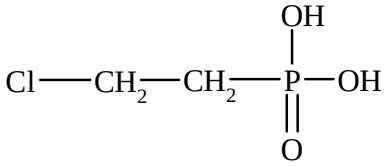
ETHEPHON
373



ISO common name	Ethephon
Chemical name	2-Chloroethyl phosphonic acid (IUPAC); (2-chloroethyl) phosphonic acid (CA; *16672-87-0*)
Empirical formula	$C_2H_6ClO_3P$
RMM	144.5
m.p.	74 - 75 °C
pK_1	2.5
pK_2	7.2
Solubility	In water: more than 1000 g/l; soluble in ethanol and propane-1,2-diol; sparingly soluble in aromatic solvents
Description	White to slightly coloured crystals
Stability	Stable at pH less than 3.5; at high pH values decomposition and release of ethene
Formulations	Soluble concentrates

ETHEPHON TECHNICAL CONCENTRATES
*373/TK/M/-

1 Sampling. Take at least 100 g.

2 Identity tests

2.1 GLC. Carry out a gas chromatographic identity test comparing the sample with a reference material. The retention time of ethephon for the sample should not deviate from that for the reference solution by more than 2.5 % obtained under the same conditions.

Chromatographic conditions (typical):

Column	glass, 180 mm x 0.6 mm (i.d.) packed with 10 %SP 2100 on Supelcoport 100 to 120 mesh, or a megabore column, 30 m x 0.53 mm (i.d.) coated wit a 1.5 µm DB-5 film
Detector	flame ionisation
Column temperature	packed column: initial: 100 °C; programmed at 8 °C/min megabore column: initial: 70 °C; hold for 2 min; to 220°C at 6 °C/min; final hold: 10 min
Detector temperature	250 °C
Injection temperature	250 °C
Carrier gas	helium at 10 and 40 ml/min for the packed column and megabore column respectively
Injection volume	2 µl for the packed column, 1 µl for the megabore column
Reference solution	Dissolve ethephon standard (50 mg) in acetone (5 ml) in a centrifuge tube (Mark the volume). Carefully add diazomethane solution (3 ml, RE 35.1), cap, shake, and place in a water bath for 40 min. Cool down, carefully vent, and evaporate the excess diazomethane and ether with a gentle stream of nitrogen to 5 ml (original volume).
Sample solution	Weigh a sample containing 50 mg ethephon and carry out the methylation as for the reference solution.
Retention time	ethephon: about 7 min

* CIPAC method 1997. Prepared by the French Committee (CFAPA). Chairman: B Declercq. Based on a method supplied by CFPI-Agro, Ffrance.

2.2 TLC. Carry out a thin-layer chromatographic test by comparing the sample with the standard using the following conditions:

TLC plate	10 × 10 cm, coated with cellulose without fluorescence indicator, 0,10 mm (e.g. Merck Darmstadt, FRG, Art No 5632)
Mobile phase	Solvent A: add to a water- acetic acid mixture, 48 + 1.6 (v/v), trichloroacetic (5 g), adjust to pH 4 with ammonia solution 30 % (about 2.5 ml) Solvent B: methanol–dioxan–propan-2-ol, 60 + 30 + 26. Mix solvent A and B in the ratio 1 : 2.
Reference solution	Dissolve ethephon standard (50 mg) in water (5 ml) in a volumetric flask (10 ml). Make up to volume with water and mix well.
Sample solution	Weigh enough sample to contain 50 mg ethephon into a volumetric flask (10 ml). Dissolve in water (about 5 ml), make up to volume with water, and mix well.
Loading	1 µl
Travelling distance	8 cm
Visualisation reagent	Dissolve ammonium molybdate (1 g), hydrochloric acid (37 %) (2 ml) and perchloric acid (70 %) (5 ml) in water (100 ml).
Visualisation	Dry the plate at 70-80°C. Spray the visualisation reagent, dry at 70-80 °C for 15 min, and put under UV light (254 nm) to obtain a blue spot.
R_F value	ethephon: about 0.8

Compare the R_F value of the sample with that of the ethephon reference solution. The major spot in the sample chromatogram should have the same R_F value as the one in the chromatogram of the ethephon reference solution.

2.3 NMR. Use a solution in deuterium oxide containing sodium 3-trimethylsilyl propionate as internal standard. The ^1H spectrum of ethephon displays the following characteristics:

a split triplet at δ 2.34 ppm J(H–H) = 7.5 Hz and J(H–C–H) = 18 Hz, corresponding to P-CH_2

a split triplet at δ 3.79 ppm J(H–H) = 7.5 Hz and J(H–C–C–H) = 14 Hz, corresponding to CH_2Cl.

OUTLINE OF METHOD The sample is neutralised to pH 9.3 to form the ethephon disodium salt, which is decomposed to ethene and sodium dihydrogen phosphate on heating. Sodium dihydrogen phosphate is determined by acidimetry.

REACTION EQUATIONS

(i) Formation of ethephon disodium salt

$$Cl\text{-}CH_2\text{-}CH_2\text{-}P(O)(OH)_2 + 2NaOH \rightarrow Cl\text{-}CH_2\text{-}CH_2\text{-}P(O)(ONa)_2 + 2H_2O$$

(ii) Thermal decomposition of ethephon disodium salt

$$Cl\text{-}CH_2\text{-}CH_2\text{-}P(O)(ONa)_2 + H_2O \rightarrow CH_2{=}CH_2 + NaCl + (HO)_2P(O)(ONa)$$

(iii) Neutralisation of sodium dihydrogen phosphate

$$(HO)_2P(O)(ONa) + NaOH \rightarrow (HO)\text{-}P(O)(ONa)_2 + H_2O$$

REAGENTS

Sodium hydroxide c(NaOH) = 0.1 mol/l, standardised solution, carbonate free; RE 25.1. It is essential that the solution is carbonate free, because the presence of carbonate will produce erroneous results. Check before each analysis by adding 1 ml $BaCl_2$ solution (0.5 mol/l) to a test tube containing the sodium hydroxide solution (9 ml). Stopper and mix. No turbidity or flocculation should occur within 10 min.

Water distilled

Buffer solutions pH 7 and pH 9

APPARATUS

pH meter or *automatic potentiograph* fitted with a 20 ml burette and suitable for carrying out titrations to a given pH. Calibrate the pH meter or the potentiograph and their electrodes at 5 °C at pH 7 and pH 9.

Glass/calomel electrode couple or *combined glass electrode*

Heated magnetic stirrer equipped with a system to keep the temperature at 90 ± 5 °C

Cooling bath e.g. water-ice bath equipped with a magnetic stirrer

Thermometer

Beaker 250 ml, tall size

PROCEDURE

(a) Preparation of sample. Weigh (to the nearest 0.1 mg) into a tall size beaker (250 ml) enough sample to contain about 250 mg (w g) of ethephon. Dilute with distilled water (150 ml) and add a magnetic stirring bar. Put the beaker in a water-ice cooling bath and cool to 5 °C while stirring.

(b) Determination. Bring the pH at 9.3 by adding sodium hydroxide solution (c = 0.1 mol/l). Carry out this operation within 10 min while keeping the contents of the beaker at 5 °C. It is, therefore, necessary to add the first 25 ml of the sodium hydroxide solution with a pipette or by pre-trickling programmed with the potentiograph, before starting the automatic titration to pH 9.3.
Remove the electrodes from the solution and rinse them with distilled water. Place the beaker on a heated magnetic stirrer and heat at 90 ± 5 °C for 30 min while stirring continuously in order to achieve the thermal degradation of the ethephon disodium salt. Cool to 5 °C by adding water and ice.
While keeping the content of the beaker at 5 °C titrate the solution again to the preset pH value of 9.3 using the pH meter or the potentiograph. Record the volume needed.

(c) Calculation

$$\text{Ethephon content} = \frac{144.5 \times N \times t}{w} \text{ 1g/kg}$$

where:
N = normality of the sodium hydroxide solution (mol/l)
t = volume required for the titration of the sodium dihydrogen phosphate formed after the degradation of ethephon (ml)
w = mass of sample taken (g)

Repeatability r = 9 g/kg at 714 g/l active ingredient content
Reproducibility R = 12 g/kg at 714 g/l active ingredient content

ETHEPHON SOLUBLE CONCENTRATES

[*] **373**/SL/M/-

1 Sampling. Take at least 1 l.

2 Identity tests. As for **373**/TC/M/2.

3 Ethephon. As for **373**/TC/M/3.

Repeatability r	=	4 g/kg at 557 g/l active ingredient content
	=	10 g/kg at 700 g/l active ingredient content
Reproducibility R	=	12 g/kg at 557 g/l active ingredient content
	=	18 g/kg at 700 g/l active ingredient content

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