

Determination of PP796 (emetic) in paraquat dichloride technical concentrates (TK)

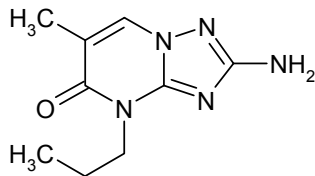
Information

IUPAC name: 2-amino-4,5-dihydro-6-methyl-4-propyl-s-triazolo-[1,5-a]pyrimidin-5-one

CA name: 2-amino-6-methyl-4-propyl-(1,2,4)triazolo[1,5-a]pyrimidine-5-(4H)-one (9CI)

CAS Registry No: [27277-00-5]

Molecular structure:



Molecular formula: C₉H₁₃N₅O

Relative molecular mass: 207.2

Scope of method

This capillary gas chromatography (GC) method is for the determination of PP796 emetic, as % w/w, in paraquat dichloride technical concentrates.

Summary of method

A portion of the TK (aqueous solution) is made basic with NaOH and partitioned into dichloromethane, containing octadecane as an internal standard. The extract is analyzed by capillary GC-FID, measuring peak areas.

Safety information

Paraquat dichloride salts are toxic, particularly by inhalation of particulates or ingestion, and, because there is no antidote or treatment for the progressive symptoms which can develop, exposure must be avoided. Paraquat dichloride solutions are irritant if splashed in the eyes and harmful if allowed to contact the skin or open cuts. Wear eye protection and protective gloves when handling paraquat dichloride analytical standards, the TK or formulated materials. Solid paraquat materials must only be handled in a fume cupboard.

If in any doubt about the nature and hazards of the chemicals used in this method, consult the Material Safety Data Sheet (MSDS) or an appropriate safety manual such as:

“Hazards in the Chemical Laboratory”, Luxon, Ed., Royal Society of Chemistry, 5th Edn, 1992, London, ISBN 0-85186-220-2.

“The Sigma-Aldrich Library of Chemical Safety Data”, Lenga, Ed., 2nd Edn, 1999, Milwaukee, WI, ISBN 0-941633-16-0.

Chemicals

Dichloromethane, HPLC grade.

Octadecane, laboratory reagent grade. Weigh approximately 50 mg into a 100 ml volumetric flask and add about 80 ml dichloromethane. Shake to dissolve, make to the mark with dichloromethane and mix well, to produce an internal standard solution of approximately 0.5 mg/ml.

Sodium hydroxide solution, 1M.

PP796 emetic, analytical standard grade (obtainable from Syngenta). Weigh accurately about 10 mg into two separate 25 ml volumetric flasks and add 5.0 ml of internal standard solution. Shake to dissolve, make to the mark with dichloromethane and mix well, to produce two solutions (Solutions A₁ and A₂) containing PP796 at 0.4 mg/ml.

Laboratory detergent, non-ionic, e.g. Decon Neutracon.

Dimethyldichlorosilane (DMCS), laboratory reagent grade.

Hexane, laboratory reagent grade.

Methanol, water-free.

Acetone, laboratory reagent grade

Apparatus

Gas chromatograph, equipped with split/splitless injection system and flame ionisation detection, operated in split mode, with automatic injector and electronic data capture and handling system. All gases should be purified through molecular sieves. The carrier gas should be further purified through an oxygen trap.

Injection Liner, straight silica liner (4 mm ID) packed with silanized fused silica wool plug (e.g. Restek cat No. 20790). Contaminated split injection liners should be treated as follows.

Immerse in detergent (10% solution) for about 1 hour, then wash in purified water and dry in an oven at 120°C. Take the liner, while still warm, and immerse in a 5% solution of dimethylchlorosilane in hexane for 5 min. Remove the liner and immerse in fresh dry methanol for 1 hour. Wash the liner with acetone and dry thoroughly. The fused silica liner is ready for packing with silanized fused silica wool.

Column, 25 m x 0.25 mm ID fused silica capillary column with 0.25 µm film of BPX-5 (ex SGE) or Chrompack CP-Sil 8CB, or equivalent. Maximum programmed operating temperature 350°C.

Typical operating conditions

Oven temperature programme: initial temperature 50°C for 2 min.
programme 1, rate 20°C min⁻¹ to 100°C, held for 2 min.
programme 2, rate 20°C min⁻¹ to 280°C, held for 10 min.
total run time, 25.5 min.

Injector temperature: 300°C

Detector temperature: 325°C

Gas flow rates: hydrogen carrier gas, 50 cm/sec (e.g. 10 psi head pressure)
nitrogen make-up gas, 30 ml/min.
hydrogen flame gas, 30 ml/min.
air, 450 ml/min.
Split flow, 50 ml/min.

Injection volume: 1 µl (by autosampler)

Typical retention times: octadecane, 12-14 min; PP796, 13-15 min.

Sample extraction

Weigh accurately, in duplicate, about 2 g of paraquat dichloride technical concentrate into two 100 ml separating funnels. In each case, add 0.5 ml 1M sodium hydroxide solution and swirl the separating funnel taking care not to foul the stopper. Add 2.0 ml octadecane internal standard solution and swirl the separating funnel, taking care not to foul the stopper. Carefully release the gas pressure, shake well and again carefully release the gas pressure. Leave standing until two clear layers are obtained.

Collect the lower (dichloromethane) layer into a 14 ml glass screw-capped (trident) vial and retain the aqueous layer in the separating funnel. Add 2 ml dichloromethane to the separating funnel and shake well. Leave standing until two clear layers are obtained. Combine the lower (dichloromethane) layer with the initial extract in the glass vial and retain the aqueous layer in the separating funnel. Repeat the extraction with a further 2 ml dichloromethane, combining all three extracts in the glass vial and add 5 ml dichloromethane to the glass vial. Identify the duplicate extracts as Solutions B₁ and B₂.

Determination

Make replicate injections of Solution A₁ and/or A₂ at about 2 min. intervals, to equilibrate the GC system. Wait 19 min. then inject Solution A₁ or A₂ again and check that the retention times of the octadecane (12-14 min.) and PP796 (13-15 min.) are within the expected time windows. If not, the column head pressure may be adjusted ± 1 psi, or column temperature programme 1 final temperature may be adjusted ± 10°C. If column performance deteriorates substantially during use, check the condition of the split injection liner and replace if necessary.

Perform replicate injections of calibration and sample solutions in an appropriate sequence, such as: A₁, B₁, A₁, B₁, A₁, B₁, A₂, B₂, A₂, B₂, A₂, B₂. Measure peak areas.

Confirm the identity of PP796 in Solution B by GC-MS or, alternatively, by spiking an aliquot of Solution B with an aliquot of Solution A and check for exact co-elution.

Calculations

Calculate the relative response factor, RF, for each injection of the standard Solution A as follows.

$$RF = \frac{A \times VI \times 100}{P \times I \times WR}$$

Where: WR = weight of PP796 standard (mg);
VI = volume of internal standard added in ml;
A = peak area of PP796 peak;
I = peak area of octadecane peak;
P = % w/w purity of PP796 standard.

Calculate the percentage PP796 content (w/w) of each sample Solution B as follows.

$$\% \text{ w/w} = \frac{A' \times VI \times 100}{I' \times WS \times RF}$$

Where: WS = weight of sample (mg);
VI = volume of internal standard added in ml;
A' = peak area of PP796 peak;
I' = peak area of octadecane peak;
RF = relative response factor for PP796 obtained from the preceding standard Solution A.

Calculate the average PP796 content from Solutions B₁ and B₂.

