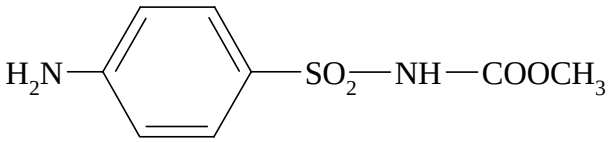
ASULAM
240



ISO common name	Asulam
Chemical name	Methyl sulphanilylcarbamate (IUPAC); methyl [(4-aminophenyl)sulphonyl]carbamate (CA; *3337-71-1*; sodium salt: *2302-17-2*)
Empirical formula	$C_8H_{10}N_2O_4S$ $C_8H_9N_2NaO_4S$ (sodium salt)
RMM	230.2 252.2 (sodium salt)
m.p.	213 ° C (with decomposition; sodium salt)
v.p.	Less than 1×10^{-3} at 20 °C (asulam)
Solubility	Sodium salt in water: 1.4 kg/l; methanol: 30 g/l; acetone: 0.9 g/l; ethyl acetate: 0.1 g/l
Description	Pale cream/buff granular powder
Stability	Stable in air and aqueous solution
Formulations	Soluble granules and soluble concentrates

ASULAM SODIUM TECHNICAL
[*] **240.011**/TC/(M)/-

1 Sampling. Take at least 100 g. If the material is granular, grind a subsample such that it will pass through a 100 µm sieve.

2 Identity tests

2.1 HPLC. Use the method described below. The relative retention time of asulam with respect to the internal standard for the sample solution should not deviate by more than 1% from that for the calibration solution.

2.2 Infrared. Prepare potassium bromide discs from the sample and from pure asulam sodium with using 1.5 mg compound and 300 mg potassium bromide. Scan the discs from 4000 to 400 cm^{-1}. The spectrum produced from the sample should not differ significantly from that of the pure asulam sodium.

3 Asulam

OUTLINE OF METHOD Asulam is determined by reverse phase high performance liquid chromatography (HPLC) using an internal standard procedure.

REAGENTS

Acetonitrile HPLC grade
Water HPLC grade
Asulam standard of known purity
4-Methoxybenzyl alcohol internal standard
Sodium dihydrogen phosphate dihydrate
Phosphoric acid
Phosphoric acid solution, 5 % (v/v) in acetonitrile

Buffer solution. Dissolve sodium dihydrogen phosphate (9.83 g) in water (1000 ml). Adjust the pH of the solution to 3.0 using phosphoric acid.

Mobile phase Add acetonitrile (150 ml) to buffer solution (850 ml) and mix well.

Internal standard solution. Dissolve 4-methoxybenzyl alcohol (10 g) in acetonitrile (100 ml).

Calibration solution. Weigh (to the nearest 0.1 mg) into two volumetric flasks (100 ml) asulam standard (150 mg, *s* mg). Add by pipette to each flask internal standard solution (10.0 ml), dilute to volume with acetonitrile, and mix thoroughly. Dilute 10.0 ml of these solutions to 100 ml with mobile phase and mix well. Finally dilute 15.0 ml of these solutions to 100 ml with mobile phase and mix well (Solutions C_a and C_b).

[*] Provisional CIPAC method 1997. Prepared by the Asulam Panel of PAC-UK. Chairman: P T Patel. Based on a method supplied by Rhône Poulenc Agriculture, UK.

APPARATUS

Liquid chromatograph equipped with a UV detector capable of measuring the absorbance at 270 nm, a constant flow pump (2.0 ml/min), and a loop injector (20 μl)

Liquid chromatographic column stainless steel, 100 × 4.6 mm (i.d.) packed with Spherisorb 5 ODS-2 or equivalent

Electronic integrator or *data system*

PROCEDURE

(a) Operating conditions (typical):

Flow rate	1.0 ml/min
Column temperature	ambient, but controlled to within 2 °C
Injection volume	20 μl
Detector wavelength	270 nm
Chromatographic run time	25 min
Retention times	asulam: 3.8 min
	internal standard: 11.5 min

(b) Preparation of sample. Weigh in duplicate (to the nearest 0.1 mg) into separate volumetric flasks (100 ml) sufficient sample to contain 200 mg asulam sodium standard (*w* mg). Add by pipette internal standard solution (10.0 ml) and acetonitrile (30 ml). Dilute to volume with water and mix well to dissolve all the solids. Pipette these solutions (10.0 ml) into separate volumetric flasks (100 ml), add 5% phosphoric acid solution (2 ml), dilute to volume with mobile phase and mix well. Finally dilute 15.0 ml of these solutions to 100 ml with mobile phase and mix well. (Solutions S_a and S_b).

(c) Determination. Inject 20 μl portions of the two calibration solutions until the consecutive asulam to internal standard ratios agree within 1%. Then inject 20 μl aliquots of the samples and one calibration solution in the order C_a, S_{a1}, S_{a1}, C_a , S_{b1}, S_{b2}, C_a, ...etc. Determine the peak areas. Calculate the asulam to internal standard ratios for the pair of calibration solution injections which bracket sample solution injections and calculate the mean. Repeat the sample analysis if the calibration response factors differ by more than ±2% of the mean.

(d) Calculation

$$\text{Content of asulam} = \frac{R' \times s \times P}{R \times w} \text{ g/kg}$$

where:

R = asulam to internal standard peak height ratio for the sample solution
R' = asulam to internal standard peak height ratio for the calibration solution
s = mass of asulam in the calibration solution (mg)
w = mass of asulam in the sample solution (mg)
P = purity of the asulam standard (g/kg)

Repeatability r = 30 g/kg at 800 g/kg active ingredient content
Reproducibility R = 33 g/kg at 800 g/kg active ingredient content

ASULAM SODIUM SOLUTION CONCENTRATES
*240.011/SL/(M)/-

1 Sampling. Take at least 1 l. Asulam sodium 50 % solutions may show some crystallisation at low temperatures. It is necessary to re-dissolve these crystals and to mix the bulk before any sub-sample is taken.

2 Identity tests.
2.1 HPLC. As for asulam sodium technical **240.011**/TC/(M)/2.1
2.2.UV spectrum. Pass the column effluent from the HPLC procedure through a diode-array UV detector. The peak at the retention time for asulam should show a very similar spectrum to that observed for the asulam peak in the calibration solution (λ_{max} =270 nm).

3 Asulam. As for asulam sodium technical **240.011**/TC/(M)/3.

Repeatability r = 8 g/kg at 340g/kg active ingredient content
= 19 g/kg at 450g/kg active ingredient content
Reproducibility R = 12 g/kg at 340 g/kg active ingredient content
= 24 g/kg at 450 g/kg active ingredient content

4 Methanol

SCOPE The method is a limit test (not exceeding 6% of the asulam content).

OUTLINE OF METHOD The methanol is distilled from the asulam sample and then determined by a colorimetric method, using decolourised magenta solution and a suitable standard.

* Provisional CIPAC method 1997. Prepared by the Asulam Panel of PAC-UK. Chairman: P T Patel. Based on a method supplied by Rhône-Poulenc Agriculture, UK.

REAGENTS

Oxalic acid
Water distilled or de-ionised
Ethanol spectroscopic grade
Methanol HPLC grade
Sulphuric acid
Hydrochloric acid 35%
Potassium permanganate
Phosphoric acid 85 %
Sodium sulphite solution. Dissolve sodium sulphite heptahydrate (20 g) or anhydrous sodium sulphite (10 g) in water (100 ml).
Oxalic acid solution 5% w/v solution of oxalic acid in 50% v/v sulphuric acid
Potassium permanganate in phosphoric acid. Dissolve 3 g potassium permanganate in a mixture of 15 ml of phosphoric acid and 70 ml water. Dilute to 100 ml with water.
Magenta Various grades of magenta are commercially available. The best grades yield a reagent that does not normally require any additional decolourising treatment. A less suitable grade of magenta can be used but the reagent will probably require additional decolourising and as a result will be less sensitive. Failing this, a poorer material may be re-crystallised until it gives a satisfactory reagent.
Decolourised magenta
CAUTION - Avoid contact of magenta with the skin

Weigh magenta (1.0 ± 0.05 g) into a ground-glass stoppered conical flask (1000 ml) previously marked at 1000 ml. Add water (600 ml), loosely stopper and swirl gently. Then heat on a steam bath with occasional swirling until dissolved (3-5 hours). Check that all crystals have dissolved by viewing against a bright light. A trace of almost black insoluble material may, however, still remain.

Cool to about 5°C and add sodium sulphite solution (100 ml). Again cool to about 5°C and add, slowly with constant swirling, hydrochloric acid (10 ml). Dilute to 1000 ml with water, stopper and set aside overnight in the dark. Filter the solution, which should be virtually colourless, through a Whatman No 1 paper on a Hartley funnel, using minimum vacuum. Immediately transfer to a stoppered amber glass bottle and store in the dark.

If the reagent is not virtually colourless, it may be necessary to treat it additionally in an attempt to decolourise it. However, such treatment usually produces a reagent of low sensitivity. To the reagent add 0.3 g decolourising charcoal, shake and immediately filter as above.

SENSITIVITY TEST

Dilute 1.0 ml of a 5% v/v solution of methanol (either aqueous or ethanolic) to 1000 ml with water. To 10.0 ml of this solution, add ethanol 95% v/v (5 ml) and dilute to 50.0 ml with water.

To 5.0 ml of this solution of methanol add of potassium permanganate / phosphoric acid solution (2.0 ml). Mix, set aside for 10 minutes and then add oxalic acid/sulphuric acid solution (2.0 ml), and again mix. To the colourless solution add 5.0 ml of the decolourised solution of magenta, mix and set aside at 15 to 30 °C.

Concurrently prepare a blank, substituting the methanol solution for 5 ml of a 10% v/v aqueous ethanol solution. Compare the colours after 10, 30, and 60 minutes. With the better grades of magenta, the colour reaches a maximum after about 30 minutes and then fades.

APPARATUS

Distillation assembly consisting of a round bottom flask (250 ml) attached to a splash-head and a vertically mounted coil condenser. The end of the condenser should be cut off obliquely and directed into the neck of a volumetric flask (100 ml).

PROCEDURE

Pipette a sample containing 10.0 g of asulam into the distillation flask and add water (100 ml.). Add a few particles of solid phenolphthalein and 5-6 granules of carborundum (14 mesh). Make just alkaline with sodium hydroxide (c = 1 mol/l) and assemble the distillation apparatus.

Distil about 90 ml into a 100 ml volumetric flask, rinse the end of the condenser into the flask with a few ml of water and dilute to the mark with water. Mix thoroughly.

Pipette 10% v/v aqueous ethanol (5.0 ml) into each of two boiling tubes. Into one tube pipette 0.25 ml of the distillate, and into the other pipette 0.37 ml of a 0.5% v/v aqueous solution of methanol and mix. To each tube add potassium permanganate/phosphoric acid solution (2.0 ml), mix and allow to stand for 10 minutes. Add oxalic acid/sulphuric acid solution (2.0 ml), mix and add decolourised magenta solution (5 ml). Mix and allow to stand at room temperature (15 to 30°C) for 30 minutes. The intensity of blue colour in the test solution should not exceed that produced in the standard.

ASULAM SODIUM S0LUBLE GRANULES
* **240.011**/SG(M)/-

1 Sampling. Take at least 1 kg. Grind the sample such that it will pass through a 100 µm sieve.

2 Identity tests.

2.1 HPLC. As for asulam sodium technical **240.011**/TC/(M)/2.1.

2.2 UV spectrum. Pass the column effluent from the HPLC procedure through a diode-array UV detector. The peak at the retention time for asulam should show a very similar spectrum to that observed for the asulam peak in the calibration solution (λ_{max} =270 nm).

3 Asulam. As for asulam sodium technical **240**/TC/(M)/3.

Repeatability r = 10 g/kg at 800 g/kg active ingredient content
Reproducibility R = 17 g/kg at 800 g/kg active ingredient content

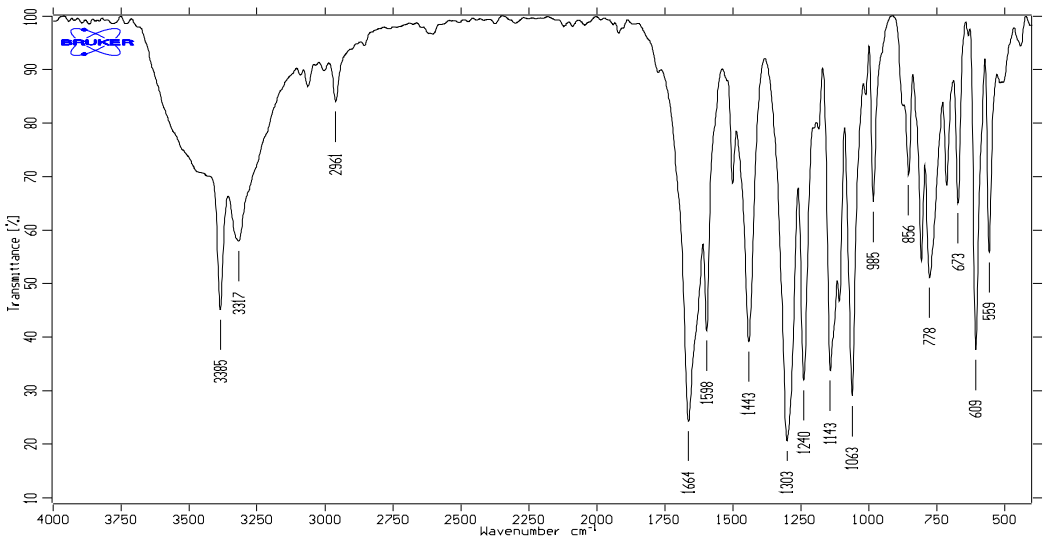


Fig. 1 Infrared spectrum of purified Asulam sodium

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