METHOD FOR THE DETERMINATION OF p-TOLUENESULPHONIC ACID IN WATER

B Crathorne, C P James and J A Stratford

November 1987

UNRESTRICTED

PERMISSION: This work was funded by the Department of the Environment whose permission to publish has been obtained

WRc Environment,
Medmenham Laboratory, Henley Road, Medmenham,
PO Box 16, Marlow, Bucks, SL7 2HD
Telephone: Henley (0491) 571531
SUMMARY

WRc, under contract to the Department of the Environment, have undertaken research into the effects of distribution on organics in water (Contract reference EHT 9155). During this work a number of analytical methods were developed including one for the determination of p-toluenesulphonic acid. An HPLC method with a detection limit of 5 μg/litre for p-toluenesulphonic acid in drinking water is described.
# CONTENTS

## SUMMARY

1. PERFORMANCE CHARACTERISTICS OF THE METHOD  
   1.1 Substances determined  
   1.2 Type of sample  
   1.3 Basis of method  
   1.4 Range of application  
   1.5 Limit of detection  
   1.6 Sensitivity  

2. PRINCIPLE OF THE METHOD  

3. REAGENTS  
   3.1 Water  
   3.2 Extraction solvents, HPLC eluent etc  
   3.3 Analytical standards  
   3.4 Standard solutions  

4. APPARATUS  
   4.1 General  
   4.2 High-performance liquid chromatography  

5. SAMPLE COLLECTION  

6. ANALYTICAL PROCEDURE  
   6.1 Extraction  
   6.2 HPLC analysis  

7. PERFORMANCE CHARACTERISTICS  

## REFERENCES

## FIGURES
1. PERFORMANCE CHARACTERISTICS OF THE METHOD

1.1 Substances determined p-toluenesulphonic acid.

1.2 Type of sample Drinking water.

1.3 Basis of method Extraction by vacuum evaporation and methanol extraction of the residue. Separation and quantification using high-performance liquid chromatography.

1.4 Range of application Up to 5 mg/litre.

1.5 Limit of detection 5 µg/litre for a 100 ml sample (see Note 1).

1.6 Sensitivity This will depend on the equipment used. With that listed under 3.2 the following was obtained.

   p-toluenesulphonic acid, 50 ng.

2. PRINCIPLE OF THE METHOD

   The water sample is evaporated to dryness using a vacuum rotary evaporator. The solid residue is extracted with methanol and the extract analysed using high-performance liquid chromatography.

3. REAGENTS

3.1 Water

   The water used for blank determinations and subsequently for recovery experiments should be tap water which has not come into contact with any epoxy resin components. This should be checked by
3.2 Extraction solvents, HPLC eluent etc
Methanol (glass distilled grade), tetrabutylammonium bromide (Aldrich Chem Co).

3.3 Analytical standards
p-Toluenesulphonic acid (BDH Chemicals).

3.4 Standard solutions
The following solutions should be prepared in clean 10 ml volumetric flasks. p-Toluenesulphonic acid, 100 mg ± 0.1 mg and 10 mg ± 0.1 mg per 10 ml methanol. A dilute standard (1 mg per 10 ml methanol) is prepared by adding 1 ml of the 10 mg/10 ml solution to a clean 10 ml volumetric flask and making up to the mark with methanol. All standard solutions should be stored in the dark at -18 °C.

4. APPARATUS

4.1 General
All glassware, including the rotary evaporator, should be washed with non-ionic detergent, 4N HCL, rinsed with deionised water (see Note 7), and finally washed with the appropriate solvent before use. General laboratory glassware will be required, plus the following, more specialised equipment.

Vacuum rotary evaporator equipped with a suitable vacuum pump (water pump or equivalent), water bath and cold finger.

A multiple nitrogen manifold (enabling a gentle stream of nitrogen to be delivered from a jet about 1 cm above the liquid surface) for evaporating partially concentrated extracts.
Precision microlitre syringes suitable for use with HPLC and for spiking experiments.

4.2 High-performance liquid chromatography

A high-performance liquid chromatograph equipped with an ultraviolet absorption detector. Various instruments, columns etc are potentially suitable for the analysis. The following was used for developing the method.

- HPLC pump: Waters 6000A
- Detector: LDC uvIII fixed wavelength (254 nm)
- Column: Spherisorb-ODS (25 cm x 4.6 mm id), 5 μm particle size
- Injector: Rheodyne valve, model 7125
- Eluent: Methanol-water (45:55)/0.005 M tetrabutylammonium bromide, pH 5.5.
- Temperature: Room temperature
- Flow rate: 1 ml/min.

Under these conditions p-toluene sulphonic acid has a retention time of 9 min (k'/=3) (see Note 2). A chromatogram from the analysis of a standard solution is shown in Figure 1. HPLC separation of an extract of water which has been in contact with epoxy resin is shown in Figure 2.

5. SAMPLE COLLECTION

The sample is collected in a 2.5 litre glass-stoppered glass bottle. This is washed with a small volume (approximately 100 ml) of sample water, which is discarded. The bottle is then filled and stoppered so as to leave no headspace (see Note 3).
6. ANALYTICAL PROCEDURE

6.1 Extraction

The water sample (100 ml) is evaporated to dryness at 55 °C using a vacuum rotary evaporator. The residue is then extracted with methanol (2 x 10 ml). Slight warming is used during the extraction to aid dissolution. The organic extracts are combined and then concentrated to approximately 3 ml on a vacuum rotary evaporator at 35 °C (see Note 4). The extract is transferred to a suitable 1 ml vial and concentrated to 0.1 ml under a gentle stream of nitrogen. Store the extract in the dark at -18 °C.

6.2 HPLC analysis

Set up the equipment according to the manufacturer's instructions. Equilibrate the column by passing eluent through the column (1 ml/min) until a reproducible retention time is obtained from repeat injections of a standard solution (see Note 2). Run a calibration standard to establish the peak height for a known amount injected. This should be repeated until a reproducible peak height is obtained. Inject the sample and measure the height if a peak is recorded at the appropriate retention (see Note 5). Calculate concentration of p-toluenesulphonic acid by comparison of peak height (see Note 6). The sample should be analysed at least twice and consistent retention time and peak height obtained.

7. PERFORMANCE CHARACTERISTICS

Before carrying out any recovery experiments a blank determination should be made on the tap water supply to be used. No interfering peaks should be observed.
Recovery experiments should be carried out on a series of water samples to which have been added a known amount of p-toluenesulphonic acid. Recovery should be checked at levels ranging from the detection limit up to the maximum value expected in the samples analysed. Table 1 lists some of the determinations carried out and the recoveries obtained.

Table 1 Results from spiking experiments

<table>
<thead>
<tr>
<th>Concentration (µg/l)</th>
<th>Recovery (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>75</td>
</tr>
<tr>
<td>10</td>
<td>75</td>
</tr>
<tr>
<td>100</td>
<td>60</td>
</tr>
<tr>
<td>500</td>
<td>62</td>
</tr>
<tr>
<td>1000</td>
<td>50</td>
</tr>
<tr>
<td>5000</td>
<td>69</td>
</tr>
</tbody>
</table>

Note 1  The limit of detection will depend on the final volume of the extract and the amount injected onto the HPLC. If the extract is concentrated to 50 µl and 10 µl is injected a detection limit of 5 µg/l will be obtained.

Note 2  The separation of p-toluenesulphonic acid is based on ion-pair chromatography. Column equilibration times are considerably longer with this type of system compared to conventional reversed-phase chromatography. In order to obtain reproducible results eluent should be pumped through the column for approximately 1½ hours or until a steady baseline is achieved and reproducible retention times are obtained. This type of chromatography is also particularly susceptible to changes in column temperature. Thus more reproducible results will be obtained if a column oven or a similar type of thermostat is used. If such equipment is not available then injection of a standard solution should be made
after every two sample injections to check on the reproducibility of the retention time.

Note 3 Samples should be processed as soon as possible after collection. Limited experiments on the stability of samples during storage have been carried out. The results indicate that storage in the dark at <20 °C for up to 24 hours will not cause significant decomposition of the determinand.

Note 4 The rotary evaporator should be rinsed with clean methanol between processing each sample and extract. This can be achieved by rotary evaporating approximately 30 ml methanol.

Note 5 The volume of extract injected will depend on the expected concentration of p-toluenesulphonic acid in the sample.

Note 6 The peak height from the standard should be as close as possible to that of the sample (at the same instrument attenuation). If there is a large discrepancy, another standard should be analysed of appropriate dilution or extract should be concentrated/diluted as required.

Note 7 More persistent stains on glassware, resulting from evaporation of samples to dryness, can generally be removed by adding a small amount of sand to the acid wash.
REFERENCES


Column: Spherisorb ODS (25cm x 4.6mm i.d.)
Eluent: Methanol - Water (45/55)/0.005M Tetrabutyl Ammonium Bromide
U.V. Detection at 254nm, 0.002 aufs

Fig. 1. Chromatogram from the HPLC separation of p-toluenesulphonic acid.
Column: Spherisorb ODS (25cm x 4.6mm i.d.)
Mobile Phase: Methanol - Water (45/55)/0.005M Tetrabutyl Ammonium Bromide
U.V. Detection at 254nm, 0.002 aufs

Fig. 2. Chromatogram from the HPLC separation of an extract of water which has been in contact with epoxy resin.
WRC ENGINEERING
P O Box 85
Frankland Road
Blagrove, Swindon
Wilts SN5 8YH
Tel: Swindon (0793) 488301
Telex: 449541

WRC ENVIRONMENT
Medmenham Laboratory
Henley Road, Medmenham
P O Box 16 Marlow
Bucks SL7 2HD
Tel: Henley (0491) 571531
Telex: 848632

WRC (Headquarters)
John L van der Post Building
Henley Road, Medmenham
P O Box 16 Marlow
Bucks SL7 2HD
Tel: Henley (0491) 571531
Telex: 848632

WRC PROCESSES
Stevenage Laboratory
Elder Way
Stevenage, Herts
SG1 1TH
Tel: Stevenage (0438) 312444
Telex: 826168

WRC SCOTTISH OFFICE
1 Snowdon Place
Stirling FK8 2NH
Tel: Stirling (0786) 71580

WRC WATER BYELAWS ADVISORY SERVICE
660 Ajax Avenue
Slough, Bucks
SL1 4BG
Tel: Slough (0753) 37277
Telex: 449541

Registered Offices:

WRC
WRC CONTRACTS
CABLETIME INSTALLATIONS LTD
Henley Road, Medmenham
P O Box 16 Marlow
Bucks. SL7 2HD
Tel: Henley (0491) 571531
Telex: 848632