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## Note

# Impurities arising from the use of XAD-2 resin for the extraction of organic pollutants in drinking water

H. A. JAMES*, C. P. STEEL and I. WILSON
*Water Research Centre, Medmenham Laboratory, P.O. Box 16, Marlow, Bucks. SL7 2HD (Great Britain)*
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The use of the XAD series of macroreticular resins for the recovery of low levels of organic pollutants from various waters and effluents is well established. Various techniques for the purification of the resins prior to use have been reported[1–4], and spiking experiments have been carried out with a wide range of organic compounds to demonstrate the utility of these resins[1,4–6].

We have been using XAD-2 resin to extract organic compounds from drinking waters, prior to gas chromatography with flame ionization detection (GC–FID) and gas chromatography–mass spectrometry (GC–MS). Initially, satisfactory blanks were obtained, but attempts to lower the detection limit of the procedure to $\approx 10$ ng/l using sample sizes of 5 l resulted in unsatisfactory blanks. The presence of impurities in blanks from XAD-2 resin has been reported[7], but no details of their identities or of ways of reducing their levels were given. We have found that a modification of a published extraction procedure[1] enables satisfactory blanks to be obtained.

It was originally assumed that poor blanks were obtained due to the incomplete removal of impurities from the resin during the initial clean-up procedure. However, various modifications of this procedure proved to be ineffective in reducing the impurity levels in the blanks. As satisfactory reagent blanks could be obtained, it became evident that the presence of these impurities was associated with the passage of a water sample through the resin. GC–MS was used to identify these impurities, and it could be demonstrated, by using alternative extraction techniques, that the laboratory tap water (derived from groundwater) used for most of these experiments did not contain detectable amounts of these compounds. The occurrence of these impurities, which presumably arise due to the fracture of some of the resin beads when water is passed through the resin (displacing the methanol in which the resin is normally stored), can be minimised by using the solvent series methanol–diethyl ether–water (sample), rather than methanol–water (sample).

## EXPERIMENTAL

Amberlite XAD-2 resin, manufactured by Rohm & Haas (Philadelphia, PA, U.S.A.), was obtained from BDH (Poole, Great Britain) and from Applied Science Europe [Pierce and Warriner (UK), Chester, Great Britain]. All solvents (Rathburn Chemicals, Walkerburn, Great Britain) were re-distilled in an all-glass apparatus

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prior to use. Pyrex glass columns (10 × 1.2 cm), fitted with glass sinters (porosity 0) and PTFE or glass stopcocks, were used for the XAD-2 resin columns. Glass reservoirs (2 l) fitted with all-glass taps and suitable ground glass joints were attached to the resin columns. Nitrogen was used to pressurise the samples to obtain the required flow-rate.

*Resin purification procedures*

(1)[1] An 18-g amount of XAD-2 resin was Soxhlet extracted (6 h) sequentially with methanol, acetonitrile and diethyl ether. The purified resin was stored under methanol.

(2) A 24-g amount of XAD-2 resin was placed in a stainless steel tube (16 × 2.2 cm I.D.) connected to a nitrogen supply. The resin was heated at 200°C for 16 h under a stream of nitrogen (100 ml/min). The resin was allowed to cool to room temperature before switching off the nitrogen. It was then slurried with methanol, placed in a glass column and washed with methanol (100 ml) prior to storage in methanol.

(3) As 1, but with an additional final Soxhlet extraction (6 h) with petroleum ether (b.p. 60–80°C).

(4) As 1, but with an additional initial Soxhlet extraction with water.

(5) A 21-g amount of XAD-2 resin, previously rinsed with methanol, was placed in a stainless steel tube (16 × 2.2 cm I.D.) and water (0.2 ml/min) pumped through, using a stainless steel diaphragm pump (Model G50.V; Wallace and Tiernan, Tonbridge, Great Britain), while the temperature of the tube was increased to 120°C. This temperature and water flow were maintained for 2 h (equivalent to ≈30 l steam). The tube was allowed to cool to room temperature, and the flow of water stopped. The resin was removed from the tube and then Soxhlet extracted (6 h) with methanol, prior to storage under methanol.

(6) A 21-g amount of XAD-2 resin, previously purified as in 1, was placed in a stainless-steel tube (16 × 2.2 cm I.D.) and water (≈10 ml/min) pumped through the resin for 1 week. (The same stainless steel diaphragm pump as in 5 was used.) The resin was removed from the stainless-steel tube, placed in a glass column and extracted with diethyl ether (25 ml) prior to storage in methanol.

*Extraction procedures*

(1) Essentially as described by Junk *et al.*[1]. Purified XAD-2 resin (≈2 g), stored under methanol, was slurried with methanol (≈15 ml), and loosely packed into a glass column (10 × 1.2 cm I.D.) to give a resin bed height of 6 cm. Resin bed heights of 3 cm and 9 cm (1 g and 3 g resin, respectively) were also used when the effect of bed height on the impurities was being studied. A glass reservoir (2 l) was attached to the column and the sample (1 l laboratory tap water for resin blank checks using GC–FID, 5 l when using GC–MS and for recovery checks with internal standards[8]) passed through the resin at a flow-rate of ≈ 30 ml/min. The reservoir was connected to a nitrogen supply which could be adjusted (up to a maximum of 2 p.s.i.g.) to give the necessary flow-rate. After most of the sample had passed through the column and the water level was at the top of the column, diethyl ether (15 ml) was added and allowed to flow through until it reached the bottom of the column. The flow was stopped and the diethyl ether allowed to equilibrate with the resin for 10

min. A further 15 ml of diethyl ether wass added to the reservoir, and all the diethyl ether allowed to flow through the resin. The ether eluate was dried by freezing out any water, and concentrated to 250 μl in a flask[1] (50 ml) fitted with a three-ball Snyder Column (Kontes Europe, Over Kellet, Great Britain), prior to GC–FID analysis. The volume of the extract was further reduced to 100 μl, using a stream of dry nitrogen, for GC–MS examination.

(2) As above *except* that after the XAD-2 resin column had been made up in methanol, the excess methanol was allowed to drain through the column until the methanol level reached the top of the resin. Diethyl ether (80 ml) was then added to the reservoir and passed through the column until the level reached the top of the resin. The sample was then passed through the column.

*GC–FID*

A Carlo-Erba Fractovap 2900 gas chromatograph was used for this work. OV-1 wall-coated open tubular (WCOT) glass capillary columns (50 m) were exclusively used [Erba Science (UK), Swindon, Great Britain; Chrompack U.K., London, Great Britain; Phase Separations, Queensferry, Great Britain].

The injector was used in a splitless mode and FID detection employed. The GC conditions were as follows: injector temperature 225°C; detector temperature 250°C; carrier gas, helium at 1.5 ml/min; oven temperature 20°C for 4 min, 8°C/min to 250°C; injection volume 2 μl.

*GC–MS*

An Hewlett-Packard 5710A gas chromatograph directly coupled to a VG Micromass 16F mass spectrometer linked to a VG Data Systems Multispec 82R was used for the identification of the impurities arising from the XAD-2 resin. OV-1 WCOT glass capillary columns (50 m) were used [Erba Science (UK)]. GC conditions were as follows: injector temperature 250°C; oven temperature 20°C for 4 min, 4°C/min to 220°C; carrier gas helium at 1.5 ml/min; injection volume 2 μl. MS conditions were as follows: source temperature 220°C; ionisation mode, electron impact; ionisation energy 70 eV; trap current 100 μA; scan speed 0.5 sec per decade.

## RESULTS AND DISCUSSION

The original XAD-2 resin clean-up procedure used at this laboratory was sequential Soxhlet extractions with methanol, acetonitrile and diethyl ether[1]. Spiking experiments at the 5–50 μg/l level indicated that satisfactory blanks could be obtained. As the majority of the organic contaminants in drinking water which are amenable to GC analysis are present at levels below 1 μg/l, an overall detection limit of 10 ng/l was considered desirable. This sensitivity can be achieved using 2-l water samples when a closed-loop dynamic headspace extraction technique[9] is used. This sensitivity should be achieved for the XAD-2 extraction technique using 5-l water samples and injection of 1/125th of the diethyl ether extract onto a GC column with FID detection (1/50th for MS detection). However the results obtained using 1-l samples of laboratory tap water as blanks were unsatisfactory, as a comparison of an extract from the dynamic headspace technique and an extract from the XAD-2 resin method indicated that additional compounds were present in the latter. From their GC retention times and mass spectra these additional compounds were a series of *n*-

alkanes, ranging from $n$-$C_{10}H_{22}$ to $n$-$C_{24}H_{50}$, as indicated in Fig. 1. As recoveries of $n$-alkanes using the dynamic headspace extraction technique are at least as good as the recoveries using XAD-2, these interferences must be produced as a result of using XAD-2.

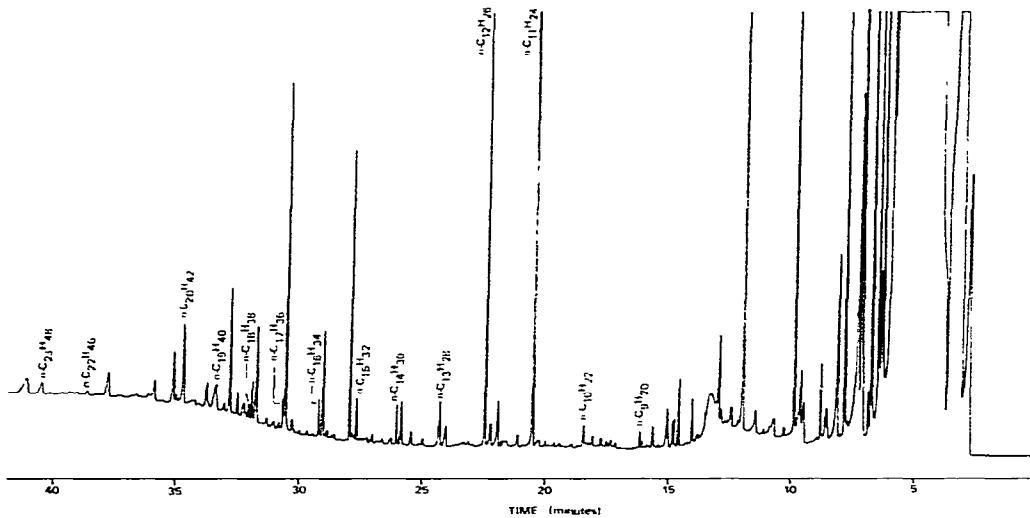


Fig. 1. FID chromatogram of XAD-2 resin extract (in diethyl ether) of laboratory tap water, with $n$-alkane interferences.

An alternative clean-up procedure using thermal desorption followed by washing with methanol gave similar unsatisfactory blanks. Sequential Soxhlet extraction with methanol, acetonitrile, diethyl ether and petroleum ether was also unsuccessful.

A satisfactory "blank" (Fig. 2) could be obtained from any of the above purification methods when no water was used in the overall procedure. It therefore ap-

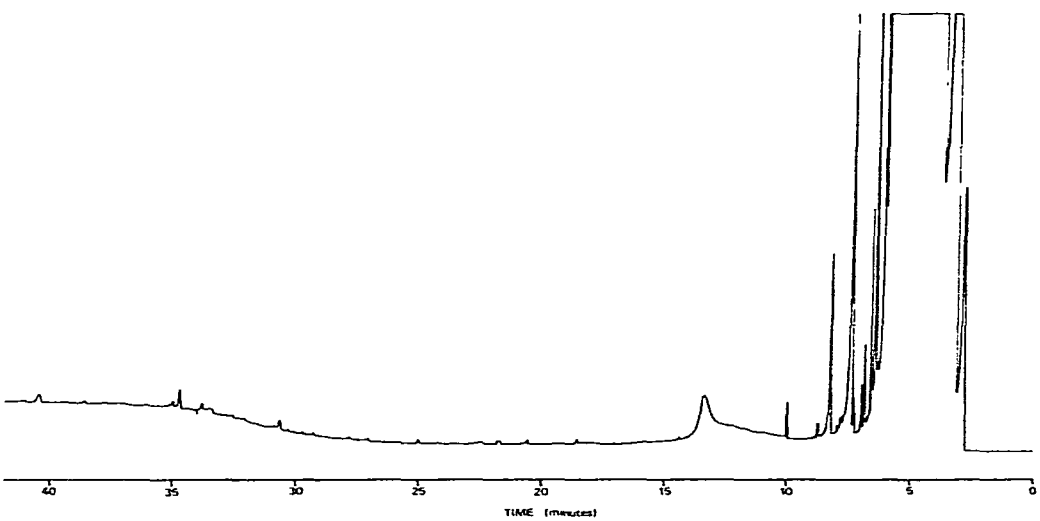


Fig. 2. FID chromatogram of XAD-2 resin "blank" without passage of water through the resin.

peared that the interferences came from the resin but were only released from the resin when it was in contact with water. A Soxhlet extraction sequence with water, methanol and diethyl ether was then carried out, but again the same impurities were found in a blank run. Steam cleaning was also unsatisfactory, as was an attempt to remove the impurities by passing a large volume of water through the resin. When the bed height of the resin was varied, using a constant volume of water for the blank, there was a corresponding change in the level of the hydrocarbons found in the ether extract. It thus appeared that merely changing the solvent from methanol to water, or from water to diethyl ether caused impurities to be released from the resin.

It had previously been noted[10] that XAD-7 and XAD-8 swelled when the solvent was changed from an aqueous to a non-aqueous solvent, so that when diethyl ether was used for desorption, some of the resin beads fractured and impurities were released. Also, when XAD resins were used for HPLC[11], it was found that the pressure drop across the column was dependent on the polarity of the solvent used for elution, the effect being more pronounced with XAD-7 than with XAD-2 or XAD-4. It was therefore thought likely that the impurities were introduced during the change from water to diethyl ether, *i.e.*, during the desorption of the organics from the resin. However, when methanol was used for desorption, a concentrated pentane extract of the methanol eluate again gave the same series of hydrocarbons. The impurities must therefore arise when the solvent change methanol to water is carried out, and will occur whether the sample, or a "blank" water, is used. From figures published[12] for the uptake of solvents by XAD-2, 1 g of resin will take up 0.07 ml of water compared to 0.089 ml of methanol. Whether the accompanying volume change is sufficient to rupture any of the resin beads is not known, but presumably the beads fracture due to either pressure or temperature changes arising from the change of solvent.

The effect of replacing the methanol by diethyl ether prior to the extraction can be seen in Fig. 3. There are still some peaks detected, most of which are from the water used for the blank, but the series of hydrocarbons is no longer detectable.

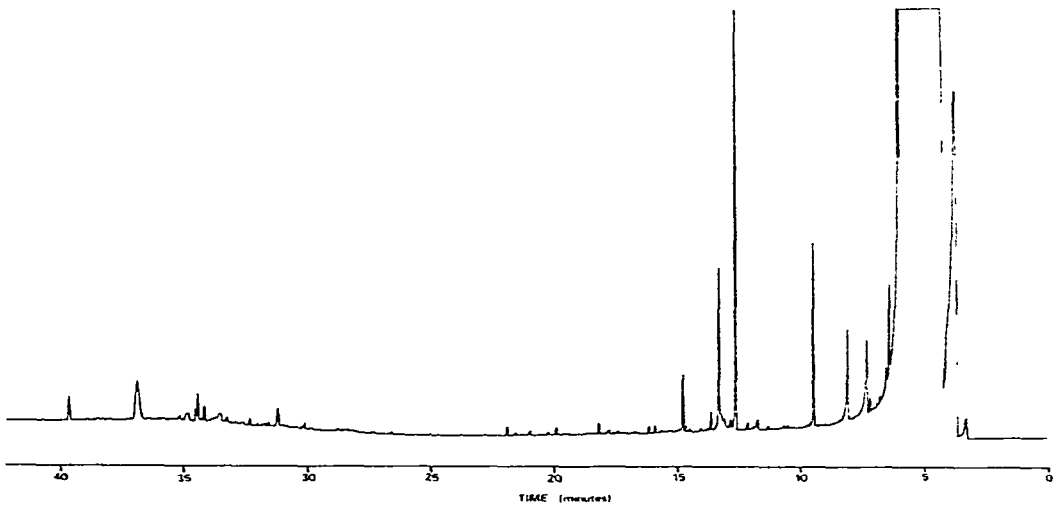


Fig. 3. FID chromatogram of XAD-2 resin extract (in diethyl ether) of laboratory tap water using modified procedure.

Naphthalene, ethylbenzene and benzoic acid have been reported[1] as being major constituents in blanks from XAD-2 purified by heat desorption or vacuum degassing, but the origin of the hydrocarbons reported here is not known. They may be incorporated into the resin during manufacture, but no data have been found to confirm this.

From estimates (GC–FID peak heights) of the quantities present in the diethyl ether extracts, it appears that the levels of hydrocarbons produced are $\approx 2.5$ $\mu$g per g resin and 1 $\mu$g per g resin for $n$-$C_{11}H_{24}$ and $n$-$C_{12}H_{26}$ respectively. The other $n$-alkane levels appear to be below 250 ng per g resin.

The possibility that the residual ether in the XAD-2 column in our modified procedure could have an effect on recoveries was considered, as experiments with methanol–water and acetone–water solutions[5] had demonstrated that low percentages of acetone adversely affected the recoveries of certain compounds when XAD-4 was used. This was checked by spiking laboratory tap water with a deuterated internal standard mixture at 100 ng/l of each compound chloro[$^2H_5$]benzene, [$^2H_{10}$]*p*-xylene, [$^2H_5$]phenol, [$^2H_8$]naphthalene, [$^2H_{34}$]hexadecane and [$^2H_{10}$]phenanthrene). The recoveries obtained, compared to those obtained when the methanol was not replaced by diethyl ether, are shown in Table I.

TABLE I
RECOVERIES OF DEUTERATED COMPOUNDS USING XAD-2 WITH AND WITHOUT DISPLACEMENT OF METHANOL BY DIETHYL ETHER PRIOR TO SAMPLE EXTRACTION

| *Compound* | *Recovery (%)* | |
|---|---|---|
| | *From methanol* | *From methanol–diethyl ether* |
| Chloro[$^2H_5$]benzene | 47 | 52 |
| [$^2H_{10}$]*p*-Xylene | 45 | 61 |
| [$^2H_5$]Phenol | 18 | 9 |
| [$^2H_8$]Naphthalene | 73 | 60 |
| [$^2H_{34}$]Hexadecane | 10 | 10 |
| [$^2H_{10}$]Phenanthrene | 60 | 60 |

The recoveries given in the table are the mean of two determinations and further work would be necessary to establish whether the two sets of results are significantly different. However, the modified procedure gives acceptable recoveries for the compounds used.

## CONCLUSIONS

A slight modification to the most widely applied procedure for the extraction of low levels ($\leqslant 100$ ng/l) of organic compounds from drinking water using XAD-2 resin enables lower detection limits to be achieved, due to the absence of interfering compounds arising from breakdown of the resin.

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