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# Use of solid-phase extraction in the determination of benzene, toluene, ethylbenzene, xylene and cumene in spiked soil and investigation of soil spiking methods

**Katie M. Meney, Christine M. Davidson* and David Littlejohn**

*Department of Pure and Applied Chemistry, University of Strathclyde, 295 Cathedral Street, Glasgow, UK G1 1XL*

**A method has been developed for the determination of benzene, toluene, ethylbenzene, xylene and cumene (BTEXC) in soils, based on methanol extraction, solid-phase extraction (SPE) of the diluted extract and gas chromatography. Quantitative recoveries of BTEXC were obtained from methanol extracts provided the solvent composition was adjusted to methanol–water (50 + 50) prior to SPE, and care was taken to avoid the development of headspace into which analytes could partition. Cartridge (500 mg) load volumes of up to 20 ml of methanol–water extract were possible for all the analytes, except benzene (7 ml), without significant loss due to volatilization. The minimum elution volume for 100% removal of the analytes from the SPE cartridge was 1.5 ml of dichloromethane. It was possible to recover $>90\%$ of analytes added as a concentrated methanolic solution to a dry, clay soil, but the recoveries decreased if field-moist soil was used and if the soil was spiked with petrol. Recoveries were also reduced if the soil and spiking solution were left in contact for extended periods (as would occur in the event of a real contaminant spillage). Over a 17 d period, more than 30% of the BTEXC added to a soil as a dilute solution in methanol–water (50 + 50) became too tightly bound for removal by a single aliquot of extractant. When the method of vapour fortification was used to produce performance evaluation materials, both uptake of BTEXC and stability of the analyte concentrations after spiking were found to depend strongly on the soil type.**

***Keywords:*** *Solvent extraction; solid-phase extraction; gas chromatography; contaminated soil; benzene; toluene; ethylbenzene; xylene; cumene; vapour fortification*

Volatile organic compounds (VOCs), such as benzene, toluene, ethylbenzene, xylene and cumene (BTEXC), are important environmental contaminants because of their toxicity and widespread occurrence. They are present in aviation fuel and petrol (gasoline) and are widely used industrial solvents and raw materials.[1] Benzene, toluene and ethylbenzene are amongst the compounds designated 'priority pollutants' by the US EPA and action levels for BTEX are listed in the Dutch Government quality standards for assessment of land contamination.[2]

Soils become contaminated with BTEXC through spillage of industrial solvents, leakage of petrol from storage facilities (particularly underground holding tanks) and deposition from contaminated air.[1] Most methods for contamination assessment are based on the extraction of VOCs from soil or sediment for quantification by GC or GC–MS. A wide variety of extraction techniques have been used, including headspace analysis,[3,4] purge-and-trap analysis,[5] thermal desorption,[6] vacuum distillation,[7] solvent extraction (including Soxhlet extraction, use of sonication[8,9] and microwave assistance[10]) and supercritical fluid extraction.[11]

Apart from solvent extraction, all of these methods suffer from the limitation that only small (typically $<5$ g) and potentially unrepresentative samples can be processed. An exception is the novel apparatus for headspace analysis of bulk sediment samples (up to 150 g) described by Bianchi and Varney.[12] An important drawback of solvent extraction is that relatively large quantities of liquid are required. A high extractant-to-soil ratio reduces the analytical sensitivity unless the extract is later concentrated. Furthermore, environmental considerations, including costs of disposal, make the large-scale use of many organic solvents unacceptable.

Solid-phase extraction (SPE) has been applied widely in clean-up and/or preconcentration of liquid samples and extracts.[13] Cartridges containing $C_{18}$ sorbent have been used in the isolation of benzene and toluene from sea-water[14] and of BTEX from acidic industrial effluents.[15] Solid-phase micro-extraction (SPME) has been applied to isolate BTEX from water samples, either by direct sorption from the liquid[16,17] or *via* sampling of headspace.[18] SPE has also found applications in soil analysis. Both Redondo *et al.*[19] and Huang[20] used SPE to collect a suite of pesticides from soil extracts, and Mills and Thurman[21] isolated triazine metabolites from soil and aquifer sediments using methanol–water (4 + 1) and automated SPE.

Few SPE methods for the collection of VOCs from soil have been reported, however. Loconto[22] used a multi-stage SPE procedure to isolate 1,4-dichlorobenzene and 1,2,4-trichlorobenzene from spiked soils, but the recoveries were poor (5.8 and 26.1%, respectively). Headspace SPME has been successfully applied to spiked soils,[23,24] but it is not yet clear whether the method can be used in quantitative analyses for VOCs in real soil matrices containing variable proportions of organic matter.

Soil sampling is a critical factor in VOC analysis, with large (up to 100%) negative biases being reported owing to loss of analytes through vaporization during sampling, transport and storage.[25] Considerable evidence exists to support the need for immediate, on-site immersion of soil samples in a stabilizing solvent such as methanol,[26] but this is not yet common practice because it lowers the sensitivity and also limits the range of extraction techniques which can be applied to the sample once returned to the laboratory.

In this paper, a method is described based on the approach recommended by Bone[27] in which methanol added to contaminated soil in the field serves as both the sample preservation medium and the extractant. Methanol extracts were diluted with water and processed by SPE, prior to quantification of BTEXC by GC. The potential to improve sensitivity *via* preconcentration during SPE was investigated and the influence on analyte recoveries of soil type, moisture content, spiking method and length of contact between analytes and the soil matrix were studied.

## Experimental

### *Apparatus*

A high-resolution gas chromatograph from Carlo Erba (Milan, Italy) capable of split, splitless and on-column injection was used with a flame ionization detector. The column used was a

CP-SIL 8 fused-silica capillary, 25 m × 0.32 mm id, 5 μm film thickness (Chrompack, Middelburg, The Netherlands). Integration was performed with a PU 4810 integrator (ATI Unicam, Cambridge, UK). The temperature programme and conditions were as follows: 100 °C for 5 min, then a ramp at 4 °C min$^{-1}$ to 180 °C; injection port temperature 225 °C; detector temperature, 225 °C; carrier gas (helium) flow rate, 1.8 ml min$^{-1}$; and splitting ratio, 45 : 1. SPE was performed with 500 mg $C_{18}$ Bond Elut cartridges (Analytichem/Varian, Harbor City, CA, USA).

### Reagents

Methanol (HPLC grade), ethylbenzene and dichloromethane (technical grade) were obtained from Fisons (Loughborough, Leics., UK). Toluene, benzene and cumene (AnalaR) were obtained from Merck (Poole, Dorset, UK) and *p*-xylene (technical grade) from Aldrich (Gillingham, Dorset, UK). The soils used in method development were a commercial peat, two typical topsoils (a sandy loam and a clay soil) and a 'made ground' sample (a mixture of topsoil, stones and clinker) obtained from a former industrial site. They either were used in a field-moist condition or were air dried at room temperature and sieved through a 2 mm mesh. Soil characteristics are summarized in Table 1. None of the soils was intrinsically contaminated with detectable quantities of the analytes. Unleaded petrol was obtained from a commercial filling station.

### Procedures

#### Solution preparation

A solution of dichlorobenzene in dichloromethane (2000 μg ml$^{-1}$) was used as an external standard for quantification of the analytes in the SPE extracts by GC. Standard solutions (approximately 150 μg ml$^{-1}$ of each analyte) were prepared by weighing accurately (by difference) benzene, toluene, ethylbenzene, *p*-xylene, cumene and dichlorobenzene into a calibrated flask containing dichloromethane and then diluting to volume with further solvent. A concentrated stock standard solution (containing about 6000 μg ml$^{-1}$ of each of the analytes in methanol) was also prepared. Aliquots of this solution were diluted with water or methanol to obtain the working standard solutions used to spike soils and during SPE method development.

#### Headspace minimization

Dilute stock standard solutions were stored for a minimum time in calibrated flasks to prevent loss of analytes through partitioning into the headspace. Once prepared, solutions used in SPE method development were immediately taken up in replicate 5 ml glass syringes, the tips of the which were then sealed with Parafilm. If this procedure was not followed it was found that significant (up to 40%) loss of analytes occurred. Syringes containing aliquots of soil extracts were also sealed in this way prior to SPE.

**Table 1** Soil characteristics

| Parameter | Sandy loam | Clay | Peat | Made-ground |
|---|---|---|---|---|
| Moisture content (%)[a] | 14–20 | 18–27 | 52–66 | 19 |
| Loss on ignition (%)[b] | 13 | 16 | 32 | 22.7 |
| pH | 5.5 | 5.3 | 3.1 | 6.0 |

[a] Obtained by drying at 105 °C overnight; a range of values indicates soil obtained on different sampling trips. [b] Obtained by ashing at 450 °C overnight.

#### Solvent extraction

Soils (25 or 50 g) spiked with solutions of the analytes or with petrol were extracted in 100 ml centrifuge tubes. Vapour fortified soils (15 g) were extracted in 50 ml centrifuge tubes. Methanol–water (50 + 50) was used to extract soils which had been spiked with solutions of the analytes, whereas methanol alone was used for soils spiked or vapour fortified with petrol.

Polyethylene centrifuge tubes were used in this study, although for some applications glass tubes would be preferable, because their caps could easily be modified to include a septum. When the extractant was added to the soil, care was taken to fill the tube completely with liquid (allowing air to escape by piercing the septum with a needle) and prevent the development of headspace into which the analytes could partition. The volume of extractant added depended on the mass of soil. For 25 and 50 g of soil in the 100 ml tubes, the volumes of extractant were about 75 and 50 ml, respectively; about 35 ml of extractant were added to the 15 g of soil in the 50 ml tube. The exact volume added to each tube was noted to permit the determination of analyte concentrations.

The centrifuge tubes were shaken for 1 h on an end-over-end shaker and then centrifuged [2000 rpm; MSE (Loughborough, UK) Mistral 1000 bench centrifuge] and aliquots of the supernatant (generally 3 ml) were taken up in 5 or 20 ml glass syringes for loading on to SPE cartridges.

#### Solid-phase extraction

The procedure was based on a method for the extraction of volatile organic compounds from acidic industrial effluents.[15] A $C_{18}$ SPE cartridge was washed with 3 ml of methanol then conditioned with 3 ml of a 1% solution of methanol in water. The standard solutions or soil extracts (3 ml unless stated otherwise) were loaded and the analytes eluted, normally in 3 ml of dichloromethane. A 100 μl aliquot of dichlorobenzene external standard solution was then added to the eluate, which was analysed by GC.

#### Vapour fortification

The procedure was derived from that described by Hewitt.[28] Multiple 15 g aliquots of soil were weighed into 20 ml glass vials and placed (uncapped) in a 400 ml glass desiccator, along with 10 ml of petrol in a shallow Petri dish. The desiccator was sealed and the soils were exposed to the vapours from the petrol for 14 days. At the end of this period, the soils were transferred to amber-glass bottles with PTFE-lined caps, which were filled to capacity to minimize the headspace.

## Results and discussion

### Optimization and characterization of solid-phase extraction procedure

Before applying SPE to soil extracts, optimum conditions for the retention of the analytes on the $C_{18}$ sorbent were determined. Mixed standard solutions (3 ml), containing 70 μg ml$^{-1}$ of each analyte, but with solvent composition varying between 100% water and 100% methanol, were passed through SPE cartridges. The best performance, *i.e.*, close to quantitative recoveries for all analytes, was obtained with methanol–water mixture (50 + 50) (Fig. 1). A higher proportion of methanol [methanol–water (45 + 65) or (40 + 60)] gave analyte recoveries $>100\%$.

The poorer recoveries obtained at $<40\%$ methanol may reflect the low solubilities of the analytes in water, which could prevent quantitative transfer of the analytes to the SPE cartridge. Higher methanol concentrations (75%) led to enhanced recoveries of the less volatile analytes but losses of benzene and toluene. At 100% methanol, the recoveries were uniformly low ( < 30%), perhaps because of poor retention of the analytes by the $C_{18}$ sorbent when methanol is used as the solvent. Therefore, when soil samples are preserved by field immersion in methanol, it will be necessary to dilute the extracts with water prior to SPE.

These recoveries are an improvement on those obtained for extraction of benzene and toluene from sea-water by Saner *et al.*[14] (22 ± 4 and 85 ± 6%, respectively, $n = 6$), and those achieved for an aqueous standard, with an internally cooled SPME device, by Zhang and Pawliszyn[23] (benzene 42 ± 18, toluene 72 ± 8, ethylbenzene 85 ± 6, xylene about 98 ± 5%, $n = 3$). However, they are similar to those reported for toluene, chlorobenzene and xylene isomers (100 ± 4, 104 ± 5 and 98 ± 5%, respectively, $n = 3$) when the minimal headspace procedure used in the current study was applied to industrial effluent samples.[15] Quantitative recoveries were also achieved when 3 ml aliquots of mixed standard solutions containing up to 650 $\mu$g ml$^{-1}$ of each analyte in a methanol–water (50 : 50) matrix were processed. This is equivalent to the concentration which would be obtained by extracting completely 25 g of a soil containing 2070 $\mu$g g$^{-1}$ of each analyte with 75 ml of methanol–water. For comparison, the current Dutch 'C' (intervention) values for benzene, toluene, ethylbenzene and xylene are 5, 50, 30 and 50 mg kg$^{-1}$, respectively.[2] The limit of detection for the same mass of soil and extractant volume was calculated to be around 0.7 mg kg$^{-1}$.

To assess the potential of the SPE method for analyte preconcentration, the maximum loading volume and minimum elution volume of the cartridge were investigated. Replicate 3 ml aliquots of mixed standard solutions containing 60 $\mu$g ml$^{-1}$ of each analyte were diluted by drawing additional methanol–water (50 + 50) into glass syringes, to give final volumes of 7, 10, 12, 15, 17 and 20 ml. No significant loss of toluene, ethylbenzene, *p*-xylene or cumene occurred when these solutions were processed by SPE, but benzene recoveries were reduced ( < 60%) when volumes greater than 7 ml were loaded. As might be expected, an important limitation of the SPE method appeared to be loss of the most volatile analyte during loading of the cartridge. When replicate cartridges loaded with 3 ml of the same mixed standard were eluted with different volumes of dichloromethane, 1.5 ml was adequate to remove all analytes. Hence preconcentration factors of approximately ×5 and ×13 could be obtained for benzene and the other analytes, respectively, without adversely affecting the efficiency of the extraction.

When mixed standard solutions [70 $\mu$g ml$^{-1}$ of each analyte in methanol–water (50 + 50)] were prepared from the 6000 $\mu$g ml$^{-1}$ methanolic stock solution and extracted in duplicate on five successive days, overall recoveries of 92–102% were obtained (RSD < 6%, $n = 10$).

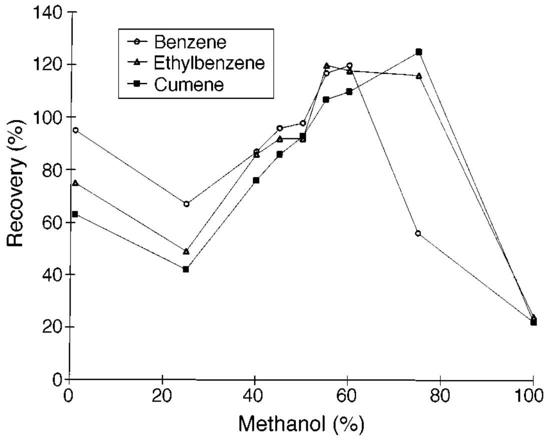

**Fig. 1** Recoveries of benzene, ethylbenzene and cumene from a standard solution using the minimum headspace SPE procedure.

### *Investigation of soil spiking methods*

It is common to validate extraction methods *via* analysis of certified reference materials or the use of 'spike and recovery' tests. Unfortunately, no soil reference materials certified for VOC content are available[28] and so soils spiked using a variety of methods were investigated using the SPE method developed.

#### *Spiking with a concentrated methanol solution*

Duplicate 25 g aliquots of dry clay soil were spiked with 1 ml of a methanol solution containing 6000 $\mu$g ml$^{-1}$ of each analyte and were extracted immediately. The extractant used was methanol–water (50 + 50), since this had been found to be optimal for SPE. Except for benzene in one sample, recoveries of > 90% were obtained (Table 2). However, up to 40% of the benzene and up to 23% of the other analytes were lost when field-moist samples (moisture content 17.5%) were used. The presence of the aqueous phase may limit analyte access to binding sites in the soil matrix, resulting in enhanced loss of, in particular, the most volatile analyte.

#### *Spiking with methanol–water (50 + 50) solution*

A solution (75 ml) with the optimum solvent composition for SPE [methanol–water (50 + 50)], containing about 60 $\mu$g ml$^{-1}$ of each analyte, was added to 25 g of field-moist clay soil in a centrifuge tube, taking care to fill the tube completely to prevent the development of headspace. Prior to addition of the BTEXC solution, a small volume of methanol was added to the tube to compensate for the soil moisture initially present and maintain a constant solvent composition. Quantitative recoveries could be obtained provided that the mixture was immediately centrifuged and an aliquot of the supernatant removed for SPE. However, if the soil and solution were shaken together, on an end-over-end shaker, for 1 h before centrifugation, losses occurred. Analyte recoveries were benzene 92, toluene 89, ethylbenzene 87, *p*-xylene 87, and cumene 89%. Recoveries of 96–98% were obtained when a tube containing the BTEXC solution but no soil was treated similarly, suggesting that losses are due to analyte–soil interactions, and not to volatilization or sorption on the centrifuge tube walls.

To investigate this further, samples of three soils were spiked with the same methanol–water solution and left to stand, in sealed centrifuge tubes with no headspace, for various periods. At the end of the contact time, aliquots of the supernatant were removed for analysis, and each soil residue was extracted with a second volume of methanol–water (50 + 50). The contents of blank tubes, containing the methanolic solution but no soil, were also analysed to assess losses due to vaporization or adsorption of the analytes by the tube walls during the experiment. These values were used to calculate the amounts of

**Table 2** Recoveries (%) obtained following spiking clay soil with a concentrated methanol solution of the analytes

| Compound | Dry soil ($n = 2$) | Field-moist soil ($n = 2$) |
|---|---|---|
| Benzene | 88, 95 | 64, 60 |
| Toluene | 103, 99 | 84, 77 |
| Ethylbenzene | 94, 96 | 84, 76 |
| *p*-Xylene | 92, 98 | 84, 78 |
| Cumene | 93, 97 | 89, 83 |

analyte adsorbed by the soils over periods of 6 and 17 d (Table 3).

After 6 d, the peat had adsorbed the largest amounts of analytes, probably owing to the larger proportion of organic matter present. Non-polar compounds are well known to have an affinity for the organic fraction of moist soil.[1] When separate tubes were analysed after 17 d, results for the peat showed little change, but further analyte sorption was evident in both clay and sandy soils. At the end of the experiment, up to 38% of the analytes added to the peat and up to 30% of those added to the other soils could neither be recovered nor accounted for by analysis of the blank. It must be presumed, therefore, that these had become too tightly bound to the soil matrix for removal with a single aliquot of methanol–water (50 + 50).

Losses from the blank tube were of the order of 20% over 17 d, and were greater for the less volatile analytes. This suggests that partitioning into the polypropylene walls, rather than volatilization, was the main mechanism responsible for analyte loss in the absence of soil.

Similar contaminant ageing experiments were carried out over a longer period. After 10 weeks, $<50\%$ of the benzene and toluene and $<30\%$ of the other analytes remained in the spiking solution. In addition to analysis of the supernatant, four consecutive extractions were performed on each soil residue, and progressively smaller amounts of the analytes were recovered by each subsequent extraction (Fig. 2). When the levels of analytes which could be recovered *via* the four extractions were added to those remaining in the supernatant at the end of the contact period and corrected for blank tube losses, recoveries $>100\%$ were obtained for some soils (Table 4). A possible explanation is overestimation of the blank, which could occur if the soil competed effectively with the tube walls for adsorption of the analytes, but retained them in forms which could be removed by the methanol–water extractant. The made-ground sample appeared less able to bind these analytes than the true soils. This is probably due to the unusual nature of this matrix, which consisted of a mixture of clinker and topsoil (sandy loam and sandy silt loam).

Alexander[29] questioned the validity of ‘spike-and-recover’ experiments for the assessment of soil extraction methods on the grounds that they do not simulate accurately the manner in which contamination occurs in the environment. When a solvent or petrol spillage occurs, the soil and VOC often have a considerable amount of time to interact. Under these conditions, ‘ageing’ effect (in which substances are gradually altered to more stable forms or diffuse into inaccessible locations, within the soil matrix) can become important. This effect is of particular concern in contaminated land clean-up, where the presence of recalcitrant forms of a pollutant may make it impossible to achieve adequate soil remediation. It is also important in analytical science. Although quantitative recoveries may be obtained when a soil is spiked and promptly extracted, use of the same method could seriously underestimate contamination in a field sample.[30]

### *Spiking with petrol*

Spillage of petrol is a common source of BTEXC in the environment, and it is important that any extraction method be applicable to petrol-contaminated soil. However, when 500 μl aliquots of unleaded petrol (of known composition) were added to 25 g samples of a field-moist clay soil (moisture content 27%), difficulties were experienced in recovering the compounds of interest using methanol–water (50 + 50). On addition of the extractant, a strong smell of petrol was immediately apparent and immiscible droplets could be seen on the surface of the liquid. A tarry residue remained in the centrifuge tube at the end of the extraction. Recoveries of the less volatile analytes were slightly reduced relative to those obtained when spiking with methanolic solutions (Table 5), presumably because of the presence of high concentrations of non-polar components in petrol, which compete effectively with the extractant for the

**Table 3** Concentrations of analytes adsorbed by soils from methanol–water (50 + 50) solutions following various contact times (μg g$^{-1}$ soil dry mass)

| | Sandy loam[a] | | Clay[a] | | Peat[b] | |
|---|---|---|---|---|---|---|
| Compound | 6 d | 17 d | 6 d | 17 d | 6 d | 17 d |
| Benzene | 3 | 10 | 2 | 8 | 19 | 16 |
| Toluene | 7 | 18 | 9 | 17 | 41 | 37 |
| Ethylbenzene | 16 | 24 | 19 | 24 | 59 | 55 |
| *p*-Xylene | 10 | 17 | 16 | 20 | 53 | 51 |
| Cumene | 13 | 13 | 13 | 12 | 52 | 38 |

[a] Spiking conditions: 75 ml of 52 μg ml$^{-1}$ (of each analyte) solution added to 50 g of soil. [b] Spiking conditions: 73 ml of 49 μg ml$^{-1}$ (of each analyte) solution added to 25 g of soil.

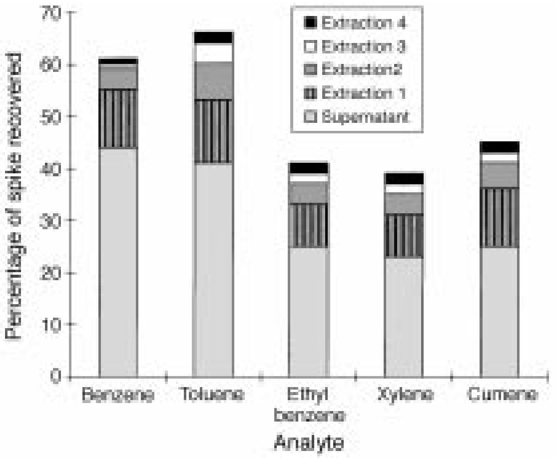

**Fig. 2** Analyte recoveries obtained by successive extraction of a clay soil spiked with a methanol–water (50 + 50) solution and left to age for 10 weeks.

**Table 4** Overall recoveries (%) of analytes from soil and made-ground following contact with a methanol–water (50 + 50) solution of BTEXC for 10 weeks. Results shown are blank corrected and represent the sum of analyte levels in the supernatant + amounts released by four consecutive extractions of the soil *versus* the spike concentration

| Compound | Sandy loam | Clay | Made-ground |
|---|---|---|---|
| Benzene | 120 | 120 | 73 |
| Toluene | 110 | 103 | 60 |
| Ethylbenzene | 119 | 113 | 78 |
| *p*-Xylene | 135 | 124 | 74 |
| Cumene | 138 | 133 | 82 |

**Table 5** Recoveries (%) obtained with different extractants following spiking of field-moist clay soil with petrol

| Compound | Methanol–water (50 + 50) (*n* = 2) | Methanol (*n* = 2) |
|---|---|---|
| Benzene | 58, 59 | 81, 86 |
| Toluene | 88, 84 | 92, 95 |
| Ethylbenzene | 76, 72 | 90, 92 |
| *p*-Xylene | 83, 74 | 93, 95 |
| Cumene | 74, 64 | 94, 98 |

analytes. Improved recoveries could be obtained if the soil was extracted with methanol alone, although there was still significant (up to 19%) loss of benzene. To achieve optimum solvent composition for the SPE procedure, a 3 ml aliquot of the methanol extract was drawn into a glass syringe and then diluted by drawing up 3 ml water.

In order to simulate more closely the manner in which soils become contaminated in the field, two large masses of soil (5 kg each of the sandy loam and the clay) were deliberately contaminated with unleaded petrol (200 ml). Each was thoroughly mixed after spiking, then transferred to a container, covered with turf and placed in the open for 8 weeks. Periodically, soil (about 80 g) was removed from each quarter of the container, quickly mixed to give a bulk sample, then four 50 g aliquots were taken for extraction.

The amounts of analytes extracted from the sandy loam in general decreased with time but no similar decrease was apparent in the clay soil. In both experiments the reproducibility was exceedingly poor (RSD up to 100% for $n = 4$). It was difficult to spike the soils homogeneously and mixing of the bulk samples had to be minimized to avoid loss of analytes *via* vaporization. Where extractable analyte levels decreased, it was not possible to determine whether this was due to conversion to recalcitrant species or to vaporization, and the initial spiking level could not be determined accurately since evaporation of the petrol occurred during the procedure. Hence, although spiking with petrol represents a close approximation of field contamination, it proved too complex a system in which to evaluate the soil extraction methodology.

### *Vapour fortification with petrol*

Vapour fortification is a spiking method developed by Hewitt.[28] Soils are exposed to VOC vapour, in a closed container, which simulates closely the manner in which contamination often occurs in the vadose zone. The absolute level of analytes taken up by the soil is unknown, but vapour fortification can produce homogeneously spiked soils which are stable for over 60 d in sealed vials, and can therefore be used in inter-laboratory trials or to compare the performance of different extraction methods.[31]

In this work, three soils (the sandy loam, clay soil and peat) were vapour fortified and used to study interactions between BTEXC and the soil matrix and to evaluate the effects of these on extraction efficiency. All extractions were performed with 100% methanol, in preference to methanol–water (50 + 50) since higher recoveries were obtained (Table 6).

The three types of soil differed in their ability to absorb BTEXC when exposed to similar amounts of petrol, and in their stability after fortification. At the end of a 14 d fortification of dry soil samples, the highest levels of all the analytes were recovered from the peat and the lowest from the sandy soil (Table 7). As noted previously for spiking with methanol–water (50 + 50) solutions, a high organic matter content appears to aid rapid sorption of the analytes.

In contrast to the work of Hewitt[28] and Hewitt and Grant,[31] these spiked soils were not stable in terms of their extractable analyte content. Significant losses (up to 27% for benzene, 17% for the other analytes) occurred on storage for only 7 d and, after 42 d, $< 50\%$ of the original extractable benzene remained in each soil. Stability varied between soils and between analytes. Recoveries for the more volatile compounds decreased more rapidly than for those with higher boiling points, suggesting that volatilization (rather than conversion to non-extractable forms) was occurring. Over time, the vapour fortified sand retained a higher proportion of the analytes initially present than the clay soil, and the lowest recoveries were obtained for the peat. Hence, although the peat soil was initially able to take up the highest amounts of analytes, these were more easily lost.

Reversible binding of the analytes to organic matter may explain the difference in stability observed for soils vapour fortified in the present work and those prepared by Hewitt and Grant,[31] who used material of low organic carbon content ($< 7\%$).[31]

Overall, however, the repeatability of the vapour fortification method was much better than for conventional (bulk) spiking with liquid petrol (RSD $< 7\%$ for sandy loam and clay, $< 15\%$ for peat). Over time, however, the precision degraded (RSD up to 44% after 42 d). As might be expected, this was most marked for the more volatile analytes and for the peaty soil.

When the experiment was repeated with field-moist soil, the peat, again, was found to contain the highest levels of extractable analytes immediately after vapour fortification (Table 7). The recoveries decreased with time and, in general, were poorest for the more volatile analytes. An exception was

**Table 6** Concentrations of analytes recovered from vapour fortified dry clay soil on extraction with different solvents (μg g$^{-1}$ soil dry mass). Results are for soils vapour fortified at the same time and in the same desiccator

| Compound | Methanol–water (50 + 50) ($n = 2$) | Methanol ($n = 2$) |
|---|---|---|
| Benzene | 206, 212 | 308, 311 |
| Toluene | 647, 666 | 954, 966 |
| Ethylbenzene | 157, 169 | 280, 297 |
| *p*-Xylene | 240, 254 | 419, 448 |
| Cumene | 171, 180 | 362, 389 |

**Table 7** Concentrations of analytes recovered from vapour fortified soils after storage for various periods (μg g$^{-1}$ soil dry mass). Values in parentheses are RSDs for $n = 6$ (*i.e.*, extraction of triplicate soil samples and duplicate analysis of each extract)

| | Sandy loam | | | | Clay soil | | | | Peat | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Compound | day 1 | day 7 | day 14 | day 42 | day 1 | day 7 | day 14 | day 42 | day 1 | day 7 | day 14 | day 42 |
| *Dry soil—* | | | | | | | | | | | | |
| Benzene | 243 (7) | 188 (4) | 168 (8) | 107 (26) | 318 (6) | 232 (11) | 255 (2) | 109 (20) | 348 (9) | 286 (10) | 268 (6) | 98 (44) |
| Toluene | 868 (4) | 761 (4) | 744 (5) | 601 (14) | 1166 (3) | 973 (8) | 937 (4) | 779 (10) | 1651 (11) | 1379 (4) | 1283 (2) | 905 (32) |
| Ethylbenzene | 348 (5) | 326 (4) | 317 (6) | 301 (9) | 480 (4) | 417 (11) | 379 (4) | 320 (3) | 657 (14) | 550 (8) | 514 (4) | 446 (23) |
| *p*-Xylene | 534 (4) | 500 (4) | 460 (11) | 480 (9) | 725 (4) | 635 (9) | 572 (4) | 579 (4) | 1072 (14) | 887 (7) | 841 (47) | 804 (21) |
| Cumene | 656 (5) | 621 (5) | 571 (11) | 590 (9) | 878 (4) | 766 (11) | 690 (5) | 715 (2) | 1287 (14) | 1077 (9) | 1010 (4.3) | 956 (19) |
| *Moist soil—* | | | | | | | | | | | | |
| Benzene | 69 (7) | | 38 (10) | 27 (23) | 66 (4) | | 56 (11) | 21 (3) | 272 (29) | | 158 (23) | 68 (10) |
| Toluene | 175 (6) | | 81 (9) | 75 (6) | 255 (6) | | 165 (10) | 127 (9) | 1125 (25) | | 885 (17) | 486 (9) |
| Ethylbenzene | 175 (7) | | 43 (10) | 36 (7) | 94 (6) | | 72 (9) | 57 (7) | 411 (22) | | 435 (10) | 285 (8) |
| *p*-Xylene | 94 (5) | | 81 (11) | 64 (8) | 157 (5) | | 133 (9) | 105 (6) | 895 (16) | | 775 (9) | 547 (5) |
| Cumene | 102 (5) | | 87 (11) | 73 (9) | 165 (6) | | 155 (11) | 122 (4) | 988 (14) | | 895 (7) | 684 (5) |

the marked loss of ethylbenzene from the sandy loam over 42 d. The soils which were vapour fortified in field-moist conditions were less able to take up and retain BTEXC over the study period than those which were previously air dried.

Soil behaves as a dual sorbent towards VOC vapour.[32] Both partitioning into organic matter and sorption on mineral matter can occur, and both processes are influenced by the presence of moisture. At high relative humidity, sorbed organic vapours are displaced from the mineral fraction by water and only uptake by soil organic matter occurs. Hence, in the presence of moisture, less VOC can be taken up. Further, if, as suggested above, binding by organic matter is relatively weak in the soils examined, then moist soils would be expected to have a lower capacity to retain BTEXC once sorbed.

Finally, a dry vapour fortified clay was extracted with four successive aliquots of methanol, each of which was diluted to methanol–water (50 + 50), processed by SPE and analysed separately. Of the total amounts of analytes which could be removed by the four extractions, the largest proportions (68–74%) were found in the first extract and significant levels (19–25%) in the second. Little additional BTEXC was removed by the third and fourth treatments (about 5% and $<2\%$, respectively). Since the initial spiking level was unknown, it was not possible to determine whether the soil had been exhaustively extracted. However, it is clear that a single methanol extraction would underestimate soil contamination, as observed for soil spiked with BTEXC in methanol–water (50 + 50).

## Conclusions

BTEXC can be recovered quantitatively and with good precision from methanol extracts of soil by SPE, provided the extract is first diluted to methanol–water (50 + 50). Analyte preconcentration is possible and the cartridge capacity is sufficient to allow analysis at levels well above legislative trigger concentrations for soil contamination. The method can also be used to quantify analytes at sub-mg $\mathrm{kg}^{-1}$ levels.

A number of difficulties were encountered when attempts were made to produce performance evaluation materials to test the method developed. Quantitative recoveries of all analytes except benzene could be obtained when soils spiked with methanolic or methanol–water (50 + 50) solutions, or with petrol, were extracted immediately. However, the extraction efficiencies were lowered, for methanol-spiked soils, by the presence of moisture and, more important, were observed to depend on the length of time for which the soil and analytes had been in contact. The existence of such ‘ageing effects’ cast serious doubt on the use of spike-and-(prompt)-recovery procedures for validation of methods to extract VOCs from soil. However, preparation of aged reference materials was limited by the volatility of analytes, and the use of blanks to quantify and correct for losses also presented difficulties since BTEXC did not behave in a similar way in the presence and absence of soil.

Studies with a methanol–water (50 + 50) spike and with petrol vapour fortification showed that soils differed markedly in their ability to take up VOCs, and also indicated that a single solvent extraction could significantly underestimate contamination. Vapour fortified soils were found to be unstable over periods of only a few days, and the stability was both soil and analyte dependent.

The study suggests that none of the spiking methods used is entirely satisfactory for these analytes and further work is necessary to develop alternative approaches. Vapour fortification is probably the best of the methods investigated, provided that soils are extracted soon after exposure, because it most closely simulates the manner in which contamination occurs in the field. The use of spike-and-(prompt)-recovery procedures produces data of little value and is to be discouraged.

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## References

1 Kliest, J. J. G., in *Chemistry and Analysis of VOCs in the Environment*, ed. Bloemen, H. J. Th., and Burn, J., Blackie, Glasgow, 1993, pp. 202–236.
2 *Environment Quality Standards for Soil and Water*, Netherlands Ministry of Housing, Physical Planning and Environment, Leidschendam, 1986 and 1991.
3 Roe, V. D., Lacy, M. J., Stuart, J. D., and Robbins, G. A., *Anal. Chem.*, 1989, **61**, 2584.
4 Kolb, B., *LC–GC Int.*, 1995, **8**, 512.
5 Yan, X., Carney, K. R., and Overton, E. B., *J. Chromatogr. Sci.*, 1992, **30**, 491.
6 Moreton, E. P., Walsh, P. R., and Lawlor, L. J., *Groundwater Manage.*, 1991, **8**, 75.
7 Hiatt, M. H., Youngman, D. R., and Donnelly, J. R., *Anal. Chem.*, 1994, **66**, 905.
8 Donaldson, S. G., Miller, G. C., and Miller, W. W., *J. Assoc. Off. Anal. Chem.*, 1990, **73**, 306.
9 US Environmental Protection Agency, *Test Methods for Evaluating Sold Waste*, Report No. SW-846, EPA, Washington, DC, 1986.
10 Poole, C. F., and Poole, S. K., *Anal. Commun.*, 1996, **33**, 11H.
11 Burford, M. D., Hawthorne, S. B., and Miller, D. J., *J. Chromatogr. A*, 1994, **685**, 95.
12 Bianchi, A., and Varney, M. S., *Analyst*, 1989, **114**, 47.
13 Berrueta, L. A., Gallo, B., and Vicente, F., *Chromatographia*, 1995, **40**, 474.
14 Saner, W. A., Jadamec, J. R., Sager, R. W., and Killeen, T. J., *Anal. Chem.*, 1979, **51**, 2180.
15 Deans, I. S., Davidson, C. M., Littlejohn, D., and Brown, I., *Analyst*, 1993, **118**, 1375.
16 Arthur, C. L., and Pawliszyn, J., *Anal. Chem.*, 1990, **62**, 2145.
17 Arthur, C. L., Pratt, K., Motlagh, S., Pawliszyn, J., and Belardi, R. P., *J. High. Res. Chromatogr.*, 1992, **15**, 741.
18 Zhang, Z., and Pawliszyn, J., *Anal. Chem.*, 1993, **65**, 1843.
19 Redondo, M. J., Ruiz, M. J., Boluda, R., and Font, G., *Chromatographia*, 1993, **36**, 187.
20 Huang, L. Q., *J. Assoc. Off. Anal. Chem.*, 1989, **72**, 349.
21 Mills, M. S., and Thurman, E. M., *Anal. Chem.*, 1992, **64**, 1985.
22 Loconto, P., *LC–GC Int.*, 1991, **4**, 10.
23 Zhang, Z., and Pawliszyn, J., *Anal. Chem.*, 1995, **67**, 34.
24 Fromberg, A., Nilsson, T., Larsen, B. R., Montanarella, L., Facchetti, S., and Madsen, J. O., *J Chromatogr.*, 1996, **746**, 71.
25 Siegrist, R. L., and Jenssen, P. D., *Environ. Sci. Technol.*, 1990, **24**, 1387.
26 Smith, J. M., Eng, L., Comeau, J., Rose, C., Schulte, R. M., Barcelona, M. J., Klopp, K., Pilgrim, M. J., Minnich, M., Feenstra, S., Urban, M. J., Moore, M. B., Maskarinee, M. P., Siegrist, R., Parr, J., and Claff, R. E., in *Principles of Environmental Sampling*, ed. Keith, L. H., Americal Chemical Society, Washington, DC, 3rd edn., 1996, ch. 34, p. 693.
27 Bone, L. I., in *Principles of Environmental Sampling*, ed. Keith, L. H., Americal Chemical Society, Washington, DC, 3rd edn., 1996, ch. 37, p. 737.
28 Hewitt, A. D., *J. AOAC Int.*, 1994, **77**, 735.
29 Alexander, M., *Environ. Sci. Technol.*, 1995, **29**, 2713.
30 Pavlostathis, S. G., and Mathavan, G. N., *Environ. Sci. Technol.*, 1992, **26**, 532.
31 Hewitt, A. D., and Grant, C. L., *Environ. Sci. Technol.*, 1995, **29**, 769.
32 Chiou, C. T., and Shoup, T. D., *Environ. Sci. Technol.*, 1985, **19**, 1196.

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