Recovery of some common solvents from protective clothing breakthrough indicator pads by microwave–solvent extraction and gas chromatography

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Evanly Vo, Stephen P. Berardinelli and Rotha C. Hall

National Institute for Occupational Safety and Health, Division of Safety Research, 1095 Willowdale Road, Morgantown, WV 26505, USA

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The efficiency of solvent adsorption using Permea-Tec general solvent pads, used for the detection of chemical breakthrough of protective clothing, was determined for methanol, acetone, ethyl methyl ketone, trichloroethylene (TriCE), tetrachloroethylene (TetCE), toluene, *m*-xylene, and D-limonene. Known volumes of single or mixed solvents were added to pads in the range 0.2–5.0 μl (0.16–8.13 μg). After microwave–solvent extraction (ME) into hexan-1-ol, the samples (0.5–3.0 μl) of the filtered and extracted solutions were analyzed by gas chromatography. All solvents exhibited > 97% adsorption on the pads at spiking levels of 0.48–0.98 μg for each solvent. The solvent recovery for the system was calculated for each solvent, with solvents with boiling points below 110 °C showing recoveries of > 90%, and with solvents with boiling points above 110 °C showing recoveries from 80 to 90%. The recovery precision was good (RSD ≤4%) for all solvents over the range 1.0–2.5 μl of applied solvents to pads for ME and 1.0 μl of extracted solutions for GC analysis.

Introduction

Respiratory and dermal exposures to chemical agents are common in the workplace.[1–4] A major occupational health focus has been respiratory monitoring and control, yet damage caused by non-respiratory exposure is also a major cause of occupational ill health.[5,6] Non-respiratory exposure is mainly through the skin and workers are required to wear protective clothing, such as gloves, to minimize the risk of exposure to chemical agents.

Protective-clothing breakthrough-indicator Permea-Tec general solvent pads, containing activated carbon, have become commercially available from Colormetric Laboratories, Inc. (Des Plaines, IL, USA). Fresh pads are attached to the hands of a worker before gloving. Permeation of chemical through the glove during workplace activities will result in adsorption on the pads which can be quantified through subsequent analysis.

In order to analyze exposed pads successfully, it was necessary to develop analytical methods for use with specific chemicals. We now report the validation of an assay for methanol, acetone, ethyl methyl ketone, TriCE, TetCE, toluene, *m*-xylene, and D-limonene, for which dermal-exposure control is advisable. The amounts of adsorbed solvents obtained from pads exposed to them had been determined using a method of thermal desorption-GC analysis.[7] However, the recovery of TriCE, TetCE, toluene, *m*-xylene and D-limonene, was not fully successful using this method. The optimum conditions for ME, GC, and analysis were determined. The MEC-GC procedure was used to determine solvent recovery following addition of known amounts of single solvents (standard solvents), unknown amounts of single solvents (exposure solvents), and known amounts of hexan-1-ol, which was used to extract exposure solvents form pads. The sensitivity and reproducibility of the procedure were also determined for these solvents when used in conjunctions with pads.

Materials and methods

Chemicals

Methanol, acetone, ethyl methyl ketone, TriCE, TetCE, toluene, *m*-xylene, and D-limonene (all ACS reagent grade) were used as standard and exposure solvents for testing pads. Hexan-1-ol (ACS reagent grade) was used as the extracting solvent. All chemicals were purchased from Aldrich Chemical Co. (Milwaukee, WI, USA).

Apparatus

A CEM Corporation (Matthews, NC, USA) microwave–solvent extraction system, Model MES-100, was used to extract sample solvents in pads. A Perkin-Elmer Corporation (Norwalk, CT, USA) gas chromatographic system, which consists of the PE Nelson Model 1022 Personal Integrator and the AutoSystem GC, was used to analyze chemicals. Permea-Tec general solvent pads were purchased from Colormetric Laboratories, Inc. (Des Plaines, IL, USA). Syringe filters, Model Cameo 25N (25 mm diameter, 0.45 μm pore size), were purchased from Fisher Scientific (Pittsburgh, PA, USA).

Spiking general solvent pads

New pads were removed from sealed packages and the adhesive areas removed with scissors. Pads were tested to determine if there was any pad–media interference. Known volumes of single or mixed solvents (methanol, acetone, ethyl methyl ketone, TriCE, TetCE, toluene, *m*-xylene, and D-limonene; 0.2–5.0 μl) were added directly to the surface of the pads using a syringe (0.1–5.0 μl). Then, the pads were inserted into the 2 ml extracting solvent (hexan-1-ol) in extraction vessels and the vessels were immediately covered with the vessel caps.

The ME process

The extraction vessels of the single solvents (methanol, acetone, ethyl methyl ketone, and TriCE) were placed into the MES and extracted for 5 min at 40 °C, 50 psi, and 20% power, while the vessels of the single solvents (TetCE, toluene, *m*-xylene, and D-limonene) were extracted for 5 min at 80 °C, 50 psi, and 20% power. The mixed solvents were extracted for 5 min at 60 °C, 50 psi, and 20% power. The extracted solutions were allowed to cool down at room temperature before opening the vessel caps in order to obtain maximum recovery of the solvents without evaporation loss. Then the extracted solutions were filtered using syringe filters and GC analysis applied.

GC conditions and exposure solvent determinations

The optimum GC conditions were as follows: column (3.05 m × 3.18 mm id, 3% SP-1500 on 80/120 Carbopack B, Supelco, Bellefonte, PA, USA); helium flow rate at 25 ml min^{-1}; oven temperature 225 °C; column temperature 225 °C; and temperature of the flame ionization detector (FID) 225 °C. The extracted samples (0.5–3.0 μl) of single exposure solvents were injected into the GC. The injector, column, and detector were all enclosed in a thermostated oven, which maintained the temperature at 225 °C. In this way, samples that would not volatilize enough at room temperature could be analyzed. The areas of the peaks in the resulting gas chromatograms were used for exposure solvent determinations.

Standard solvent determinations

Standard solvent determinations were performed using the same procedure, but without using pads. Known volumes of single solvents (methanol, acetone, ethyl methyl ketone, TriCE, TetCE, toluene, *m*-xylene, and D-limonene; 0.2–5.0 μl) were added directly into the 2 ml of extracting solvent in the extraction vessels using a syringe (0.1-5.0 μl). The samples (0.5–3.0 μl) of the extracted solutions were injected into the GC. The peak of the standard solvent was called a standard peak. The areas of the standard peaks in the resulting gas chromatograms were used for standard solvent determinations.

Efficiency of multiple solvent adsorption

The efficiency of solvent adsorption on pads was determined with solvent spiking. In the first extraction vessel, 5 μl of a mixture of the eight solvents pre-mixed in equal volumes were added to a pad and the vessel was immediately covered with the vessel cap. The vessel was left at room temperature for 30 min before the pad was inserted into the 2 ml of extracting solvent in the second vessel. Then, 500 μl of the extacting solvent were added directly into the first vessel to extract excess solvents which did not adsorb on the spiked pad. These vessels were then used for the extraction process and GC analysis.

Single solvent recovery

Known volumes of single solvents (0.25–5.0 μl) were added to pads. The pads were then inserted into the 2 ml of extracting solvent in the vessels for the extraction process. The samples (0.5–3.0 μl) of the extracted solutions were then used for GC analysis up to four times. The areas of the peaks in the resulting gas chromatograms were determined and correlated with volumes of solvents added to pads and volumes of extracted solutions subjected to GC analysis to assess the efficiency of solvent recovery during the ME-GC process. Solvent recovery for each solvent was calculated as the percentage of exposure solvent peak area divided by standard solvent peak area.

Results

Resolution

Good resolution of the eight solvents and the extracting solvent was achieved by seting the optimum GC conditions as described above. None of the blanks (unexposed pads in the extracting solvent) produced chromatograms containing peaks corresponding to the eight solvents used in this study. The gas chromatogram shown in Fig. 1 was obtained using 0.5 μl of the filtered extracted solution of a mixture of seven solvents (methanol, acetone, ethyl methyl ketone, TriCE, toluene, *m*-xylene, and D-limonene) and the extracting solvent (hexan-1-ol). The GC retention times for the solvents and the extracting solvent obtained under these conditions are given in Table 1.

Efficiency of solvent adsorption

Excess solvents which did not adsorb on the spiked pad in the first vessel were low, being < 3% for all solvents. No significant peaks were observed in the chromatogram for acetone, ethyl

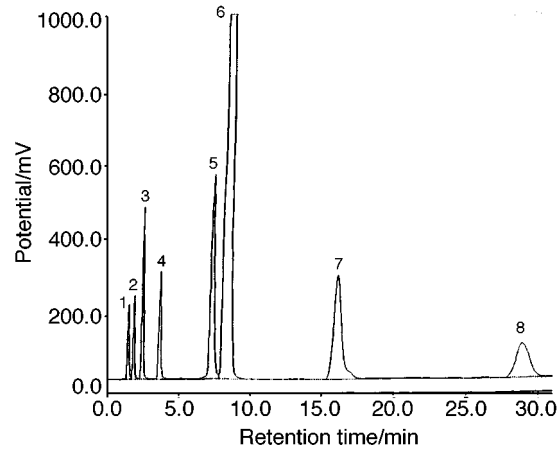

Fig. 1 A gas chromatogram obtained following the microwave–solvent extraction for 5 min at 60 °C, 50 psi, and 20% power. 5 μl of an equivalent volume mixture of methanol, 1; acetone, 2; ethyl methyl ketone, 3; TriCE, 4; toluene, 5; *m*-xylene, 7; and D-limonene, 8 added to the pad. 2 ml of hexan-1-ol (6) were used to extract the mixed solvents from the pad. 0.5 μl of the filtered–extracted solution was analyzed by GC.

Table 1 Retention times and efficiency of adsorption on the spiked pad. 2 ml of hexan-1-ol (retention time, 8.43 min) were used to extract an equivalent volume mixture of eight solvents, 5 μl of which were added to the pad. 1 μl of the filtered extracted solution was analyzed by GC [n.s.: not significant (the peak area < 1% of the area peak for the solvent found in vessel no. 2)]

Solvent	Mass of solvent applied to pad/g	Excess solvent found in the first vessel (%)	Retention time/min
Methanol	0.49	1.13	1.45
Acetone	0.49	n.s.	1.84
Ethyl methyl ketone	0.48	n.s.	2.43
TriCE	0.91	n.s.	3.65
TetCE	0.98	2.25	6.85
Toluene	0.54	n.s.	7.16
m-Xylene	0.54	2.86	15.9
D-Limonene	0.52	n.s.	28.9

methyl ketone, TriCE, toluene, and D-limonene in the first vessel (the area peak < 1% of the area peak for the solvent found in vessel no. 2). Generally, all solvents exhibited > 97% adsorption on the pads at spiking levels of 0.48–0.98 μg for each solvent (Table 1).

Calibrations of pads

For experiments performed with the ME–GC process, no peaks at 1.45, 1.84, 3.65, 15.9, and 28.9 min, corresponding to methanol, acetone, TriCE, *m*-xylene, and D-limonene, respectively, were detected in the chromatograms for the 0.2 μl or lower volumes of these single solvents added to pads in the 2 ml of extracting solvent. All solvents with the single solvents added to pads in the range 1.0–2.5 μl produced high recoveries. No significant improvement in the recovery of the eight solvents was observed when 3.0 μl or larger volumes of these solvents were added to pads.

A relationship between signals (peak area) from gas chromatograms and volumes over the range 0.2–5.0 μl (n = 5) of solvents applied to pads for eight solvents was analyzed using Microsoft Excel software. Linear correlations for these solvents were obtained over the range 1.0–2.5 μl of single solvents added to the pads (methanol, R^2 = 0.9936; acetone, R^2 = 0.9878; ethyl methyl ketone, R^2 = 0.9926; TriCE, R^2 = 0.9794; TetCE, R^2 = 0.9789; toluene, R^2 = 0.9797; *m*-xylene, R^2 = 0.9782; and D-limonene, R^2 = 0.9784) (in all cases p < 0.001). No such linear correlations for methanol, acetone, TriCE, *m*-xylene, and D-limonene were obtained when 0.8 μl of lower volumes of these solvents were applied to pads, while no correlations between volume and areas of the resulting peaks were obtained when 0.5 μl or lower volumes of ethyl methyl ketone, TetCE, and toluene were added to pads.

Solvent recovery

For experiments performed with repeated ME–GC measurements, higher recovery values were observed for all solvents over the range 1.0–2.5 μl of applied solvents to pads and 0.5–3.0 μl of filtered–extracted solutions for GC analysis. Solvent recovery was dependent on the volume of solvent applied to pads, the ME process, and the volatility of the solvents. Solvent recovery was calculated for each solvent, with solvents at boiling points below 110 °C showing recoveries of > 90%, and with solvents at boiling points above 110 °C showing recoveries from 80 to 90% (Table 2).

Precision

The ME–GC process was analyzed for each solvent at a variety of solvent volumes. The recovery precision was good, with the root mean square deviation (RSD) ≤4% for all solvents over the range 1.0–2.5 μl of solvent applied to pads and 1.0 μl of filtered–extracted solutions for GC analysis.

Sensitivity

The gas chromatogram shown in Fig. 1 was obtained with 5 μl of an equivalent-volume mixture comprising 0.6 μl of each solvent applied to a pad and 0.5 μl of the filtered–extracted solution comprising 0.001 μl of each solvent applied for GC analysis. These volumes represent 0.48–0.98 μg of each solvent component per pad and 0.8–1.6 ng of each solvent applied for GC analysis.

Discussion

The results obtained with the ME–GC procedure were consistent for reproducible recovery of eight common solvents from a pad which had been exposed to these solvents. The efficiency of adsorption of these solvents on the pads was also assessed.

It was shown that acetone, ethyl methyl ketone, TriCE, toluene, and D-limonene were nearly completely adsorbed (99–100%) on the pads at spiking levels of 0.48–0.98 μg for each solvent. For methanol, TetCE, and *m*-xylene, the corresponding values were 98.9, 97.8, and 97.1%, respectively.

It has been demonstrated that all solvents from the pads were extracted by the extracting solvent but that the recovery depends on the volatility of the solvent, with decreasing recovery observed with increasing solvent boiling points, as seen in Table 2. For the low-boiling solvents (methanol, acetone, ethyl methyl ketone, and TriCE), excellent recovery was obtained over the range 1.0–2.5 μl of solvents applied to pads and 0.5–3.0 μl of the filtered–extracted solutions for GC analysis. For the other solvents with higher boiling-points, an increased extraction temperature gave higher recovery. Recovery was also dependent on the volume of solvent applied to pads, with increasing recovery observed with increasing volume; however, no significant improvement in the recovery of the solvents was observed when 3 μl or larger volumes of these solvents were added. For some of these solvents, the recovery from the pad at a spiking level of 2.0 μl produced higher recoveries in comparison with those at a spiking level of 3.0 μl, indicating that at this high level of spiking some of these solvents were not completely adsorbed on contact with the pad.

No such linear correlations for methanol, acetone, TriCE, *m*-xylene, and D-limonene were obtained when 0.8 μl or lower volumes of these solvents were added to pads. Excellent linear correlations and a significant improvement in the recovery (*p*

Table 2 Recovery of eight common solvents (1.0–3.0 μl of single solvents added to pads). 2 ml of extracting solvent was used to extract single sample solvents from the pads. 1 μl of the filtered–extracted solutions was applied to GC analysis

Solvent boiling-point/°C	Mass of solvent applied to pad/μg	Recovery (%)
Acetone (56.0)	0.8	83 ± 3.2
	1.6	97 ± 3.7
	2.4	98 ± 3.9
Methanol (65.5)	0.8	94 ± 3.6
	1.6	98 ± 2.3
	2.4	98 ± 3.5
Ethyl methyl ketone (80.0)	0.8	92 ± 3.4
	1.6	92 ± 3.1
	2.3	91 ± 4.1
TriCE (87.0)	1.5	89 ± 3.3
	2.9	91 ± 2.5
	4.4	89 ± 3.8
Toluene (110.6)	1.6	84 ± 2.3
	3.3	91 ± 3.4
	4.9	87 ± 3.6
TetCE (121)	0.6	86 ± 2.8
	1.3	90 ± 2.7
	1.9	88 ± 3.1
m-Xylene (138–139)	0.9	85 ± 3.1
	1.7	89 ± 3.3
	2.6	80 ± 3.6
D-Limonene (175.5–176)	0.8	76 ± 3.0
	1.7	81 ± 2.1
	2.5	82 ± 3.4

< 0.001) were obtained for eight solvents over the range 1.0–2.5 μl of solvents applied to pads and 0.5–3.0 μl of the filtered–extracted solutions for GC analysis.

It was shown that the GC system is sensitive enough to detect the presence of these solvents in extracted solutions. Fig. 1 demonstrated that low-nanogram amounts (0.8–1.6 ng for each solvent in mixed solvents in the extracted solution) of all solvents except D-limonene can be easily detected and that they are clearly resolved under the GC conditions described.

The recovery for the eight solvents from pads using ME–GC analysis was compared with the recovery for these same solvents and pads using thermal desorption–GC analysis.[7] The results of two different methods of analysis (ME–GC analysis against thermal desorption–GC analysis) for measuring the recovery for methanol, acetone, and ethyl methyl ketone from pads produced similar high recoveries. Although the thermal desorption–GC method was quicker and simpler than the ME–GC method when measuring the recovery for methanol, acetone, and ethyl methyl ketone from pads, the ME–GC method is a valuable technique for the quantitative study for TriCE, TetCE, toluene, *m*-xylene, and D-limonene (high-boiling solvents). The recovery for TriCE, TetCE, toluene, and *m*-xylene from the pads produced higher recoveries in comparison with those from a prior study.[7] Interestingly, the quantitative data were obtained for D-limonene when a pad exposed to D-limonene was analyzed under the conditions for the ME–GC analysis described, while Rowell *et al*.[7] reported that the quantitative data for D-limonene could not be obtained when a pad exposed to D-limonene was analyzed under the conditions for thermal desorption–GC analysis.

The quantitative data were obtained for the eight common solvents. The results indicate that general solvent pads exposed to the solvents studied can be analyzed for these solvents under the conditions for the ME–GC analysis described. As a follow on to this study, these results will be used to evaluate worker's gloves for breakthrough exposure to these chemicals.

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