Talanta 82 (2010) 739–744

Contents lists available at ScienceDirect

Talanta

journal homepage: www.elsevier.com/locate/talanta

Rapid removal of selected volatile organic compounds from gaseous mixtures using a new dispersive vapor extraction technique: A feasibility study

E.S. Farrell[a,*], G.E. Pacey[b]

[a] Department of Health and Biomedical Sciences, Florida Hospital College of Health Sciences, Orlando, FL 32803, United States
[b] Department of Chemistry, Miami University, Oxford, OH 45056, United States

ARTICLE INFO

Article history:
Received 28 February 2010
Received in revised form 18 May 2010
Accepted 19 May 2010
Available online 26 May 2010

Keywords:
VOCs
Extraction
Pre-concentration

ABSTRACT

A new dispersive vapor extraction (DVE) technique for rapid removal of selected volatile organic compounds (VOCs) from gaseous mixtures was investigated. In this technique, less than 1.0 mL of a volatile solvent was vaporized for 8 min in a 250-mL flask containing a gaseous mixture. The flask was then cooled under running tap water for 2–3 min to induce condensation of the vapor and co-extraction of the VOCs from the headspace. The technique was tested over a concentration range of 4–23 ppb, and resulted in extraction efficiencies ranging from 80 to 97% for the VOCs tested. Because of its simplicity and the relatively short sampling time, DVE could potentially lead to high sample throughput and rapid air analysis.

1. Introduction

There is a growing need for rapid analysis of volatile organic compounds (VOCs) in ambient air. This is principally due to the fact that airborne VOCs are implicated in everything from respiratory disorder and lung cancer to stratospheric ozone depletion and global warming [1,2]. It is also driven by national security concerns and the potential to compromise air quality through acts of terrorism. Because of the sensitivity limitations of most VOC detectors, and the low levels of VOCs in the environment (mostly $\mathrm{pg\,L^{-1}}$ to $\mu\mathrm{g\,L^{-1}}$) [3], sample pre-concentration remains a critical step in any VOC monitoring methodology. However, as Santos and Galceran observed, the sampling bottleneck is the most protracted task in the entire analytical scheme [4]. Most VOC pre-concentration techniques involve some aspects of cryogenic trapping or adsorptive sampling [1,3]. Despite its prevalence, cryogenic trapping of VOCs from air must incorporate a pre-cooling and refocusing stage to remove water vapor and refocus the VOCs [5]. Another limitation is the logistic problems created by the low temperature (typically -150 to $-170\,^{\circ}$C) of the cryogenic fluids [1]. Peltier-based cryogenic techniques allow trapping to occur in the 10 to $-30\,^{\circ}$C temperature range, but not without the use of sorbent materials [6].

Solid sorbents are widely used as effective agents to trap VOCs from air [7,8]. Porous organic polymers such as Tenax, graphitized carbon such as Carbopack, carbon molecular sieves (CMS), glass fiber (GF) filters, and carbon nanotubes are some of sorbent materials that are commercially available for this purpose [9–12]. However, if the sorbent capacity is exceeded or the collection rate is too high, analyte breakthrough is likely to occur [13]. While higher sampling rates could lead to a loss of the volatile components in a mixture, a less than optimum sampling rate is known to have caused poor retention of some analytes [10]. The high moisture content associated with CMS and other sorbents is another setback. Another concern with this method of VOCs enrichment is the high temperature that is sometimes needed to desorb the analyte from the solid phase. The process is slow and often requires some level of analyte refocusing. A workable solution to this problem involves the use of Peltier devices to reduce the sorption temperatures of the solid phase. This reduces the amount of sorption material needed for trapping, improves sorption capacity, and reduces the desorption time. Another solution is to desorb the analytes into a headspace vial for subsequent analysis by solid phase microextraction (SPME) [14]. Some applications utilize polyvinylfluoride bags in conjunction with SPME to collect the VOCs [15]. SPME is a solvent-free enrichment technique that requires less sampling time and is compatible with traditional VOCs detectors. While the technique has been used to collect volatile and semivolatile organic compounds [16–20], some setbacks remain. Among these are limited sorption capacity, poor retention of less volatile compounds, bleeding of the SPME coating into the gas chromatograph (GC), short fiber lifetime, artifact formation arising from sample carryover, and poor fiber-to-fiber reproducibility [21,22].

Ultraviolet differential absorption spectroscopy (UV-DOAS) is cited in the literature as a technique that allows direct measurement of VOC in air without sample enrichment [23–25], but it is only applicable to a limited number of analytes.

---

[*] Corresponding author. Tel.: +1 407 303 7747x110 4448; fax: +1 407 303 8136.
E-mail address: sebastian.farrell@fhchs.edu (E.S. Farrell).

0039-9140/$ – see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.talanta.2010.05.043

Table 1
A summary of the volumes and concentrations (conc.) for the analytes in the 2, 4, and 24 ppm gas standards.

Compounds	Volume (μL)	Conc. (ppm)	Volume (μL)	Conc. (ppm)	Volume (μL)	Conc. (ppm)
Ethyl acetate	5.0	2.25	10.0	4.50	55.0	24.75
Isopropyl acetate	5.0	2.25	10.0	4.50	55.0	24.75
Toluene	5.0	2.15	10.0	4.30	55.0	23.65
p-Xylene	5.0	2.20	10.0	4.40	55.0	24.20
o-Xylene	5.0	2.20	10.0	4.40	55.0	24.20

Some applications utilize impingers and denuders to transfer airborne VOCs to extracting solvents [1,26–30]. Impingers harvest the VOCs from gaseous mixtures by dispersing or passing the air through the extracting solvent. For applications using denuders, the VOCs are pre-concentrated by dispersing the extracting solvent as a flowing film along the inner walls of the extracting vessels, but in a direction counter to the airflow. While these techniques are amendable to a variety of solvents, their pre-concentration power is limited. Kalnes et al. described a method for the removal of polynuclear aromatic hydrocarbons (PAHs) from a hot vapor containing a mixture of mono-, poly- and olefinic hydrocarbons [31]. The method is comparable to the denudation technique described above in that it allows the hot vapor effluent to contact a cool liquid stream flowing in the opposite direction. In the process of doing so, a portion of the PAHs is transferred from the hot vapor to the cool liquid. The mixture is then directed to a vapor–liquid separator to bring about separation between a vapor stream that is richer in olefinic hydrocarbons, and a liquid stream that contains mostly mono- and polynuclear aromatic compounds. If necessary, the vapor stream can then be re-extracted. Other pre-concentration techniques have been reported in the literature [32–36].

As an initial report, this paper describes the viability of a new procedure called dispersive vapor extraction (DVE) for the rapid removal of selected VOCs from gaseous mixtures. The procedure adds 1.0 mL of a suitable solvent to a sample chamber containing a gaseous mixture, vaporizes it, and rapidly condenses the mixture to extract the analytes from the headspace. DVE combines the power of solvent extraction with the speed of SPME, while using significantly less solvent than traditional extraction techniques. The technique can potentially be automated and coupled to a GC to allow real-time VOC monitoring. It is anticipated that use of more efficient heating technology would lead to further reduction in the heating and incubation time. Because of its simplicity and the relatively short sampling time, rapid analysis and high sample throughput would be possible.

2. Experimental

2.1. Reagent and apparatus

All solvents and VOCs used in this study had purity >99%, and were obtained from either Sigma–Aldrich (Milwaukee, WI), or Fischer Scientific (Fair Lawn, NJ). The 250 mL extraction flask, Thermogreen half-hole septa, Mininert valve and needle-seal septa, along with the 2-L static dilution bottle were purchased from Supelco Inc. (Bellefonte, PA). Standard 100 and 500 mL round bottom flasks were used for the extraction of 100 and 500 mL gas samples, respectively. Suba seals for these flasks were obtained from Aldrich (Milwaukee, WI). All syringes, including the 10 μL fixed needle design and the 250 and 5000 μL gastight samplelock syringes, were obtained from Hamilton Company (Reno, Nevada).

2.2. Instrumentation

Samples were analyzed using a Shimadzu GC-17A gas chromatograph that was controlled by Class-VP Chromatography Data Station, version 4.2. The GC was equipped with a split/splitless injector, a flame ionization detector (FID), and a Restek Corporation capillary column (Rtx-1701, 30.0 m × 0.53 mm i.d. × 1.0 DF). The column temperature was initially set to 40 °C for 2 min. Following this, the temperature was increased at a rate of 15 °C/min to a final temperature of 200 °C for 2 min. The carrier gas flow rate was set to 10 mL/min. Both the injector and the detector were held at a constant temperature of 225 °C. The GC was operated with air, N_2, and H_2, respectively set at 20, 40, and 50 psi. The thermal energy required during solvent volatilization or standard incubation was provided with a Fischer Scientific Isotemp standard laboratory oven.

2.3. Preparation and secondary dilution of gas standards

Due to availability problems [3], the gas standards used in these experiments were prepared in-house according to the basic guideline of (USEPA) method TO-15 [37]. A 2-L static dilution bottle (SDB) retrofitted with a Teflon stir bar and a Mininert valve was purged with a stream of nitrogen for 2 min. Helium and simulated air containing 79% N_2 and 21% O_2 are alternative diluents that can be used for this purpose [37,38]. The closed SDB was allowed to equilibrate in an oven at 60 °C for 15 min. To achieve the concentration range shown in Table 1, the SDB was spiked with between 5 and 25 μL of each of the targeted compounds. The SDB was then returned to the 60° oven for a minimum of 1 h prior to use. The final concentration of each component in the mixture was determined using the following equation:

$$\text{Concentration}\left(\frac{\text{mg}}{\text{L}}\right)=\frac{V_s d}{V_f}$$

where V_s is the volume of liquid standard in μL, d is the density of the liquid standard in mg/μL, and V_f is the volume of the SDB in L.

As a part of the daily protocol for using the gas standard, the SDB was subjected to 15 min of heating along with 15 min of cooling and mixing prior to sampling. In keeping with good laboratory practice for using gas standards, single aliquots larger than 2% of the total gas volume were not drawn. Also, the combined aliquots drawn from the SDB did not exceed 50% of its total overall volume. Secondary dilutions of the gas stock were prepared by purging the extraction vessel as described above, adding the appropriate volume of the stock standard, and equilibrating the mixture in the 60° oven for 15 min.

2.4. Extraction and analysis procedure

Each extraction vessel was retrofitted with a Suba seal or a Thermogreen half-hole septum. These septa provided a tight enough seal for the experimental conditions used in this study. Metal retainers can be used if larger volumes and higher pressures are required. A gastight syringe was used to transfer the required volume of the gas standard from the SDB to the nitrogen-purged extraction vessel. The extraction vessel with the gaseous mixture was then equilibrated in the 60° oven for 15 min. Before the extracting solvent was added to the vessel, a gastight syringe was used to secure 200 μL aliquots of its headspace for GC characterization. As

Table 2
Average daily area response (AR) and %RSD for analytes in the headspace of a 4 ppm gas standard ($n = 5$). The last column shows the between-days (BD) %RSD ($n = 4$). The data was generated using injection volumes of 100 μL of the headspace.

Compounds	Day 1 AR	%RSD	Day 2 AR	%RSD	Day 3 AR	%RSD	Day 4 AR	%RSD	BD%RSD
Ethyl acetate	4443	3.1	4262	1.5	4175	1.0	4065	0.8	4
Isopropyl acetate	5180	1.8	5047	1.1	4971	0.8	4839	0.9	3
Toluene	11,202	2.1	10,902	1.5	10,762	1.3	10,454	0.8	3
p-Xylene	10,801	2.6	10,503	1.8	10,415	2.3	10,077	0.5	3
o-Xylene	11,370	2.7	11,078	1.7	10,991	1.8	10,662	0.7	3

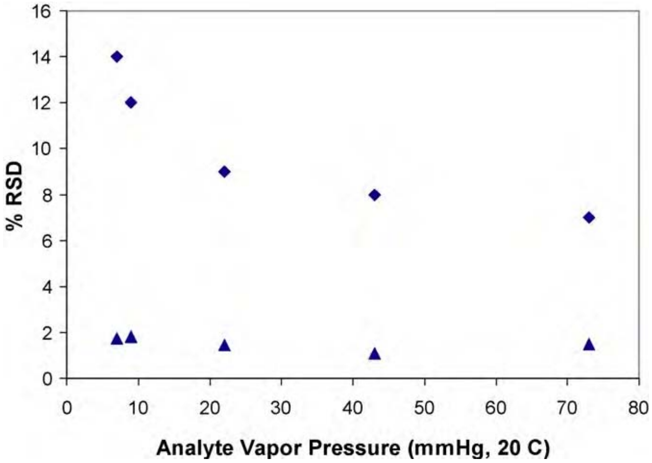

Fig. 1. A plot of %RSD as a function of compound vapor pressure for the 4 ppm (▲) and 24 ppm (♦) gas standards.

a general rule, the syringe plunger was allowed to move up and down for a minimum of five times before a final aspiration was made. Once the pre-extraction analysis was completed and the appropriate volume of extractant was added, the flask was placed in the preheated oven for 8 min. The oven was preheated to 63 °C for acetone, and 73 °C for methanol. This allowed solvent vapor to saturate the headspace of the extraction vessel. To induce rapid condensation and co-extraction of headspace analytes, the flask was removed from the oven and placed under running tap water for 2–3 min. Following a 1–2 min equilibration period, 200 μL aliquots of the headspace were subjected to GC analysis. Prior to collection, the condensate was swirled gently to ensure proper mixing with the droplets. By gently swirling or rotating the flask, the condensate was allowed to mix with any droplets adhering to the walls of the extraction vessel. The 250-mL extraction flask includes valved outlet ports to facitate collection of the condensate. For the round bottom extraction flasks, the condensate was siphoned off with a syringe before removing the Suba seals. 1 μL aliquots of the liquid collected from each extraction vessel was then analyzed by GC.

2.5. Safety considerations

To minimize the safety risk from accidental breakage of pressurized glassware, large volumes of solvent should be avoided, and the extraction flask should be wrapped with duct tape. To avoid the inhalation of solvent or solute vapor, all procedure related to DVE should be conducted in a fume hood. Also, the oven used to heat the extractor should be equipped with a hood extractor.

3. Results and discussion

3.1. Gas standard reproducibility study

If the concentration of VOCs or the vapor load in the SDB is too high, condensation of the less volatile components in the gas stream is likely to occur. A state of high vapor load can persist if too many analytes are added to the SDB. This could potentially impact the relative concentration and the %RSD of each analyte in the gas standard. For this reason, a study was conducted to monitor both the %RSD and the relative chromatographic response of each component in the gas standard over the course of 4 days. It was clear from the outset that a state of over saturation existed for the 24 ppm standard, as some level of condensation was observed. This was later confirmed by the GC data which yielded a %RSD ($n = 5$) ranging from 6.8% for ethyl acetate to 13.9% for o-xylene. Furthermore, a plot of this data as a function of vapor pressure for the 24 ppm standard (Fig. 1, upper trace), confirmed our expectation that the lower vapor pressure analytes resulted in higher %RSD. It also suggests that the %RSD is a useful indicator of gas phase integrity.

To test this premise, the study was repeated using a 4 ppm standard. Compared to the profile of the 24 ppm standard depicted in Fig. 1, the %RSD of the 4 ppm standard appears to be less sensitive to changes in vapor pressure. In the case of the latter, condensation was not observed, the within-day %RSD was consistently lower, and the process was repeatable from day to day (see data in Table 2). It is reasonable to expect that any significant changes in the equilibrium concentration of the analytes should be reflected in a corresponding change in the relative area percent of the peaks in the chromatogram. In this case, however, there were no substantial changes in peak profile during the testing period (see Table 3). Rather, the relative area percent for all analytes remained consistent from run to run. These results confirm that at the 4 ppm concentration level, the total vapor load in SDB is not high enough to compromise the integrity of the analytes in the gas phase.

3.2. Solvent considerations

In a volume of air at standard pressure and ambient temperature, the molecules would typically occupy approximately 0.2% of the overall volume, but as much as 50% of the volume in the liquid phase [39]. Thus, one obvious advantage of a pre-

Table 3
The relative area percent (RAP) for the compounds in the headspace of the 4 ppm gas standard ($n = 5$). The GC data were generated over a period of 4 days using injection volumes of 100 μL.

Compounds	RAP Day 1	%RSD	RAP Day 2	%RSD	RAP Day 3	%RSD	RAP Day 4	%RSD
Ethyl acetate	10.3	2.3	10.2	0.6	10.1	0.6	10.1	0.3
Isopropyl acetate	12.1	1.2	12.1	0.5	12.0	0.9	12.1	0.2
Toluene	26.1	1.0	26.1	0.2	26.0	0.4	26.1	0.2
p-Xylene	25.1	0.7	25.1	0.3	25.2	0.7	25.1	0.3
o-Xylene	26.4	1.7	26.5	0.4	26.6	0.3	26.6	0.1

Table 4
Extraction efficiencies (%EF) and area response (AREA) data for analytes in the headspace of a 92 ppb gas standard before and after treatment with 0.60 mL of acetone in a 250 mL extraction flask ($n = 3$).

Compounds	AREA before	%RSD	AREA after	%RSD	%EF	%RSD
Ethyl acetate	156	1	24	5	85	1
Isopropyl acetate	207	4	22	12	89	1
Toluene	380	1	33	10	91	1
p-Xylene	361	1	14	11	96	0
o-Xylene	384	2	11	17	97	1

Table 5
Extraction efficiencies (%EF) and area response (AREA) data for analytes in the headspace of a 92 ppb gas standard before and after treatment with 0.60 mL of methanol in a 250 mL extraction flask ($n = 3$).

Compounds	AREA before	%RSD	AREA after	%RSD	%EF	%RSD
Ethyl acetate	158	3	31	2	80	1
Isopropyl acetate	210	2	30	12	86	2
Toluene	399	2	75	4	81	1
p-Xylene	377	1	33	5	91	1
o-Xylene	404	1	28	11	93	1

concentration scheme based on a gas-to-liquid transition is that it could lead to significant and efficient pre-concentration of airborne analytes. However, the choice of solvent is critical to the success of DVE. In addition to solubility considerations, the extracting solvent should produce a high enough vapor pressure to satisfy the high partial pressure and the high saturation level required for condensation. Also, the chromatographic profile of the solvent should be such as not to interfere with the other peaks in the chromatogram. While other solvents can be used to harvest the VOCs, acetone and methanol are two solvents that meet the above criteria without causing significant chromatographic interference or significant safety risk. However, since acetone resulted in higher overall extraction efficiencies (see Tables 4 and 5) than methanol, most of the activities in this feasibility study was centered around acetone. To optimize the volume of acetone needed for dispersive vapor extraction of the headspace, a 92 ppb standard was prepared by diluting 10.0 mL of the 2.3 ppm gas standard in a flask containing 250 mL of nitrogen. This mixture was treated and analyzed according to the extraction and analysis procedure outlined in this paper. A graph of the area response of headspace analytes as a function of acetone volume is shown in Fig. 2. The graph shows a progressive decrease in area response of headspace analytes with increasing acetone volume, up to about 500 μL. Beyond this point, the response begins to plateau, as the optimum volume is approached. Prior to this, the volume of acetone is too small to bring about vapor saturation and condensation. Consequently, very little extraction occurs. For safety reasons, volumes larger than 700 μL were not used. A pressure-reinforced vessel is needed to capitalize on the benefits of larger extraction volumes. However, given the flatness of the response in this region of the curve, and the extraction efficiencies shown in Table 4, the modest gains from the additional volume is not worth the potential safety risk. It should also be noted that the flat region of the curve represents the equilibrium limit of the system, not the solubility limit of the solvent. If necessary, it would be more practical to remove the condensate and re-extract the headspace, but the overall extraction efficiency must be weighed against possible dilution effect from the combined extract.

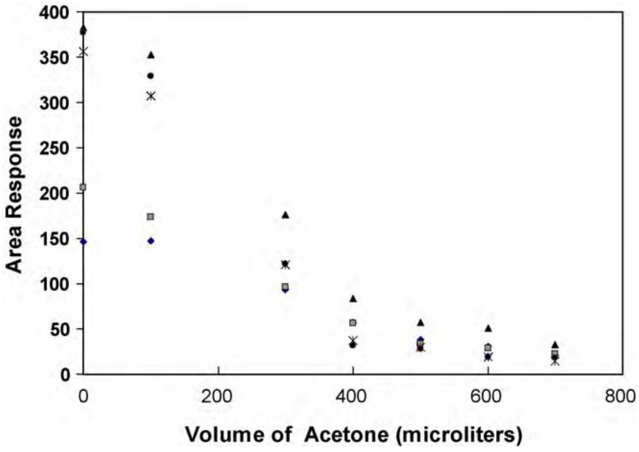

Fig. 2. The effect of acetone volume on the removal of the ethyl acetate (♦), isopropyl acetate (■), toluene (▲), p-xylene (*), and o-xylene (●) from the headspace of a 92 ppb gas standard in a 250-mL extraction flask.

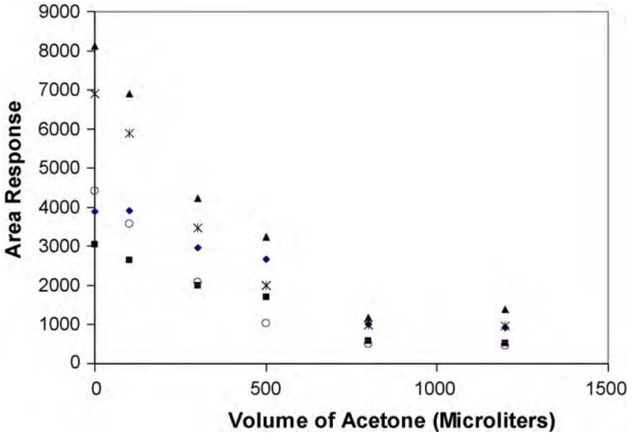

Fig. 3. The effect of acetone volume on the removal of the ethyl acetate (♦), isopropyl acetate (■), toluene (▲), p-xylene (*), and o-xylene (○) from the headspace of a 1.3 ppm (1.6 for p-xylene) gas standard in a 500 mL extraction flask.

An analysis of the graph in the region from 0 to about 400 μL shows that the slopes are steeper for the less volatile compounds, suggesting that the method would be more sensitive to less volatile analyte if the solvent volume is inadequate. However, that discrimination breaks down between 500 and 700 μL where the slopes flatten and begin to converge. This suggests that if larger volumes (and possibly higher pressures) are used, and the point of total convergence is achieved, the method should be equally sensitive to the type of compounds it is designed to extract. As Fig. 3 shows, a similar trend was observed for a 500 mL flask in which a 1.3 ppm standard (1.6 ppm for p-xylene) was extracted and 500 μL aliquots were analyzed. While the trend appears to be independent of concentration and the slopes did flatten out as anticipated, the convergence was not as noticeable, a subtle hint to the superiority of smaller extraction flasks. Similar optimization profiles were obtained for methanol in a 250 mL flask. Changing the flask size required a proportionate change in the solvent volume.

The above observations are consistent with expected distribution of VOCs between a liquid and gas. At low concentration, the partitioning of VOCs between the solvent and the gas phase is governed by Henry's law:

$$S_A = K_A P_A$$

where S_A is the solubility of solute A in solution, K_A is Henry's constant for solute A, and P_A is the partial pressure of solute A. Moreover, the mole fraction for a given VOC in the gaseous mixture can be predicted using the relationship:

$$\frac{n_A}{n} = \frac{P_A}{P}$$

where n_A is the mole of solute A, n is the total mole, and P is the total pressure. By combining these equations as shown below:

$$S_A = \frac{K_A n_A P}{n}$$

the solubility of the analyte in the solvent can be expressed in terms of the total overall pressure. Based on this combined relationship, the solubility of the solute is expected to increase as the overall pressure increases. Since the solvent is the largest contributor to the overall pressure of the gas, the increased solubility would largely be the result of the vapor pressure of the solvent. Therefore, at low solvent volumes where the vapor pressure is not particularly high, the extraction efficiency is observed to be relatively low. Under the given experimental condition, the highest extraction is achieved when the volume of the solvent is large enough to saturate the gas phase.

3.3. *Cooling consideration*

The flask is cooled with running tap water for about 2 min to remove the latent heat from the vapor, and bring about vapor saturation and condensation. When sufficient cooling has occurred, aerosol-like nuclei or possibly microscopic solvent droplets are formed within the vapor. Once formed, these entities can induce condensation and co-extraction of airborne VOCs at much lower partial pressure than is normally required for the pure VOCs. Interaction of the solvent aerosol with the bulk vapor would eventually lead to mass transfer of VOCs to the solvent, and aggregation of the small droplets into larger ones. It is important that a state of saturation/over saturation is maintained if the aerosol nuclei are to survive. If the vapor is unsaturated because the volume of solvent it less than ideal, the nuclei will evaporate when the flask returns to ambient temperature, and very little VOCs will be removed from the headspace.

3.4. *Extraction efficiency*

The headspace extraction efficiency was determined by analyzing the headspace composition of the analytes before and after treatment with either acetone or methanol. All standard were prepared and analyzed according to the procedure described in this paper. Tables 4 and 5 summarize results obtained using a 92 ppb standard in the 250 mL flask and 0.60 mL of solvent. The extraction recoveries ranged between 85 and 97% for acetone, and 80 and 93% for methanol. Acetone appears to be more effective at removing analytes from the headspace. This is partly due to better solvent–solute interaction, and higher solvent vapor pressure. The high volatility of acetone allows it to saturate the headspace above the condensate and, as a corollary benefit, minimize the amount of analyte returning to the headspace. While other solvents may just be as effective at dissolving the solute, vapor pressure and chromatographic concerns may limit their usefulness. The chromatograms in Fig. 4 were generated using a 40 ppb standard. They show the typical profile of the analytes in the headspace before and after treatment with acetone. Using this solvent for DVE resulted in a significant reduction of the analytes in the headspace. For comparison purposes, 1 μL of the condensed phase was also analyzed. The resulting chromatogram is shown in Fig. 5. The upper trace represents the analytes in the condensed phase. The lower trace is a profile of the analyte remaining in or returning to the headspace. From these chromatograms it can be shown that a reduction of analytes from the headspace resulted in a corresponding increase of the same analytes in the condensed phase.

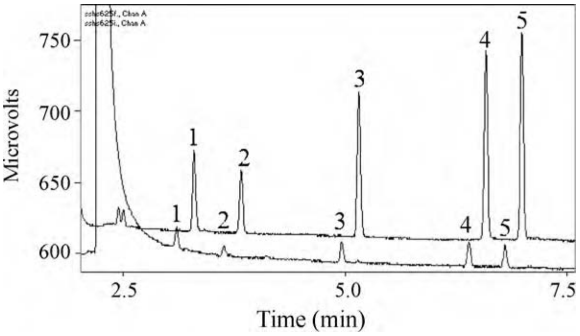

Fig. 4. Typical chromatograms of a 40 ppb mixture showing headspace analyte response before (upper trace) and after (lower trace) acetone treatment. The analytes are ethyl acetate (1), isopropyl acetate (2), toluene (3), p-xylene (4), and o-xylene (5).

3.5. *Calibration and flask volume consideration*

The calibration study was conducted using the 250 and 500 mL extraction flasks. Each flask was spiked with a proportionate amount of solvent, and analyte, and then subjected to the experimental protocol described in this paper. On closer examination of the calibration data in Table 6, it can be seen that the slope sensitivity increased with decreasing vapor pressure and decreasing flask volume. Similar trends were observed in preliminary data generated using a 100 mL flask. The vapor pressure trend is not unexpected since analytes with lower vapor pressure would condense first. The flask volume trend points to a space dependence effect. The smaller flask lends itself to more rapid heat reduction, with proportionately more of the vapor being condensed. Also,

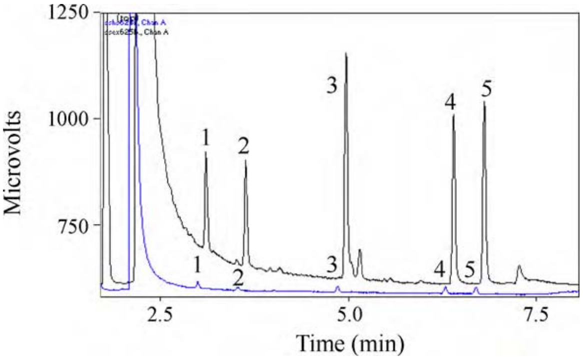

Fig. 5. Typical chromatograms of a 40 ppb mixture showing the analytes in the condensed phase (upper trace) and the headspace (lower trace) following acetone treatment. The analytes are ethyl acetate (1), isopropyl acetate (2), toluene (3), p-xylene (4), and o-xylene (5).

Table 6
A summary of the calibration and vapor pressure data for analytes extracted in the 250 mL flask (F250) and the 500 mL flask (F500).

Compounds	Vapor pressure (mm Hg, 20 °C)	F250 slope	F250 R-squared	F250 intercept	F500 slope	F500 R-squared	F500 intercept
Ethyl acetate	73	18.953	0.9968	−61.386	14.946	0.991	−7.625
Isopropyl acetate	43	22.724	0.9922	−40.829	19.152	0.9624	4.45
Toluene	22	56.096	0.9942	−42.243	33.598	0.9924	93.35
p-Xylene	9	40.686	0.9939	−108.06	26.913	0.9927	0.85
o-Xylene	7	42.031	0.9908	−90.943	28.163	0.9927	9.975

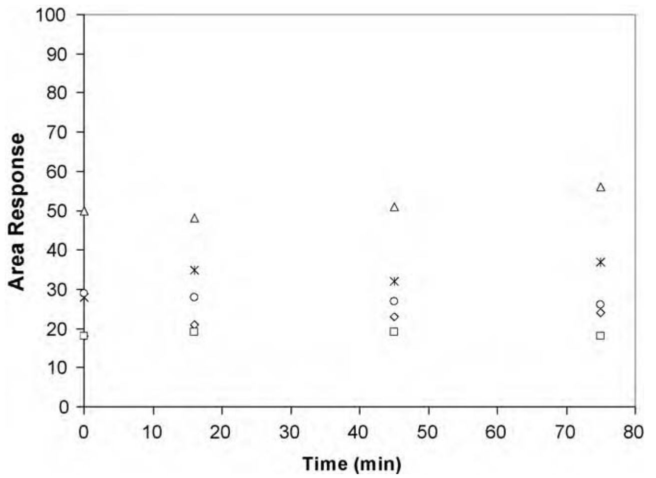

Fig. 6. Graph of headspace analyte response as a function of time following methanol extraction. The analytes include ethyl acetate (◇), isopropyl acetate (□), toluene (△), o-xylene (*), and p-xylene (◯).

because condensation is initiated on the walls of the extracting vessel, a smaller flask facilitates faster transport and uptake of analytes into the droplets. These findings suggest that temperature reduction and vapor condensation are critical factors in the dispersive vapor extraction cycle. Future efforts would be directed to creating a series of smaller extraction vessels in which air samples can be extracted and the extract combined. It is anticipated that use of more efficient heating and cooling technology would reduce analysis time and enhance sensitivity.

3.6. *Other considerations*

Concerns about whether or not the condensate was losing significant amounts of analytes to the headspace following extraction were ruled out by the work illustrated in Fig. 6. This experiment was conducted over a longer period of time than is required to process the sample. However, if a leak occurs in the extraction vessel or the headspace pressure decreases substantially before the condensate is removed, some loss can be realized as equilibrium is re-established. It is therefore important that the system is routinely and carefully checked for leaks.

4. Conclusion

The foregoing study demonstrates that DVE is a feasible extraction procedure for the removal of selected VOCs from gaseous mixtures. Compared to traditional solvent extraction procedures, DVE provides an alternative technique for the rapid and efficient removal of VOCs from gaseous matrices, without the use of large volumes of solvents. The technique resulted in extraction efficiencies between 80 and 97% for the analytes tested. Because of its simplicity and the relatively short sampling time, rapid analysis and high sample throughput would be possible. Also, because the general trend in slope sensitivity favors analytes of lower vapor pressure, the application would be broadened to include more semi volatiles organic compounds (SVOCs). These studies will include the quantitation of simulated and real-world samples.

References

[1] K. Demeestere, J. Dewulf, B. De Witte, H. Van Langenhove, J. Chromatogr. A 1153 (1–2) (2007) 130–144.
[2] L.C.A. Amorim, Z. Cardeal, L. de, J. Chromatogr. B 853 (1–2) (2007) 1–9.
[3] K. Demeestere, J. Dewulf, K. De Roo, B. De Witte, P. De Wispelaere, H. Van Langenhove, J. Chromatogr. A 1186 (1–2) (2008) 348–357.
[4] F.J. Santos, M.T. Galceran, Trends Anal. Chem. 21 (2002) 672.
[5] N. Ochiai, S. Daishima, D.B. Cardin, J. Environ. Monit. 5 (2003) 997.
[6] M. Navazo, N. Durana, L. Alonso, J.A. García, J.L. Ilardia, M.C. Gómez, G. Gangoiti, Int. J. Environ. Anal. Chem. 83 (2003) 199.
[7] US EPA Method 0030, US Environmental Protection Agency, Cincinnati, OH, 1986.
[8] US EPA Method 0031, US Environmental Protection Agency, Cincinnati, OH, 1996.
[9] S.L. Trabue, K.D. Scoggin, H. Li, R. Burns, H. Xin, Environ. Sci. Technol. 42 (10) (2008) 3745–3750.
[10] W.K. Reagen, K.R. Lindstrom, K.L. Thompson, J.M. Flaherty, J. Occup. Environ. Hyg. 1 (9) (2004) 559–569.
[11] K. Dettmer, W. Engewald, Anal. Bioanal. Chem. 373 (2002) 490.
[12] Q.-L. Li, D.-X. Yuan, Q.-M. Lin, J. Chromatogr. A 1026 (2004) 283.
[13] US EPA Method 5035, US Environmental Protection Agency, Cincinnati, OH, 1996.
[14] R. Barro, S. Ares, C. Garcia-Jares, M. Llompart, R. Cela, J. Chromatogr. A 1045 (2004) 189.
[15] G.M. Polzin, R.E. Kosa-Maines, D.L. Ashley, C.H. Watson, Environ. Sci. Technol. 41 (4) (2007) 1297–1302.
[16] V. Larroque, V. Desauziers, P. Mocho, J. Environ. Monit. 8 (2006) 106.
[17] V. Larroque, V. Desauziers, P. Mocho, J. Chromatogr. A 1124 (2006) 106–111.
[18] M. Hippelein, Chemosphere 65 (2006) 271.
[19] L.S. Ritter, E.C. Meurer, I. Cotte-Rodriguez, M.N. Eberlin, R.G. Cooks, Analyst 128 (2003) 1119.
[20] N.C. Bouvier-Brown, R. Holzinger, K. Palitzsch, A.H. Goldstein, J. Chromatogr. A 1161 (1–2) (2007) 113–120.
[21] V.G. Berezkin, E.D. Marakov, B.V. Stolyarov, J. Chromatogr. A 985 (2003) 63.
[22] Y. Saito, I. Ueta, K. Gotera, M. Ogawa, H. Wada, K. Gino, J. Chromatogr. A 1106 (2006) 190.
[23] J. Dewulf, H. Van Langenhove, G. Wittmann, Trends Anal. Chem. 21 (2002) 637.
[24] T.-Y. Lin, U. Sree, S.-H. Tseng, K.H. Chiu, C.-H. Wu, J.-G. Lo, Atmos. Environ. 38 (2004) 4111.
[25] K.C. Clemitshaw, Crit. Rev. Environ. Sci. Technol. 34 (2004) 1.
[26] M. Michulec, W. Wardencki, M. Partyka, Namiesnik, J. Crit. Rev. Anal. Chem. 35 (2005) 117.
[27] S. Naquin, Z. Frensley, N. Chong, B. Ooi, Abstracts 55th Southeast Regional Meeting of the American Chemical Society, Atlanta, GA, November 16–19, 2003, p. 203.
[28] C.-T Chang, B.-Y. Chen, J. Hazard. Mater. 153 (3) (2008) 1262–1269.
[29] L.N Moskvin, T.G. Nikitina, J. Anal. Chem. 59 (2004) 2.
[30] A. Kloskowski, M. Pilarczyk, Namiesnik, J. Anal. Chem. 32 (2002) 301.
[31] T.N. Kalnes, B.K. Glover, L.F. Smith, N.H. Scott, United States Patent 5,849,979, December 15 (1998).
[32] B. Zabiegala, T. Górecki, Namiesnik, J. Anal. Chem. 75 (2003) 3182.
[33] B. Zabiegala, M. Partyka, T. Górecki, J. Namiesnik, J. Chromatogr. A 1117 (2006) 19.
[34] S. Zampolli, P. Betti, I. Elmi, E. Dalcanale, Chem. Commun. (2007) 2790–2792.
[35] US EPA Method 0040, US Environmental Protection Agency, Cincinnati, OH, 1996.
[36] US EPA Method 5021A, US Environmental Protection Agency, Cincinnati, OH, 1996.
[37] US EPA Method TO-15, US Environmental Protection Agency, Cincinnati, OH, 1999.
[38] B.W. Jervis, J. Destieux, J. Jimenez, D. Martinez, IEE Proc. Sci., Meas. Technol. 150 (3) (2003) 97–106.
[39] J.R. Holton, J.A. Curry, J.A. Pyle, Encyclopedia of Atmospheric Science, vol. 1, Academic Press, New York, London, 2003, p. 351.