Use of sequential purging with the static headspace method to quantify gasoline contamination

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Abstract

The static headspace method used with portable gas chromatographs has become an important means of field screening environmental samples for gasoline contamination. A major limitation in using this method is the simultaneous detection (coelution) of other volatile gasoline constituents with those of interest. This is particularly problematic in the quantitation of methyl-t-butyl ether (MTBE), benzene and toluene. A sequential purging technique was used with static headspace analysis to remove coeluting compounds and to improve the accuracy in the quantitation of MTBE and aromatic constituents. Aqueous constituent concentrations determined using sequential purging were generally within 20% of those determined from laboratory purge and trap/gas chromatography (EPA method SW 846-602) analyses. Without sequential purging, constituent concentrations determined using the static headspace method were found to be 2 to over 10 times that of laboratory analyses. Further, in very contaminated samples, sequential purging permitted quantitation of constituents which were not resolvable in the initial headspace analysis due to coelution.

1. Introduction

In performing site assessments for gasoline contamination, environmental samples are usually analyzed for benzene, toluene, ethylbenzene, and the xylene isomers (collectively referred to as BTEX). Frequently, methyl-t-butyl ether (MTBE), an octane enhancing additive in gasoline, is also a target compound. These compounds are typically analyzed in the laboratory by purge and trap concentration (EPA

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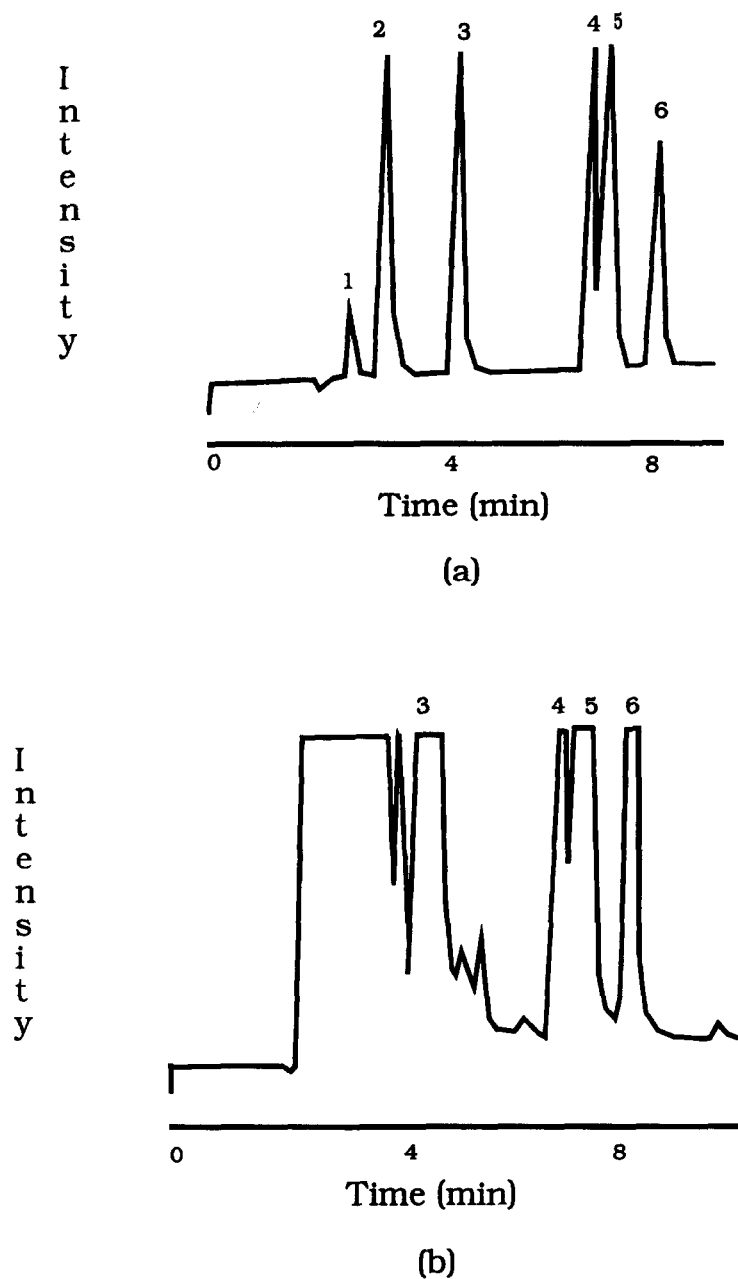
Fig. 1. Chromatograms of (a) an aqueous standard headspace and (b) a highly gasoline-contaminated groundwater sample headspace. Peak numbers: 1 – MTBE; 2 – benzene; 3 – toluene; 4 – ethylbenzene; 5 – *m,p*-xylene; 6 – *o*-xylene.

method SW 846-5030), followed by gas chromatography or gas chromatography/mass spectroscopy, using EPA methods SW 846-602 or -624 for wastewater and -8020 or -8240 for soil [1]. To obtain real-time data to guide field investigations at sites contaminated with volatile organic constituents, the static headspace method with portable gas chromatography is increasingly being used [2–7]. We have found two major disparities between the results obtained from these methods. Firstly, highly contaminated samples can yield unresolved analyte peaks (non-detections) with the static headspace method. Secondly, the static headspace quantitation of MTBE, benzene and toluene are often elevated relative to purge and trap results. This second disparity tends to increase as the contamination level increases [8].

One possible cause of the above disparities is the coelution (simultaneous detection) of target compounds with other constituents of gasoline. Fig. 1 illustrates headspace chromatograms of a gasoline contaminated groundwater sample and an aqueous standard. The groundwater chromatogram clearly exhibits many gasoline constituent peaks, in addition to those of MTBE and BTEX. As illustrated in Fig. 1, coelution may cause non-detections, if the apex of the total response from the target analyte and coeluting constituent(s) falls outside the analyte's retention time window. In this case, MTBE (peak 1) and benzene (peak 2) were not resolved. Elevated analyte concentration will occur if the apex of the total response of the target analyte and coeluting constituent(s) falls within the analyte's retention time window. Here, toluene (peak 3) exhibits coelution and, hence, an elevated concentration.

An earlier study was conducted to identify the constituents in gasoline which coeluted with MTBE and BTEX using gas chromatography–mass spectroscopy [9]. The coeluting compounds identified by the GC/MS analysis are presented in Table 1.

Table 1
Compounds found to coelute with MTBE, benzene, toluene, ethylbenzene and the xylene isomers

Compound	H_i^{11}	Coeluting compound	H_j^{10}
MTBE	0.02^{11}	*n*-pentane	50.5
		2-methylpentane	68.7
		3-methylpentane	68.5
		2-methyl-1-pentene	11.4
		Cyclopentene	NA
		2,3-dimethylbutane	52.5
		n-hexane	68.7
Benzene	0.22	1-methylcyclopropane	NA
		Cyclohexene	NA
		Cyclohexane	7.3
		2-methylhexane	140
Toluene	0.27	2,3,3-trimethylpentane	NA
		2,3,4-trimethylpentane	76.8
		2,3-dimethylhexane	NA
Ethylbenzene	0.32	NF	
m-, *p*-xylene	0.28	NF	
o-xylene	0.20	NF	

H_i: dimensionless Henry's law constant; NA: not available; NF: no coelution found.

The major coeluting constituents were found to be light hydrocarbons, predominantly alkanes and alkenes. These compounds are known to have relatively high Henry's law constants compared to MTBE and BTEX [10, 11]. McAullife [12] presented a technique of successive multiphase equilibrations (termed here sequential purging) to separate and quantitate a mixture of constituents that have contrasting Henry's law constants. A variation of this technique is presented in this study that is applicable to the commonly used static headspace method. The method was tested using standards and gasoline contaminated groundwater to evaluate its effectiveness to circumvent coelution and improve constituent quantitation.

2. Sequential purging theory

For analyzing water samples, the static headspace method consists of filling a 40 ml volatile organic analysis (VOA) vial with sample, bringing the sample to constant temperature, creating a headspace in the vial, agitating and equilibrating the vial at constant temperature, and analyzing the vapor phase. Quantitation is achieved through comparison of peak areas with those of aqueous standards. For soil analysis, the same general procedure is followed but here a known mass of contaminated soil is added to a vial containing a known amount of deionized water. To remove coeluting constituents from the aqueous phase and to better quantitate target analytes, an additional step is added to the above method. Following the initial vapor phase analysis, the headspace of the vial is purged with clean air. The sample is then reagitated, thermally re-equilibrated and reanalyzed. This procedure is repeated until there is a log-linear decrease in detector response versus purging increment. The log-linear response may then be extrapolated to the zeroth purging increment, and the coelution-free response determined for the target analyte. The theory underlying this procedure is developed below.

In an agitated vial of aqueous sample, equilibrium mass partitioning between the vapor and aqueous phases is described by

$$m_{io} = m_{iwe} + m_{ihse},$$ (1)

where m_{io} is the original mass of constituent i in the aqueous phase, m_{iwe} is the equilibrium mass of i in the aqueous phase and m_{ihse} is the equilibrium mass of i in the headspace (vapor phase). If each term in Eq. (1) is divided by the volume of water in the vial (V_w), Eq. (2) results:

$$m_{io}/V_w = m_{iwe}/V_w + m_{ihse}/V_w.$$ (2)

Multiplication of the right-hand-term by V_{hs}/V_{hs} (where V_{hs} is the volume of headspace) yields Eq. (3), written in terms of concentration:

$$C_{iwo} = C_{iwe} + (C_{ihse} \cdot V_{hs}/V_w),$$ (3)

where C_{iwo} is the original aqueous concentration of i, C_{iwe} is the equilibrium aqueous concentration of i and C_{ihse} is the equilibrium headspace concentration of constituent i. The equilibrium between the vapor phase concentration of a dilute solution and its aqueous phase concentration is described by Henry's law:

$$C_{ihse} = H_i \cdot C_{iwe},\tag{4}$$

with H_i representing the dimensionless Henry's law constant. Substituting Eq. (4) into Eq. (3), factoring and rearranging yields Eq. (5):

$$C_{iwe}/C_{iwo} = 1/(1 + H_i \cdot V_{hs}/V_w).\tag{5}$$

Eq. (5) shows that the relative volatile loss of a constituent from the aqueous phase, following equilibrium vapor partitioning, is a function of the Henry's law constant and the ratio of headspace volume to water volume. Given the Henry's law constants tabulated in Table 1, relative to MTBE and BTEX, the aqueous concentrations of the coeluting compounds would be expected to be significantly depleted following vapor phase equilibration for a given headspace to water ratio. The preferential partitioning of the coeluting compounds into the vapor phase explains why coelution is a significant problem in performing headspace analysis on materials contaminated with gasoline.

It should be realized that if the headspace of the vial was subsequently purged with clean air and the aqueous and vapor phases re-equilibrated, the remaining aqueous concentrations would again decrease by the same concentration fraction as described by Eq. (5). The change in aqueous concentration following purging and re-equilibration can be expressed by an expansion of Eq. (5), as follows:

$$C_{iwe}(n) = C_{iwo} \cdot [1/(1 + H_i \cdot V_{hs}/V_w)]^{n+1},\tag{6}$$

where n is a purging and re-equilibration increment (i.e., $n = 0$ would apply to the initial headspace equilibration). Substitution of the Henry's law constants in Table 1 into Eq. (6) reveals that only several purging increments would be needed to essentially rid a gasoline contaminated sample of coeluting compounds; yet, significant concentrations of target analytes would remain in the sample.

In order to quantify the original amount of a target analyte in the sample, Eq. (6) may be rewritten as:

$$C_{ihse}(n) = H_i \cdot C_{iwo} \cdot [1/(1 + H_i \cdot V_{hs}/V_w)]^{n+1}$$
$$= C_{ihse}(0) \cdot [1/(1 + H_i \cdot V_{hs}/V_w)]^n.\tag{7}$$

Eq. (7) relates the coelution-free vapor concentration at the nth purging interval to the initial coelution-free vapor concentration (at $n = 0$). This equation is the more general form of that developed by McAullife [12] which was restricted to a V_{hs}/V_w equal to 1. Taking the logarithm of both sides of Eq. (7) yields:

$$\log[C_{ihse}(n)] = \log[C_{ihse}(0)] + n \cdot \log[1/(1 + H_i \cdot V_{hs}/V_w)].\tag{8}$$

Eq. (8) predicts a log-linear change in coelution-free vapor concentration with purging increment. Eq. (8) may be written in terms of the GC detector response:

$$\log[R(n)] = \log[R(0)] + n \cdot \log[1/(1 + H_i \cdot V_{hs}/V_w)], \tag{9}$$

where R is expressed as peak area and equals $C_{ihse} \cdot Rf_i$, within the linear detector response range, and Rf_i is a response factor unique to the analyte. Eq. (9) predicts a log-linear change in coelution-free response with purging increment. As developed in McAullife [12], a plot of the logarithm of the response versus purging increment may therefore be used to determine when the response is coelution free, as well as the coelution-free response prior to purging. If there is coelution, the measured response is a summation of individual responses for the target and coeluting constituents (i.e., $R = C_x \cdot Rf_x + C_y \cdot Rf_y + \cdots$, where x and y refer to individual constituents). Since the target analyte and coeluting constituents will partition by different amounts, the measured response will not be log-linear until the coeluting constituents are purged. Once the plot becomes log-linear, it may be extrapolated to determine the y-intercept $(R(0))$.

Fig. 2 is an illustration of a theoretical sequential purging curve, generated using Eq. (9), of a headspace sample which initially had equal aqueous concentrations of benzene and one of its identified coeluting compounds, cyclohexane (assuming equal response factors), for a $V_{hs}/V_w = 0.33$. Included in Fig. 2 is the ratio of aqueous benzene concentration to aqueous cyclohexane concentration after each headspace purging increment. After only two purging increments, benzene would be expected to constitute 91% of the total remaining aqueous concentration. Following six purgings,
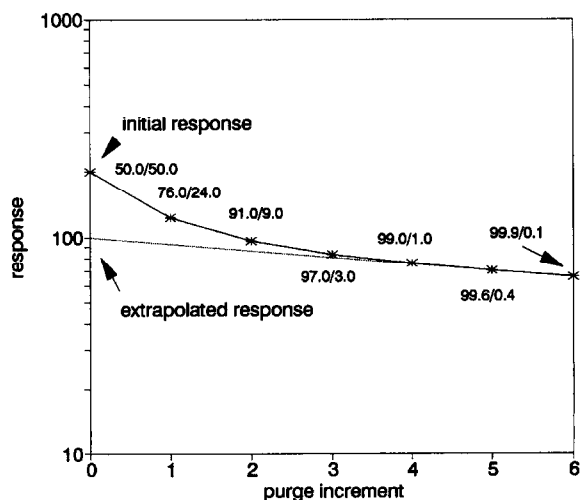

Fig. 2. Theoretical sequential purging curve of benzene and cyclohexane assuming equal response factors: $V_{hs}/V_w = 0.33$. Numbers indicate ratio of benzene/cyclohexane remaining in the aqueous phase at each purge interval.
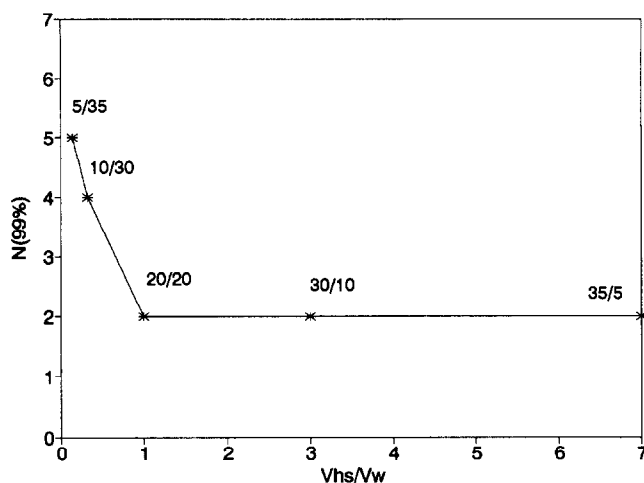
Fig. 3. Theoretical number of purging increments ($N(99\%)$) necessary to attain an aqueous phase consisting of $99^+\%$ benzene in an initially equal mixture of benzene and cyclohexane ($\#$s $= V_{hs}/V_w$).

benzene should constitute 99.9% of the total aqueous concentration. The regression of purging increments 4–6 resulted in the dashed line shown, extrapolating back to the coelution-free benzene response. The actual amount of purging necessary to achieve log-linearity will depend on the response factors for coeluting and target constituents, their concentrations and the volume of headspace/water ratio.

With respect to the volume of headspace/water ratio, increasing the ratio would require fewer purging increments to remove coeluting compounds. A theoretical sample, again containing benzene and cyclohexane, was assessed in order to determine the number of purging intervals for different V_{hs}/V_w ratios needed to achieve a sample where benzene was at least 99% of the mixture. As can be seen in Fig. 3, for a $V_{hs}/V_w > 1$, the number of sequential purgings needed to essentially deplete the cyclohexane to negligible levels was 2. The calculation assumed equal initial aqueous concentrations and equal response factors for the two compounds.

3. Experimental

An HNU Systems, Inc. portable GC (model 311) was used to conduct the sequential purging experiments. It contained a Restek MXT-1® capillary column (30 m × 0.28 mm with a 1 μm polydimethyl-siloxane film). The injector temperature was set at 90 °C while the oven temperature was 75 °C. The instrument was equipped with an HNU Systems photoionization detector (PID) with a 10.2 eV lamp which was heated to 90 °C.

Aliquots of gasoline contaminated groundwater were analyzed using both the static headspace method and a purge and trap system consisting of a Perkin-Elmer model

3920B GC, an HNU PI-52-02 PID with a 10.2 eV lamp and a Perkin-Elmer flame ionization detector connected in series. Samples were introduced onto the column using a Tekmar Dynamic Headspace Concentrator (model 4000) and a Tekmar Automatic Laboratory Sampler (model ALS®). The column was packed, stainless steel (8 ft × 0.125 in. i.d.) containing 1% SP-1000 on 60/80 mesh Carbopack B.

Monthly, concentrated standards were made by placing 100 μl each of benzene, toluene, ethylbenzene and *m*- and *o*-xylene, and 200 μl of MTBE in purge and trap grade methanol to a total volume of 10 μl. The weight of each standard added was recorded in order to calculate the final concentrations. Daily standards were made by diluting 25 μl of concentrated standard to 250 ml in distilled, deionized water. One point calibrations were utilized on the portable GC while a five point calibration was utilized on the laboratory GC with an established QA/QC program.

Samples and standards were analyzed using 40 ml VOA vials from Supelco, Inc. (cat. no. 2-3298). Before sampling, 100 μl of a 24 000 ppm solution of mercuric chloride was added to each vial as a preservative [4]. The final preservative concentration was 60 ppm. Each vial was filled to overflowing with standard or sample and then capped with a Teflon®-lined silicone septum (Supelco cat. no. 2-3281) and a holed screw-cap (Supelco cat. no. 2-3283). After collection, field samples were placed, inverted, in either a portable water bath in the field for subsequent analysis, or in an ice-filled cooler and returned to the laboratory for analysis. When a sample was to be analyzed by the static headspace method, it was placed inverted in a temperature controlled water bath, 25.0 ± 0.2 °C. After thermal equilibrium had been established (approximately 15 min), a 22 gauge × 3.5″ spinal needle (Popper & Sons, Inc. no. 7307) was inserted through the septum of the inverted vial. A second needle (23 × 1.5″, no. 7039), with a 10 ml syringe, was then inserted through the septum. Care was taken to assure the tip of the spinal needle was at the highest point in the inverted vial to minimize bubbling within the sample vial. Ten ml of liquid was then withdrawn and both needles removed. The vial was then shaken by hand for 2 min to speed phase equilibrium. After shaking, the vial was replaced in the bath and allowed to achieve chemical and thermal equilibrium (generally in 5 min).

To perform sequential purging, the vial was righted, two short needles were inserted through the septum and 50 ml of clean air (5 · V_{hs}) was injected through the headspace using a syringe attached to one of the needles. Following purging, the vial was again inverted, shaken for 2 min and placed back in the water bath. Between purging and/or analysis increments, vials were allowed to re-equilibrate for a minimum of 5 min in the water bath.

The peak areas versus the number of purging increments for MTBE and BTEX were plotted on semi-log paper. Purging was continued until three peak areas for each constituent decreased in a log-linear fashion. Log-linear regressions were performed, using the three linear points for each constituent, to determine the *y*-axis intercepts (i.e., the coelution-free responses). These responses were then used to calculate the concentrations of each target analyte (Eq. (10)):

$$C_{iso} = C_{istd} \cdot (R_{isx}/R_{istd}), \tag{10}$$

where C_{iso} is the original concentration of constituent i in the sample, C_{istd} is the concentration of i in the standard, R_{isx} is the extrapolated response of i in the sample and R_{istd} is the standard response of i.

4. Results and discussion

Aqueous standards containing MTBE and BTEX of differing concentrations were analyzed to initially test the sequential purging method. The method was initially tested at a low V_{hs}/V_w ratio of 0.33 to obtain a sufficient number of purging increments for regression analysis, to perfect experimental procedures and to evaluate the extent to which experimental results fit the above theory for sequential purging. A typical plot of log response versus purging interval for a MTBE and BTEX aqueous standard is shown in Fig. 4. The responses were found to decrease in a log-linear fashion, as predicted by the theory (Eq. (9)). Extrapolated responses were found to be within 2% of the initial responses. Also, the slopes of the best-fit lines were proportional to their Henry's law constants, as predicted by theory.

Water samples from three groundwater wells at a site of subsurface gasoline leakage were tested with the sequential purging method. One well was located near the source area of the leak and the other two wells were further downgradient, referred to here as the near-, mid- and far-field wells, respectively. Table 2 shows a comparison of sample concentrations from the wells as determined by the static headspace method with only a single equilibration, the sequential purging headspace method and purge and trap/GC. As can be seen by the reduction in percent difference values in Table 2, the
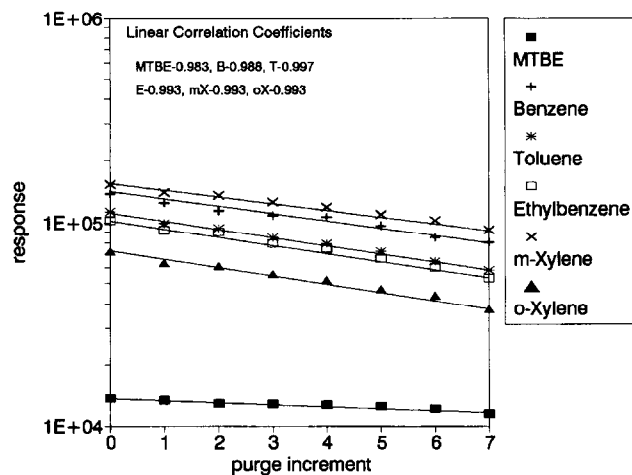

Fig. 4. Sequential purging curves for MTBE and BTEX standards. Absolute percent differences of extrapolated purging response vs. original response: MTBE – 0.41; B – 1.25; T – 0.93; E – 1.66; m,p-X – 0.73; o-X – 0.81.

Table 2

Comparison of concentrations (μg/l) of MTBE and BTEX for three groundwater samples as determined by single equilibration static headspace, sequential purging static headspace, and purge and trap

	Near-field			Mid-field			Far-field		
	HS_0	HS_{sp}	P&T	HS_0	HS_{sp}	P&T	HS_0	HS_{sp}	P&T
Response as concentration (μg/l)									
MTBE	25033	4251	3740	4681	896	775	0	0	40
Benzene	3810	3301	2548	906	592	646	62	62	57
Toluene	12088	10938	7741	179	76	83	88	10	7
Et-benzene	1667	1347	1258	126	104	135	66	63	62
Tot. xylene	12394	9599	8832	47	13	48	56	50	54
% difference vs. purge and trap									
MTBE	569.3	16.7		504.0	15.6		− 100	− 100	
Benzene	49.5	29.6		40.3	− 8.4		8.8	8.8	
Toluene	56.2	41.3		115.7	− 8.4		1157	42.9	
Et-benzene	32.5	7.1		− 6.7	− 23.0		6.4	1.6	
Tot. xylene	40.3	8.7		− 2.1	− 72.9		3.7	− 7.4	

% difference [(HS − P&T)/P&T] · 100; HS_0: single equilibration static headspace method; HS_{sp}: sequential purging static headspace method; P&T: purge and trap method.

correlation between purge and trap concentrations and those from the headspace method are greatly improved by performing sequential purging.

Fig. 5 compares chromatograms from the initial headspace injection (a) and an injection following the sixth headspace purging interval (b) from a highly contaminated monitoring well sample. It should be noted that coelution in the initial sample injection made the retention time identification of MTBE and benzene impossible. Following sequential purging all the target analytes were now resolved and could be quantitated.

Figs. 6–8 show representative sequential purging plots for MTBE, benzene and toluene, respectively, from one of the wells. Initial MTBE headspace concentrations were often more than an order of magnitude greater than coelution-free values as exemplified by Fig. 6. As illustrated in Fig. 7, initial benzene values were usually twice the coelution-free values, or were not initially detected at all. Fig. 8, the sequential purging plot for toluene, shows no detection until the fourth purging increment, and exemplifies the extent to which coelution may mask a target compound. Ethylbenzene and the xylenes were not noticeably affected by coelution in the mid- or far-field; however, there did appear to be some minor coelution occurring in the near field. As reported in Table 1, there were no compounds identified as coeluting with either ethylbenzene or the xylene isomers. The GC/MS analysis was performed using a fresh gasoline spiked sample whose composition may have differed from that of the gasoline at the contamination site. Alternatively, the coeluting compounds may be the products of microbial degradation of gasoline constituents.

An experiment was performed to evaluate how the volume of headspace in a vial may be adjusted to reduce the number of purge increments necessary to produce
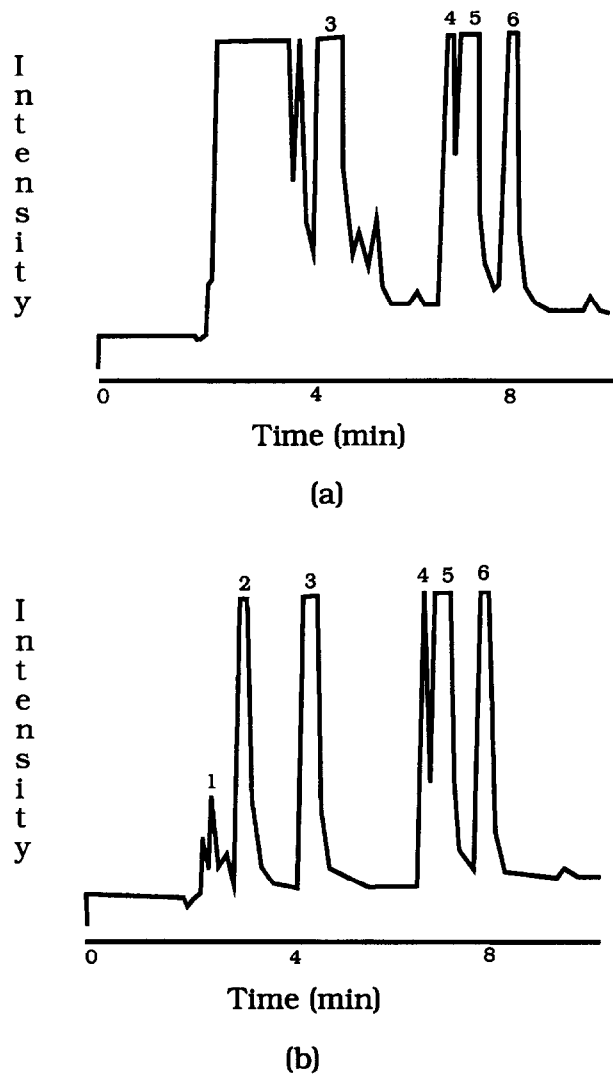
Fig. 5. Headspace chromatograms of a highly contaminated groundwater sample: (a) initial analysis and (b) after six sequential purgings. Peak numbers: 1 - MTBE; 2 - benzene; 3 - toluene; 4 - ethylbenzene; 5 - m,p-xylene; 6 - o-xylene.

linearity in the detector response. A split of an aqueous sample was then analyzed using both the 10/30 and 20/20 V_{hs}/V_w ratios. Five sequential purgings were required to achieve linear detector response for MTBE in the 10/30 sample but only three sequential purgings were needed in the 20/20 sample (Fig. 9). Peaks were identified with retention times that corresponded with benzene and toluene in the initial analysis of each headspace. The vial with the 20/20 ratio showed no peaks for benzene or
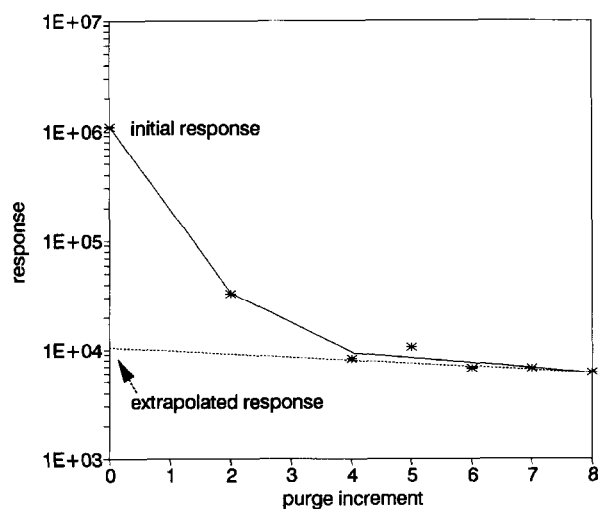
Fig. 6. Sequential purging curve of a gasoline contaminated groundwater sample containing MTBE.
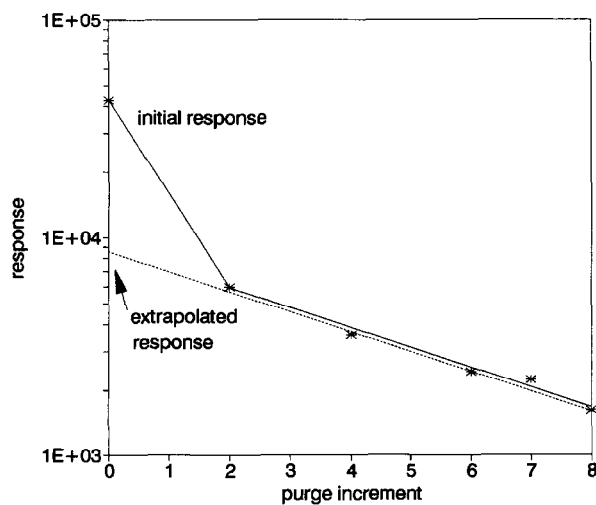

Fig. 7. Sequential purging curve of a gasoline contaminated groundwater sample containing benzene.

toluene after the first sequential purge. The 10/30 vial continued to show benzene and toluene until the fourth purge interval, when no peaks were recorded at the retention times for benzene or toluene. In terms of practical application, the use of V_{hs}/V_w ratios of one or greater can reduce the number of purgings needed to obtain coelution-free response.
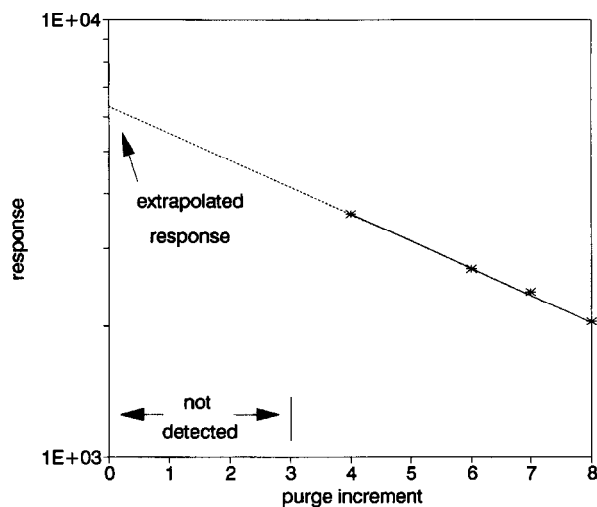
Fig. 8. Sequential purging curve of a gasoline contaminated groundwater sample containing toluene.
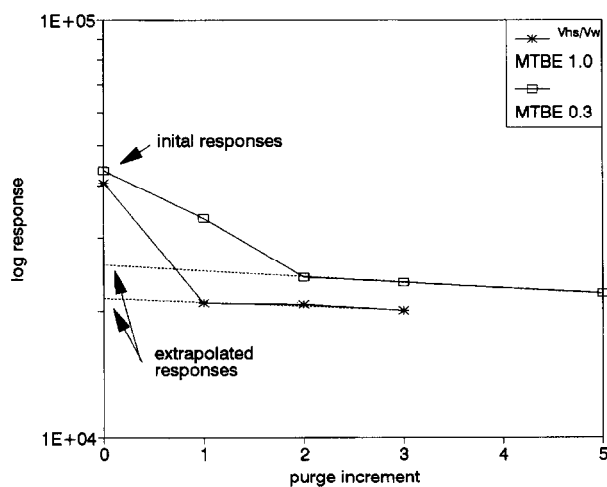

Fig. 9. A comparison of the log of the detector response for a sample containing MTBE at V_{hs}/V_w ratios of 0.3 and 1.0.

5. Conclusion

A sequential purging method has been shown to be useful in alleviating difficulties associated with coelution when analyzing gasoline contaminated environmental samples with the static headspace method and a portable gas chromatograph. The results obtained from sequential purging are generally within 20% of those obtained from

purge- and-trap analysis. In using the sequential purging method, it should be kept in mind that the efficiency of removing coeluting compounds will depend on the difference between the Henry's law constants of the target analytes and the coeluting compounds. For gasoline contamination, the contrast in Henry's law constants between target analytes and coeluting compounds is sufficiently large to permit purging of the coeluting compounds in just a few purging increments. The smaller the difference in Henry's law constants, the more purgings will be required to remove the coeluting compound(s). To increase the efficiency of the method in removing coeluting compounds, purging can be performed using a V_{hs}/V_w ratio equal to or greater than 1. Even then, sequential purging will require at least three headspace analyses per sample to verify and determine coelution-free response. Given this additional effort, the use of sequential purging and the number of analyses to be performed to improve quantitation will depend on data quality objectives.

Acknowledgements

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