Available online at www.sciencedirect.com
SCIENCE DIRECT®
Journal of Chromatography A, 983 (2003) 205–214
JOURNAL OF CHROMATOGRAPHY A
www.elsevier.com/locate/chroma

Headspace microdrop analysis—an alternative test method for gasoline diluent and benzene, toluene, ethylbenzene and xylenes in used engine oils

John M. Kokosa*, Andrzej Przyjazny
Science and Mathematics Department, Kettering University, 1700 West Third Avenue, Flint, MI 48504-4898, USA

Received 5 August 2002; received in revised form 7 October 2002; accepted 7 October 2002

Abstract

The primary standard test method used for the determination of gasoline diluent in used engine oils is method D 3525-93 of the American Society for Testing and Materials (ASTM), which involves direct injection of used oil onto a packed GC column and flame ionization detection. Recently, we have utilized a new headspace sampling method: headspace solvent microextraction (HSM), for GC and GC–MS analysis of gasoline diluent in used engine oils. High resolution capillary columns can be used without the necessity for the use of inlet cryogenic cooling or expensive sampling interfaces. This analytical method, which we generically refer to as headspace microdrop analysis yields results comparable to those obtained using the ASTM method, with the added benefit that it allows the quantification of individual volatile diluent components, including benzene, toluene, ethylbenzene and the xylenes.

Keywords: Headspace analysis; Microdrop analysis; Solvent microextraction; Extraction methods; Gasoline; Oils; Benzene; Toluene; Ethylbenzene; Xylenes

1. Introduction

The standard test method for the determination of gasoline diluent in used engine oils is method D 3525-93 [1]. The ASTM method involves analysis of oils by packed column gas chromatography using a flame ionization detector. Quantification of the gasoline content is accomplished by adding a known mass of tetradecane to the oil before injection. Comparison of the integrated peak areas of the gasoline fraction to the peak area for the tetradecane yields the fuel dilution percentage according to Eq. (1):

$$F = \frac{A_1 \cdot W_1 \cdot 100}{X_1 \cdot A_2} \quad (1)$$

where: F = fuel dilution, mass %; A_1 = area counts for the chromatographic peaks before the *n*-tetradecane peak; A_2 = area counts for the *n*-tetradecane peak; W_1 = mass of *n*-tetradecane used; and X_1 = mass of the sample used.

*Corresponding author. Tel.: +1-810-762-7929; fax: +1-810-762-9796.
E-mail address: jkokosa@kettering.edu (J.M. Kokosa).

0021-9673/02/$ – see front matter
PII: S0021-9673(02)01686-2

The repeatability expected in the method is 0.28% (m/m; absolute deviation values). The reproducibility expected in the method is 1.64% (m/m). The method states that bias cannot be estimated, however, since the method is considered to be empirical.

When the ASTM method was originally put into effect (as D 3525-76), and for following revisions, packed GC columns were chosen for the analysis since they were rugged and able to handle the relatively large amounts of sample injected. However, even packed columns are subject to contamination and degradation by the presence of oxidation products, including corrosive acids, as well as metal particulates, sludges, polymers and organometallic additives in the used oil [2]. Packed columns are also low resolution and do not allow acceptable separation and quantification of important contaminants, including benzene, toluene, ethylbenzene and the xylenes (the BTEX components).

High resolution chromatography capillary columns are not a good alternative for the method, however, since they are very susceptible to degradation by the types of contaminants present in used oils. A possible alternative to direct injection of the oil onto the GC column is to use headspace analysis [3]. Headspace analysis also has several deficiencies, however. Manual headspace sampling is difficult since the sample usually has to be heated and relatively large volumes of gas injected to increase sensitivities. Capillary columns also usually require the use of cryogenically cooled GC inlets to improve the resolution of low boiling constituents. Autosamplers are available for headspace analysis, but are expensive.

These problems can be overcome by the use of solid-phase microextraction (SPME) of the oil headspace, which can be accomplished with manual injection or with a specialized autosampler [2]. This technique does require good operator technique when performed manually, however. In addition, the fibers are expensive, fragile, have a relatively short life (~50–100 injections), and must be conditioned before each injection to avoid sample carryover. Furthermore, only a limited selection of stationary phases are available for the fibers.

An alternative to SPME is liquid-phase microextraction (LPME), which has been recently successfully developed through work in several labs to extract aqueous samples [4–19]. In its simplest form, LPME consists of suspending a microdrop of organic solvent at the tip of a syringe, which is immersed in the aqueous sample [5,6,8]. The analytes are extracted into the drop, which is then withdrawn into the syringe. The extract is then analyzed using GC or GC–MS. LPME is a very efficient, cost effective and simple extraction technique, which avoids any carryover problems associated with SPME, since the extracting solvent is replaced after each extraction. More recently, work in our [20–23] and other laboratories [24,25] has extended this technique to include headspace analysis, which can be rigorously described as headspace solvent microextraction (HSM). HSM is very similar to LPME except that microdrop of high boiling extracting solvent is exposed to the headspace of a sample. The drop is then withdrawn into the syringe and injected into the GC. The microdrop performs essentially the same function as the fiber in SPME: to extract and concentrate headspace components into a small volume of solvent, which can then be injected into the GC and analyzed. Since HSM and LPME are very similar extraction methods and are followed by GC, GC–MS, HPLC [16,17,19], capillary electrophoresis [18] or some other analysis method, we refer to these methods generically as microdrop analysis (MDA) and headspace microdrop analysis as HMDA.

2. Experimental

2.1. Extraction apparatus

The following work was accomplished using manual sampling and injection. A 2 ml PTFE–silicon–PTFE septum crimped autosampler vial (MicroLiter Analytical Supplies, Suwanee, GA, USA), containing a weighed sample of oil (0.5 ml) and 2.0 μl of ethyl acetate as an internal or surrogate standard, was allowed to equilibrate for 30 min with stirring (PTFE-coated micro-stir bar, Fisher Scientific) at 1200 rpm while clamped over a Barnstedt/Thermolyne (Dubuque IA, USA) digital stirrer, or without stirring at 50 °C in a Lab-Line (Rosemont, IL, USA) multi-well heater. After equilibration, the

headspace was sampled by puncturing the septum with a 10 μl Hamilton 701 syringe (No. 2 point style) containing 1 μl of extracting solvent. The tip of the needle was positioned 1 cm below the septum, and the syringe clamped in place. The solvent was slowly expelled from the syringe (approximately 3 s) to form a microdrop at the tip of the needle. Following the extraction (3 min), the drop was slowly withdrawn into the syringe, the syringe needle removed from the vial, and the solvent injected into the GC system for analysis. Syringes were cleaned between runs first with pentane using aspirator vacuum followed by drawing in and expelling out several portions of the extraction solvent, just before the following extraction.

2.2. Reagents and chemicals

Oil standards were prepared with SAE 10W-30 automotive oil (Citgo). The gasoline used for the vehicles in the study and for preparing standards was unleaded regular (Shell) purchased locally in the spring. Aromatic standards (benzene, toluene, ethylbenzene, and *o*-, *m*-, *p*-xylenes: BTEX), the extracting solvents (1-octanol and hexadecane), ethyl acetate and pentane were purchased from Sigma–Aldrich (HPLC grade or 99% minimum purity). Extracting solvents were distilled under vacuum (1 mm) to remove low-boiling impurities and stored in 0.5 ml fractions in 2 ml screw-top vials with a PTFE-lined septum. The vials were, in turn, stored in a polyethylene screw-top container in a sub-zero freezer, to minimize cross contamination. An extraction solvent vial for an experiment was stored in a capped polyethylene container at room temperature while being used.

Gasoline and BTEX standards were prepared in unused Citgo 10W-30 oil and vacuum distilled hexadecane. All standards were prepared by weighing samples before and after adding components. A 1.71% (m/m) gasoline in oil sample, used for extraction optimization, was prepared by adding 500 μl of gasoline to 25 ml of oil. Calibration curve standards were prepared by adding 500 μl of gasoline to 10 ml of oil and serially diluting by 1/2 to 4.199%, 2.213%, 1.052% and 0.4949% gasoline in oil.

BTEX calibration curve standards in oil were prepared by adding 25 μl of each BTEX component to 25 ml of oil and then serially diluting by 1/2 to 0.599%, 0.295%, 0.146% and 0.0711% total BTEX in oil.

A 1.83% mass % gasoline in hexadecane standard, used for direct-injection retention time calibration of the GC and GC–MS, was prepared by adding 100 μl of gasoline to 5 ml of hexadecane.

Prepared standards were stored at −20 °C in glass containers, which were, in turn, sealed in metal canisters.

Used oil samples were obtained from three vehicles, which used the same gasoline fuel. Two vehicles used 10W-30 oil and the third 5W-30 oil. Oil samples were obtained from the oil pan during oil changes and stored in completely filled 500 ml capped glass containers.

2.3. Instrumentation

The GC system used in this study was an Agilent 6890 equipped with a split–splitless injector and a flame ionization detection (FID) system. The fused-silica column used was 30 m length×0.25 mm diameter with 1.2 μm HP-5 (5% phenyl, dimethylsilicone) coating. The flow-rate was set at a constant 2.0 ml/min. The injector was operated in split mode (25/1 split) during the injection. The injector was set to 250 °C and the detector to 300 °C. The oven was programmed as follows: 35 °C for 5 min, 10 °C/min to 135 °C, 25 °C/min to 260 °C and held for 5 min (25 min run). The GC–MS used for analyte confirmation was an Agilent 5973 N. Chromatographic conditions for the GC–MS were identical to those used for GC. The mass spectrometer was operated in full scan mode from 35 to 350 amu.

ASTM method 3525-93 was modified to use the capillary column for HMDA chromatography. Oil samples (0.5 ml) were diluted with hexadecane (0.5 ml) and 10 μl of tetradecane then added with a syringe. A 0.1 μl portion of the diluted oil was injected under splitless conditions. Chromatographic conditions remained the same as for HMDA except the GC oven was ramped to 310 °C and held for 15 min to rid the column of oil.

3. Results and discussion

3.1. HMDA principles

Successful use of headspace microdrop analysis requires careful consideration of several parameters to ensure reproducible sampling. These include the sample/headspace volumes and their ratio, sampling temperature, sample agitation, equilibration time, sampling time, volume of the extracting solvent, the type of extracting solvent, the nature of the liquid or solid being extracted (in this case oil), and the volatility and concentrations of the analytes. A detailed description of the theory of HSM, which is included in a separate paper [23], is based on SPME theory [26]. While the theory shows that a larger sample volume increases extraction efficiency, the concentrations of gasoline diluent normally found in used engine oil are relatively high. We therefore decided to use standard crimp capped 2 ml autosampler vials for the extraction, to minimize waste and cost.

The extracting solvent should be high boiling and contain very low levels of volatile impurities, if lower boiling extractants are to be analyzed. The analytes should also have high solubility in the extracting solvent. Several extracting solvents were investigated, including 1-octanol (b.p. 196 °C), diethyl phthalate (b.p. 298 °C), tetradecane (b.p. 252 °C) and hexadecane (b.p. 287 °C). Hexadecane was finally chosen since it has a high enough boiling point that all but the highest boiling constituents of gasoline (components with boiling points higher than the dimethylnaphthalenes, b.p. 262–270 °C) can be analyzed. It also has a favorable partition coefficient for the gasoline constituents, and it can be purchased relatively pure, has low toxicity, and is easily further purified by vacuum distillation.

Drop size and syringe type are also important factors. The amount of analyte extracted increases as the volume of the microdrop increases. However, gasoline concentrations in used oil are relatively high, ranging from 0.2 to 5 mass percent. Thus, the extracting microdrop need not be large and, as a practical matter, a 1.0 μl microdrop was used since this volume can be reasonably reproduced manually. The syringe type is crucial to reproducibility, however. Several styles and brands of syringes were examined. It was found that a standard Hamilton 10 μl syringe with a number 2 bevel point needle gave the most reproducible results with manual sampling and injection. The relatively large surface area of the needle bevel retains the microdrop, so that it can be retracted into the syringe after sampling. Other needle point styles, including a standard autosampler cone style, allow the microdrop to wick out onto the outer surface of the needle so it cannot be fully retracted back into the needle.

Finally, good syringe handling and sampling practices are also necessary for repeatable results. It was found that using the same syringe for a set of analyses gave the most reproducible results, presumably due to slight variations in the dead volumes of needles. The syringe was cleaned by rinsing the needle and plunger with pentane and then placing the needle under aspirator vacuum and rinsing the barrel with pentane, followed by an additional 10 min, vacuum drying. The hexadecane extraction solvent was then drawn into the syringe and discarded 6 times, before drawing 1 μl into the syringe. The solvent was withdrawn into the barrel to prevent loss during injection of the needle through the vial septum. The needle tip was positioned 1 cm within the vial for each sample and sampling time precisely reproduced. The syringe plunger must be slowly and evenly injected and withdrawn to obtain a reproducible volume of solvent which ultimately is injected into the GC. The solvent must also be completely withdrawn into the barrel after sampling in order to avoid losses in transport to the GC. The following sections describe the optimization of the remaining extraction parameters.

Analysis parameter considerations are also important. The use of a high boiling extracting solvent requires the use of a split injection for column bore sizes smaller than 0.53 mm. For the 0.25 mm column used in this study an inlet split ratio of 25/1 was used for GC analysis to avoid overloading the column with gasoline components and to ensure sharp, symmetrical, resolved peaks.

3.2. Extraction optimization

The overriding goal of this study was to generate a general working procedure using modern, high-resolution capillary columns for the GC analysis of the

volatile contaminants in used motor oil. A simple, reproducible method which could be carried out with manual sampling and injection was desired for occasional sample analyses. The method should also allow for eventual adaptation to fully automated sampling and injection. To this end, extraction parameters were chosen to allow a minimum of instrumentation requirements.

3.2.1. Temperature optimization

Initial extractions were carried out at room temperature in a standard PTFE-lined septum-capped 2 ml autosampler vial containing a 7 mm×2 mm PTFE-coated stir bar (Fisher Scientific). A 0.5 ml sample size was found to be sufficient, given the relatively high concentrations of gasoline expected in the used oil samples. Extraction reproducibilities were found to be acceptable for the prepared standards, but were not acceptable for actual used oil samples. Due to the higher viscosities of the used oil samples, partitioning between the oil and headspace was much slower than for the standards prepared from unused oil. Studies at several temperatures showed that samples heated at 50 °C, without stirring, yielded an equilibrated headspace sample within a reasonable time (30 min).

3.2.2. Equilibration and extraction time optimization

A series of experiments were performed to determine the optimum equilibration and extraction times for a 1.71% gasoline in oil standard heated without stirring at 50 °C. The results are shown in Figs. 1–3. Fig. 1 shows the total area-count (averages for 3 runs) for all gasoline components extracted (4 min) by the microdrop versus equilibration time. Fig. 2 shows the corresponding individual curves for the BTEX components in the gasoline. These results indicated that 30 min would provide an equilibrated headspace sample. Fig. 3 shows the total area-count (averages of 3 runs) for all extracted gasoline components versus extraction time for samples equilibrated for 30 min. These studies showed that a 3 min extraction time was appropriate. Higher temperatures and longer extraction times were avoided to lessen the chance that the headspace sample would leak past the syringe needle. Fig. 4 shows a typical chromatogram for a used oil sample

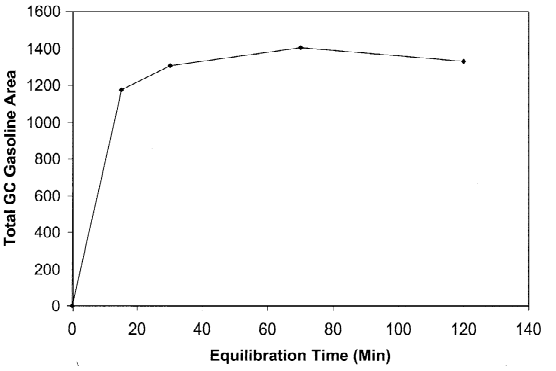

Fig. 1. Equilibration times (min) versus total GC FID area counts ($\times 10^6$) for 0.5 ml oil samples in 2 ml vials containing 1.71% gasoline. Extraction conditions: Microdrop volume 1 μl, non-stirred, 50 °C, 4 min sample time. Area counts corrected for differences in sample masses by dividing each area by the mass for the sample.

(in this case for the 1986 GMC van) extracted and analyzed with the optimized conditions. For comparison, a chromatogram (using the same GC conditions) for an extract of an unused oil sample containing 2.213% fresh gasoline is shown in Fig. 5. Next, Fig. 6 shows the chromatogram for a direct injection of 1 μl of a 1.8% solution of gasoline in hexadecane. Finally, a traditional headspace GC run for a sample of 2.213% fresh gasoline in unused oil is shown in Fig. 7. Comparison of these four chromatograms illustrates the advantages of HMDA over traditional headspace sampling for gasoline in oil analysis. It can be seen in Figs. 4 and 5 that HMDA yields a chromatogram with sharp, resolved

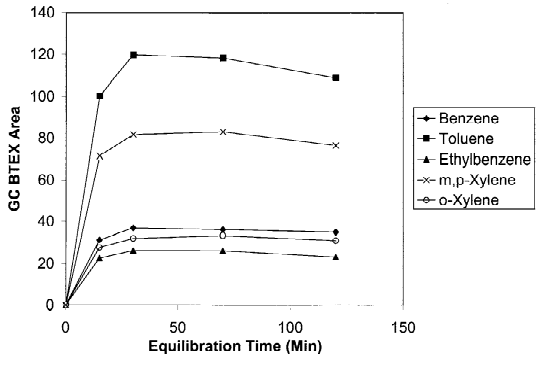

Fig. 2. Equilibration time versus GC FID area counts ($\times 10^6$) for individual BTEX components present in gasoline standards graphed in Fig. 1.

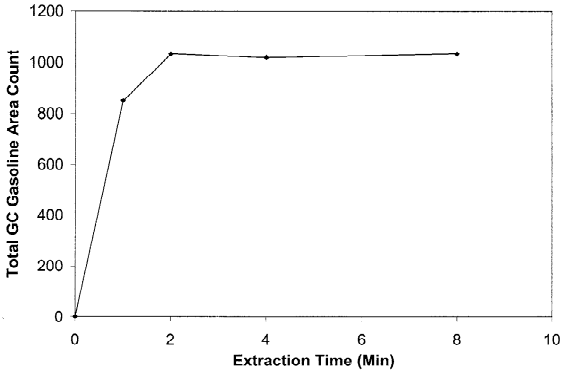

Fig. 3. Extraction time versus total GC FID area counts ($\times 10^6$) for 0.5 ml oil samples containing 1.71% gasoline. Extraction conditions: Microdrop volume 1 μl, non-stirred, 50 °C, 4 min equilibration time. Area counts corrected for differences in sample masses by dividing each area by the mass for the sample.

peaks using a standard capillary GC column with no need for cryogenic cooling of the inlet. In addition, the relative intensities of the component peaks for a standard gasoline in oil sample obtained by HMDA (Fig. 5) are very similar, though not identical, to those obtained with a direct split injection of neat gasoline (Fig. 6). In comparison, traditional headspace analysis (Fig. 7), as might be expected, has the largest peak areas for the most volatile components.

3.3. Quantitative analysis

An attempt was made to use the ASTM D-3525-93 calculation method to determine the fuel dilution mass percent, for standards analyzed using HMDA. The internal standard chosen was ethyl acetate, which has minimal interference with components in the gasoline extract and is volatile enough to be extracted into the microdrop. Thus, 2 μl of ethyl acetate was added by syringe to each sample immediately before crimping the sample vials. While the results yielded a linear calibration plot ($R^2 = 0.9998$, $y = 529.5x - 3.3034$), the calculated values [using Eq. (1)] for the fuel dilution mass percents were consistently 20–50% higher than the actual values for the prepared oil calibration standards. This is not surprising, given the fact that the composition of the vapor in the headspace is not the same as the

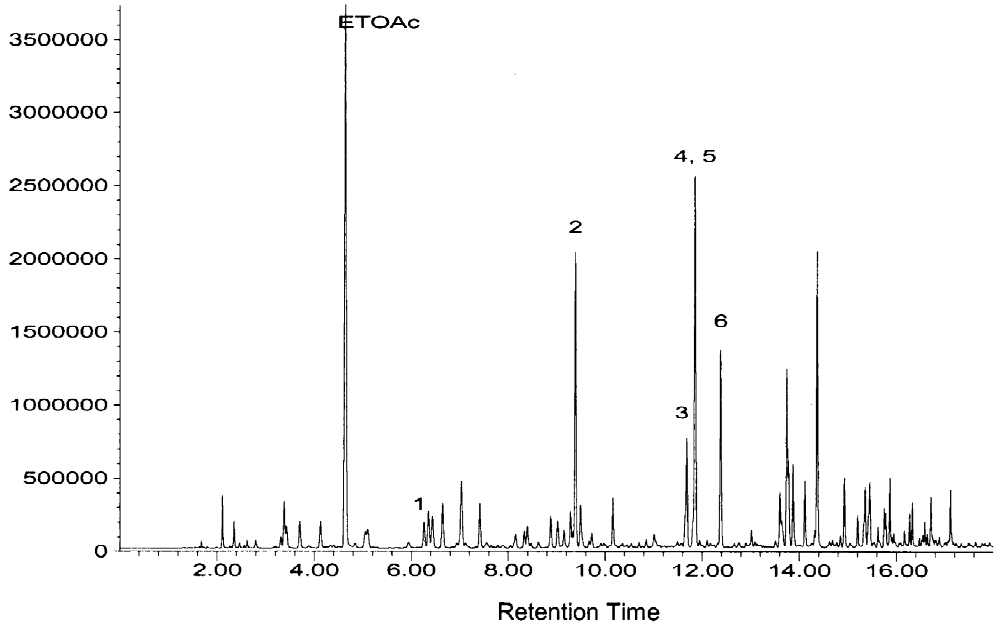

Fig. 4. HMDA of used oil sample from a 1986 GMC van, extracted and analyzed under optimized conditions: 0.5 ml oil sample in a 2 ml crimped vial, non-stirred at 50 °C for 30 min, extracted for 3 min with 1 μl hexadecane. Two μl of ethyl acetate added to the sample as a surrogate. Labeled GC peaks: 1 (benzene), 2 (toluene), 3 (ethylbenzene), 4, 5 (*m*-xylene + *p*-xylene), 6 (*o*-xylene). Split injection (25/1). Remaining conditions are given in the Experimental Section. Time scale in min.

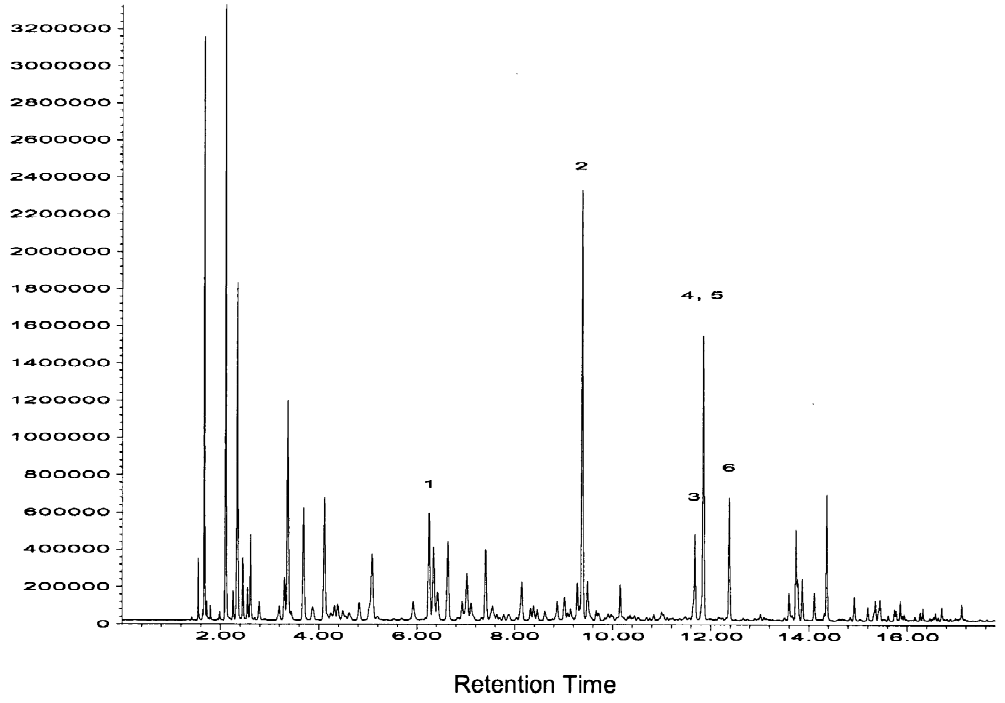

Fig. 5. HMDA of a 2.213% gasoline in oil standard. Conditions and labeled peaks are identical to those given for Fig. 4. Time scale in min.

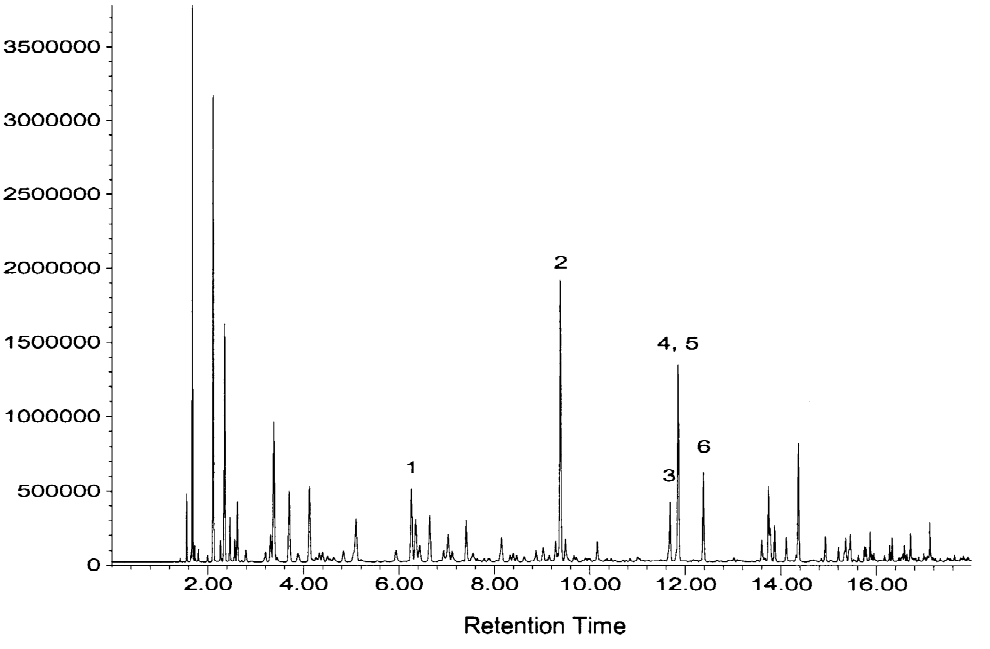

Fig. 6. GC analysis of 1 μl of a 1.8% solution of gasoline in hexadecane. GC conditions are identical to those used in Fig. 4. Time scale in min.

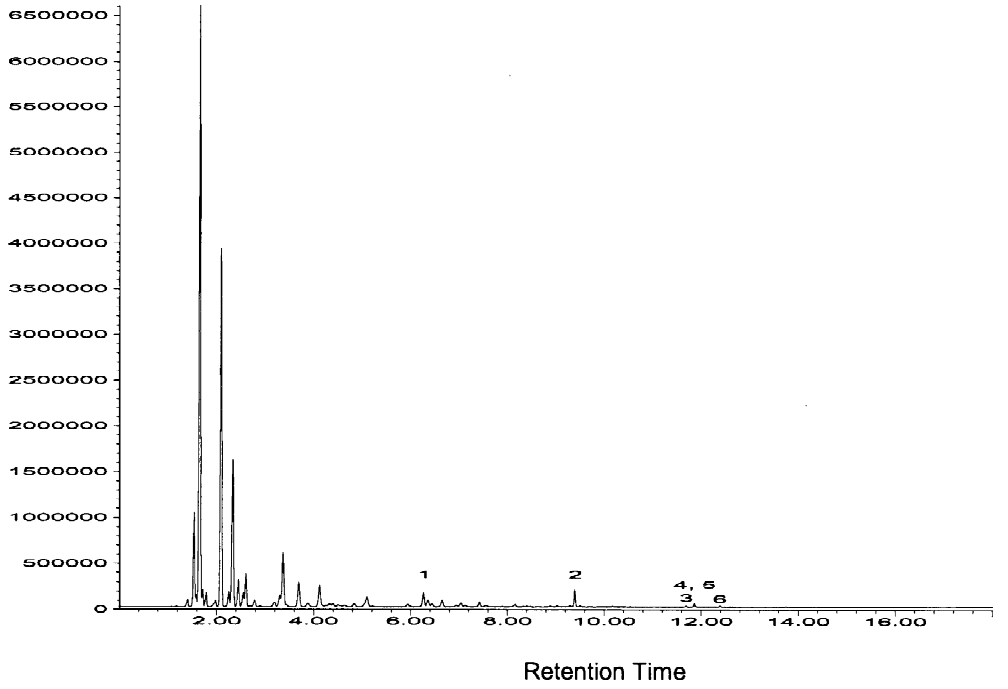

Fig. 7. GC analysis of a 100 μl sample of headspace extract for a sample prepared and analyzed using the conditions given in Fig. 4.

composition of components in the oil and the ASTM method directly measures components in the oil. In a study using traditional headspace analysis of gasoline diluent in oil, Ichikawa and co-authors derived an equation to correlate (by retention time) the relative response for each component, in headspace GC, to the responses for C_5–C_{12} *n*-alkane standards in oil [2]. While gasoline diluent concentrations obtained by Ichikawa and co-authors were in reasonably good agreement with the ASTM method results (with an average deviation of 13%), this method does not necessarily yield accurate concentrations for individual non-alkane components, such as the aromatics. We therefore sought a simpler and more traditional approach, using an external standard calibration curve. This involved generation of 4-point calibration curves for gasoline and BTEX standards prepared in oil using HMDA. While an internal standard was not used, a 2 μl aliquot of ethyl acetate was added to each sample, as a surrogate (a quality control agent), to ensure that no leakage occurred in the vial septum during the analysis. Samples were prepared by adding weighed aliquots of unleaded regular gasoline (Shell 87) or individual BTEX components to unused 10W-30 oil (Citgo), and diluting weighed primary standards with additional oil. Gasoline concentrations ranged from 0.5 to 4%. Total BTEX concentrations ranged from 0.1 to 0.6%. Extractions were carried out at 50 °C. The gasoline and BTEX calibration curves were obtained by plotting, respectively, the total integrated areas for all extracted gasoline or BTEX components, minus the hexadecane baseline blank, versus concentrations. The average of three calibration runs (corrected for differences in masses of oil used) for four standards yielded a gasoline in oil calibration curve with a correlation coefficient of $R^2 = 0.9983$ ($y = 722.3x - 37.343$). The BTEX in oil calibration curve had a correlation coefficient of $R^2 = 0.9971$ ($y = 846.04x - 3.4739$).

3.4. Analytical results

Used oil samples were obtained from three passenger vehicles. The results of the oil analyses for these vehicles are shown in Table 1. Vehicle 1 was a 2000 GM Pontiac Montana with a 3.4 l V6 fuel injection engine. The total mileage on the vehicle

Table 1
Percent gasoline and BTEX in oil determined by HMDA and ASTM methods

Vehicle	HMDA mass % gasoline (23 °C)	HMDA mass % gasoline (50 °C)	HMDA mass % BTEX (50 °C)	BTEX in diluent (%)	ASTM mass % gasoline
2000 GM Montana	0.64	1.11	0.23	21	1.30
1986 GMC Van	1.19	1.49	0.33	22	1.61
1992 GM Le Sabre	1.47	2.47	0.52	21	2.81

was 23 000 miles and the oil change interval was 10 000 miles (1 mile = 1.609 km). The second vehicle was a 1986 GMC van with a 5.0 l V8 carbureted engine. The total mileage on the vehicle was 104 000 miles and the oil change interval was 3400 miles. The third vehicle was a 1992 GM Buick Le Sabre with a 3.8 l V6 fuel injection engine. The total mileage on the vehicle was 112 000 miles and the oil change interval was 3600 miles. Vehicles 1 and 3 had a total history of both highway and city usage, Vehicle 2 was used principally on the highway. All three vehicles, however, had been used in a similar mix of commuter and highway mileage during the period leading to the oil collection.

Column 2 of Table 1 shows the mass percent of gasoline diluents in the used oil samples for the three vehicles obtained by HMDA at room temperature. Column three shows the results obtained at 50 °C. Room temperature results were consistently lower, since the headspace for these samples did not reach equilibrium after 30 min, due to the increased viscosities for the samples. Column four shows the HMDA results at 50 °C for mass percent of BTEX in the used oil samples and column five gives the mass percentages for BTEX components in the total oil diluent mass. Column six contains the results for gasoline in oil found for these three vehicles using ASTM method D-3525-93.

3.5. Discussion

To determine whether the reproducibility of HMDA compares favorably with that of the ASTM method, eight replicate analyses were carried out on the used oil for vehicle 2 (the 1986 GMC van). Four analyses were conducted on 1 day. The remaining 4 analyses were repeated on the 4 subsequent days. The results yielded a standard deviation of the mass percent of 0.035%, and a relative standard deviation of 2.5%. In addition, the absolute deviation of mass % was ±0.10%. These results fall well within the ASTM method requirements of 0.28 mass % for repeatability and 1.64 mass % for reproducibility [1]. For comparison purposes, the ASTM method was also used to determine the percent gasoline in the used oil samples. Direct injection of hexadecane diluted oil samples under modified ASTM conditions (to allow for the use of the same capillary GC column which had been used for HMDA) gave gasoline percentages ranging from 7 to 15% higher than HMDA values (Table 1, column three). The average difference between the two methods was 11%, which is approximately the same average difference for results Ichikawa obtained (average 13% difference) [2]. This difference is likely due, in part, to the use of fresh, unleaded gasoline to generate the HMDA calibration curves. The gasoline standard contains significant amounts of volatile components (Fig. 5), while the diluent found in the used oils has higher percentages of aromatic and higher boiling alkane components (Fig. 4). These differences would likely be smaller if a standard ‘weathered’ gasoline (containing less volatile material) were used to generate the calibration curves. However, this method does yield results consistent with the ASTM method, and an accurate BTEX composition can be determined using the external calibration curve method. One additional interesting and useful result of this method is the ability to

obtain a gas chromatogram (Fig. 5) with a component composition almost identical to that found by direct injection of an oil sample (Fig. 6), unlike the chromatogram obtained when using standard headspace analysis (Fig. 7). As a result, a gas chromatogram obtained by HMDA gives a reasonably accurate picture of the composition of the diluent present in used engine oils. Unlike the direct injection method, however, HMDA allows large numbers of oil samples to be analyzed using a high resolution capillary column, without the need for the use of cryo-focusing, and without contamination of the GC inlet or column.

4. Conclusions

HMDA using an external calibration curve provides a useful alternative to ASTM method 3525-93 for the analysis of gasoline diluent and BTEX components in used engine oil. HMDA yields chromatograms with sharp, resolved GC peaks with standard capillary chromatography columns, without the necessity for the use of inlet cryogenic cooling. The reproducibility and repeatability for HMDA also fall within the parameters of the ASTM method. The present work was accomplished with manual extraction and injection. It is expected that automation of the method may be possible. This avenue is presently under investigation.

Acknowledgements

We wish to thank the Ford Foundation for funds used for the purchase of the GC–MS instrumentation used in this research.

References

[1] Standard Test Method for Gasoline Diluent in Used Gasoline Engine Oils by Gas Chromatography, ASTM Test Method D-3525-93, American Society for Testing and Materials
[2] M. Ichikawa, N. Nanaka, M. Nomura, I. Takada, S. Ishimori, J. Anal. Appl. Pyrolysis 32 (1995) 233.
[3] D.M. Levermore, M. Josowicz, W.R. Rees Jr., J. Janata, Anal. Chem. 73 (2001) 1361.
[4] M.A. Jeannot, F.F. Cantwell, Anal. Chem. 68 (1996) 2236.
[5] M.A. Jeannot, F.F. Cantwell, Anal. Chem. 69 (1997) 235.
[6] M.A. Jeannot, F.F. Cantwell, Anal. Chem. 69 (1997) 2935.
[7] Y. He, H.K. Lee, Anal. Chem. 69 (1997) 4634.
[8] L.S. de Jager, A.R.J. Andrews, Analyst 125 (2000) 1943.
[9] T. Ligor, B. Buszewski, Chromatographia 51 (2000) S279.
[10] H. Zang, A.R.J. Andrews, J. Environ. Monit. 2 (2000) 656.
[11] L.S. de Jager, A.R.J. Andrews, J. Chromatogr. A 911 (2001) 97.
[12] L. Zhao, H.K. Lee, J. Chromatogr. A 919 (2001) 381.
[13] L. Zhao, H.K. Lee, J. Chromatogr. A 931 (2001) 95.
[14] L. Zhao, H.K. Lee, Anal. Chem. 74 (2002) 2486.
[15] T.S. Ho, S. Pedersen-Bjergaard, K.E. Rasmussen, J. Chromatogr. A 963 (2002) 3.
[16] L. Zhu, C.B. Tay, H.K. Lee, J. Chromatogr. A 963 (2002) 231.
[17] L. Zhao, L. Zhu, H.K. Lee, J. Chromatogr. A 963 (2002) 239.
[18] S. Andersen, T.G. Halvorsen, S. Pedersen-Bjergaard, K.E. Rasmussen, J. Chromatogr. A 963 (2002) 303.
[19] L. Zhu, K.H. Ee, L. Zhao, H.K. Lee, J. Chromatogr. A 963 (2002) 335.
[20] A. Przyjazny, J.F. Austin, A.T. Essenmacher, in: Proceedings of the 6th Polish Conference on Analytical Chemistry, Gliwice, Vol. 2, 2000, p. 135.
[21] J.M. Kokosa, American Chemical Society, Petroleum Chem. Div. Prepr. 47 (2002) 15.
[22] A. Przyjazny, J.M. Kokosa, Am. Chem. Soc., Environ. Chem. Div. Prepr. 42 (2002) 569.
[23] A. Przyjazny, J.M. Kokosa, J. Chromatogr. A 977 (2002) 143.
[24] A.L. Theis, A.J. Waldback, S.M. Hanson, M.A. Jeannot, Anal. Chem. 73 (2001) 5651.
[25] A. Tankeviciute, R. Kazlauskas, V. Vickackaite, Analyst 126 (2001) 1674.
[26] T. Gorecki, J. Pawliszyn, Analyst 122 (1997) 1079.