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VAPOR-PRESSURE MEASUREMENT OF COMPLEX HYDROCARBON MIXTURES BY HEADSPACE GAS CHROMATOGRAPHY

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SUMMARY

Headspace gas chromatography was used to measure the vapor pressures of single *n*-alkane hydrocarbons and their binary, ternary and quaternary mixtures at various temperatures in the range 38–107°C. In addition, diesel fuel, gasoline and crude oil vapor pressures were measured at 38 and 70°C. The microprocessor-controlled headspace gas chromatograph automatically thermostated the samples contained in septum-sealed glass vials to equilibrate the vapor and liquid for a pre-set period of time (usually 60 min), pressurized the vials to a pre-set pressure (at least 138 kPa gauge) by inserting a hollow needle through the septum, and sampled the vapor for a pre-set period of time (0.01 min) by allowing the pressure in the vial to drive an aliquot of the vapor (*ca.* 9 μl) through the needle and onto the analytical column. Using this technique, single *n*-alkane hydrocarbon vapor pressures, measured by totally vaporizing μl aliquots in the vials, agreed, on the average, to within 1% with calculated values based on hydrocarbon properties. Likewise, measured total vapor pressures of the binary, ternary, and quaternary mixtures compared well with calculated values, assuming ideal behavior for the mixtures, and the measured vapor pressures of diesel fuel, gasoline, and several crude oils showed good precision and accuracy.

INTRODUCTION

Evaporation of constituents of petroleum mixtures may contribute reactive hydrocarbons to the atmosphere. In order to assess the potential for evaporation from fuels and crude oil compositions, a test method for vapor pressure is required. The vapor pressure of a hydrocarbon mixture represents the sum of contributions from its hydrocarbon and related organic constituents —disproportionately so for the more volatile constituents. Methods that rely on measurement of total pressure within a sealed container (*e.g.*, the Reid vapor pressure method[1]) will also include contributions from dissolved air and water in crude oil, for example, and require at least equilibration of the container with water before a vapor-pressure measurement can be made. In order to separate the contributions of organic from inorganic constituents, an approach is needed whereby the organic constituents only are

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measured and the results then combined to calculate total vapor pressure for the organic fraction of the crude.

Of the methods available for vapor pressure determination —isoteniscope[2], Knudsen effusion[3,4], gas saturation[5,6], and gas chromatographic (GC) techniques[7]—GC offers advantages in terms of speed, solute sample size, purity, and stability requirements. Furthermore, vapor-density determination through headspace sampling and GC analysis affords the best approach for complex hydrocarbon mixtures. The principles and application of headspace sampling for GC analysis have been extensively reviewed[8–13]. A solid or liquid sample (single component or mixture) is placed in a glass container sealed with an inert septum which can be later punctured with a syringe needle. The container is then maintained at a constant temperature until vapor–liquid equilibration occurs. An aliquot of the headspace is then withdrawn with a syringe and injected into a gas chromatograph. The analyte concentration in the headspace can be determined by calibration of the gas chromatograph with suitable standards yielding, in the present case, the vapor density from which vapor pressure may be determined.

The technique of manipulation can vary from a manual syringe removal of headspace via the container septum and then injection of the contents on the gas chromatograph column to fairly sophisticated automated techniques accomplishing basically the same purpose. In this report, we describe a procedure which employed an automated headspace sampler and analysis system, with the goal of developing a relatively fast and accurate method for determining vapor pressures of complex mixtures, such as fuels and crude oils. The procedure was validated using single *n*-alkanes, their simple mixtures and diesel fuel, as a model petroleum mixture.

EXPERIMENTAL

Equipment

Analysis was accomplished using the Perkin-Elmer (Norwalk, CT, U.S.A.) Model HS-100 headspace sampler coupled to the Model Sigma 2000 gas chromatograph (flame ionization detector) and Model LCI-100 laboratory integrator. The gas chromatograph was equipped with a 30 m × 0.25 mm I.D. fused-silica open tubular (FSOT) column coated with phase-bonded silicone oil (DB-1; J&W Scientific, Rancho Cordova, CA, U.S.A.).

Materials

The glass headspace vials (22 ml), Teflon®-coated butyl rubber septa, aluminum caps, and vial cap crimping tool were supplied by Perkin-Elmer. The crimping tool was lubricated with fluoro-Glide (Chemplast, Wayne, NJ, U.S.A.) film bonding lubricant. Pure (at least 99+%) *n*-alkane hydrocarbons (Aldrich, Milwaukee, WI, U.S.A.), pentane through hexadecane, were used as received, diesel fuel and gasoline were obtained from local fueling stations, and crude oil samples were obtained from the McKittrick oil field near Bakersfield, CA, U.S.A. All bottled gases (hydrogen, helium, nitrogen), except compressed air, were at least 99.995% pure (Liquid Carbonic, Chicago, IL, U.S.A.). Glass syringes (μl), with fixed needles, were obtained from Hamilton (Reno, NV, U.S.A.).

Methods

The FSOT column was placed in the gas chromatograph oven, one end was connected to the detector and the other was directly connected without a splitter to the end of the transfer line containing a section of wide-bore (0.32 mm) FSOT column coated with phase-bonded silicone oil (DB-1). The headspace vials were sealed with the crimping tool by alternating between rotating the vial and squeezing the tool; if the vial cap could be moved, the crimping tool was applied again. Before use, the crimping tool was sprayed with a fluorocarbon lubricant to make sure the cap was properly crimped and the septum not wrinkled.

Into a series of separate, sealed vials were injected, using fixed-needle syringes at ambient temperature, increasing μl amounts of the hydrocarbon series pentane through hexadecane. The samples were thermostated at various temperatures in the range 38–107°C for 15 min prior to sampling. Binary (hexane–decane), ternary (hexane–decane–dodecane), and quaternary (hexane–decane–dodecane–hexadecane) mixtures and a seven-component mixture (hexane through dodecane) were prepared in bulk and aliquots were transferred to the vials using pipettes followed by immediate sealing of the vials. The mixtures were thermostated at temperatures in the range 38–107°C for 60 min prior to sampling. The binary and ternary mixtures consisted of approximately equimolar amounts of the constituents, the quaternary mixture consisted of about 10 mol% hexane and 30 mol% of each of the other constituents, and the seven-component mixture consisted of less than 10 mol% of each of the components in a matrix of hexadecane at greater than 50 mol%. Aliquots of diesel fuel were transferred to the vials using pipettes followed by immediate sealing of the vials. The fuel samples were thermostated at 38 and 70°C for 60 min prior to sampling. For all of the mixtures, the vials were filled to different extents to give vapor volume-to-liquid volume (V/L) ratios of 4:1 (4.4 ml), 2:1 (7.3 ml), and 1:1 (11.0 ml). After vapor–liquid equilibration, the vial septa were punctured by the instrument using a hollow sampling needle, the internal pressure of each vial was raised to at least 138 kPa gauge with helium, and the vapor sampled for 0.01 min (*ca.* 9 μl vapor). In most cases, the transfer line temperature was set at 150°C, and the column oven was operated isothermally at 50, 80, 110 or 130°C and was also temperature programmed (2°C/min, 5°C/min) beginning at 40°C and ending in the range 80–130°C, depending on the type of sample.

RESULTS AND DISCUSSION

Analysis using headspace sampling and GC requires thermodynamic equilibrium between a condensed phase (liquid or solid) and its vapor phase in a sealed container so that aliquots of the vapor can be removed for quantitative GC analysis. For a liquid mixture in equilibrium with its vapor in a sealed container, GC response of a component in the vapor is proportional to the vapor density:

$$A_i = c_i(n_i/V)$$

where A_i = GC response of component i, c_i = a calibration factor, n_i = number of moles in the vapor, and V = volume of the vapor space. Furthermore, since

$$(n_i/V)RT = P_i$$

then

$$A_i(RT) = c_i P_i$$

where P_i = the partial pressure of component i in the vapor, R = the gas constant, and T = the absolute temperature. Therefore, measuring the GC response implies measuring the partial pressure if the calibration factor is known. The calibration factor has a specific value for each component in the mixture and depends on the characteristics of the detector used. However, a complex hydrocarbon mixture can be represented by a relatively small number of *n*-alkane reference standards[14,15] and the properties of the standards can be attributed to the mixture. Also, GC detector response can be calibrated with these standards by relating GC response to vapor density. The form of the relationship would be

$$A_r = a_r + b_r(n_r/V)$$

where the constants a_r and b_r are the intercept and slope, respectively, and r stands for reference. The slope is actually a calibration factor and if detector response is linear ($a_r = 0$), this expression will have the form

$$A_r = b_r(n_r/V)$$

which is essentially the same as

$$A_i = c_i(n_i/V)$$

A_i then becomes a summation of GC responses for a series of components represented by a single *n*-alkane reference standard. Then, the partial pressure corresponding to each subsection is obtained from

$$P_i = (n_i/V)RT$$

where $(n_i/V) = A_i/(b_r M_r)$ and M_r = the molecular weight of the reference standard representing the subsection, and total pressure (P_t) of the mixture from

$$P_t = \sum P_i$$

The equation for partial pressure is the ideal gas equation. No correction for real gas behavior was necessary since total pressure in the sealed vials remained below about 304 kPa, above which gases become non-ideal[16].

A major objective of this study was the development of a method for headspace GC analysis of the vapor phase of equilibrated complex hydrocarbon mixtures, such as fuels and crude oils. Using individual pure hydrocarbons and their simple mixtures to validate the method, calculation of vapor pressure of these complex mixtures could then be done using the analytical results. Obviously of critical importance in accomplishing the objectives was the analytical instrumentation, which needed to be able to handle a large number of samples at one time, individually thermostat the samples, and achieve acceptable reproducibility through automatic control. A commercial programmable multisampling system composed of a pneumatically operated injection system, a thermostated carousel for up to 15 sample vials, and an electronically controlled sample magazine was employed. Sampling was based on a pneumatic-balanced pressure principle which avoids the disadvantages associated with gas syringes, such as change of partial pressures of the volatiles due to reduced pressure in the syringe. The system allowed pressurization of the sample vial to any pressure independent of the column head pressure. Thus, the operator was able to control the sample size, a feature that would be especially useful for low-volatility substances. In a typical operation, the septum of the thermostated sample was pierced by the hollow sampling needle, the vial was pressurized, and then an aliquot of the headspace was injected onto the FSOT column using the vial pressure as the driving force[10].

Instrument conditions

Relating response to hydrocarbon amount (*µl vs.* GC response) up through vapor saturation in the headspace vial resulted in a sigmoid curve for hexane at 38°C (Fig. 1A). This shape was less pronounced for heptane and octane (Fig. 1C, D) and the phenomenon was not observed for decane. The sigmoid shape was eliminated entirely for hexane by inserting a section of wide-bore (0.32 mm) FSOT into the transfer line (Fig. 1B). The presence of a wide-bore insert also served to improve compound peak resolution, a result to be expected from reducing the dead volume of the transfer line.

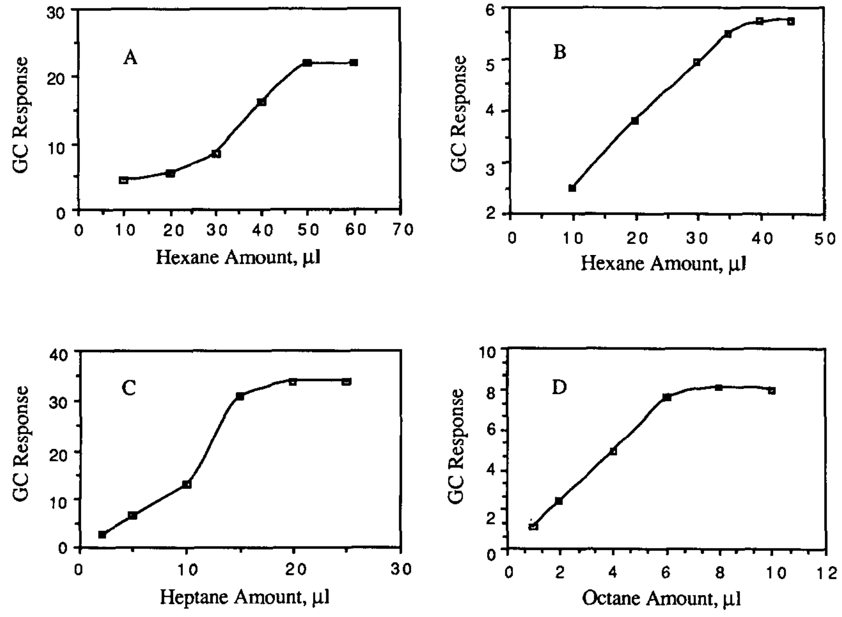

Fig. 1. Isothermal (50°C) gas chromatographic responses of hexane (A, B), heptane (C), and octane (D). Only hexane (B) had transfer line insert.

TABLE I

GC RESPONSE VARIATION FOR TOLUENE AT 38°C AND THREE TRANSFER LINE TEMPERATURES

V/L = Vapor volume-to-liquid volume ratio.

V/L	*GC Area (× 10^7), average (± relative S.D., n = 3)*		
	Transfer line temperature (°C)		
	68	*100*	*150*
4:1	2.99 (±2.6%)	3.76 (±0.9%)	4.13 (±1.8%)
1:1	2.74 (±1.3%)	3.49 (±0.6%)	4.10 (±1.9%)

All vapor pressure determinations for single hydrocarbons, their simple mixtures, and petroleum mixtures were made with a wide-bore insert in the transfer line.

Another important consideration was the transfer line temperature. Instrument default temperature was 30°C above the sample temperature. However, average differences in instrument response for V/L = 4:1 and 1:1 (single hydrocarbons and mixtures) were always significant. Using toluene as a model[17], transfer line temperature was set at 68, 100 and 150°C for a sample temperature of 38°C. When the transfer line temperature was increased (starting at 68°C), absolute response increased for both V/L = 4:1 and 1:1, but their differences at 100 and 150°C were 7.6% (significant) and 0.9% (not significant), respectively (Table I). Precision was 0.6–0.9% (100°C) and 1.8–1.9% (150°C). It may be important that toluene GC response for V/L = 4:1 and 1:1 did not begin to agree until the transfer line temperature was increased to above the boiling point of toluene (110.6°C). All vapor pressure determinations for single hydrocarbons and the mixtures were made with the transfer line temperature set at 150°C. It was possible to set the temperature at a higher value; however, the time

TABLE II

VAPOR PRESSURES OF PURE HYDROCARBONS AT THREE TEMPERATURES

ND = Not determined (either vapor density was below detection limit or it was too high for accurate measurement and safety).

Hydrocarbon	*Vapor pressure ± S.D. (n ≥ 3) (kPa)*					
	38°C		*70°C*		*107°C*	
	Experimental	*Calculated**	*Experimental*	*Calculated**	*Experimental*	*Calculated**
Hexane	34.00 ± 0.63	34.19	103.91 ± 0.53	104.69	ND	291.44
Decane	0.43 ± 0.01	0.43	2.50 ± 0.05	2.52	12.45 ± 0.12	12.48
Dodecane	ND	0.05	0.42 ± 0.005	0.42	2.75 ± 0.01	2.78
Hexadecane	ND	0.0009	ND	0.01	0.15 ± 0.02	0.16

* Calculated using the Harlacher equation: $\ln P = A + B/T + C \ln T + DP/T^2$, where P is pressure, T is temperature and A, B, C and D are constants taken from ref. 16.

required for the instrument to become ready to process samples increased dramatically, and in some cases the instrument failed to become ready at all. This might have been due in part to the close proximity of the hot transfer line to the cooler sample set. The microprocessor controlling the instrument would not process the samples until the operator-set temperatures were reached; the microprocessor could not be overridden or by-passed.

Single hydrocarbons

The capabilities of the technique were partly evaluated by determining accuracy and precision through measurement, with replication, of the vapor pressures of a series of pure *n*-alkane hydrocarbons (hexane, decane, dodecane and hexadecane) at 38, 70 and 107°C. The results are summarized in Table II, which also includes vapor pressure values calculated using the Harlacher equation[16]. Agreement between experimental and calculated values was good. Differences ranged from about 0.3 to 5.7% at 38°C, from about 0.6 to 1.3% at 70°C, and from about 0.2 to 4.2% at 107°C. Precision of the average values fell in the ranges ±1.6–1.9% at 38°C, ±0.5–2.0% at 70°C, and ±0.2–9.6% at 107°C. The high values for the two ranges at 107°C were due primarily to the difficulty in accurately measuring small volumes of hexadecane (*ca.* 0.3 μl injected into sealed vials for vapor saturation). Vapor pressures were not measured for all compounds at all temperatures because of either the inability to measure very small volumes of the low volatility hydrocarbons (0.10 μl for dodecane and 0.002 μl for hexadecane at 38°C and 0.03 μl for hexadecane at 70°C for vapor saturation) or the chance of saturating the GC detector and generating unsafe pressures in the vials with the more volatile hydrocarbons, especially at 107°C.

Varying vial V/L, using the neat hydrocarbons, did not significantly affect instrument response for samples at 43°C (Table III). However, at 72 and 107°C, all differences between V/L = 4:1 and 1:1 were significant. The greatest differences between V/L = 4:1 and 1:1 were exhibited by dodecane and hexadecane, in part because their boiling points were, respectively, about 76 and 137°C greater than the transfer line temperature (see Table I). In spite of this, their use as standards for

TABLE III

GAS CHROMATOGRAPHIC RESPONSE OF PURE HYDROCARBONS

V/L	*Temp. (°C)*	*GC Response (× 10³), average (± relative S.D., n = 3)*			
		Hexane	*Decane*	*Dodecane*	*Hexadecane*
4:1	38	13.36 (±0.59%)	1.04 (±5.52%)	–	–
2:1		13.32 (±0.79%)	0.99 (±5.56%)	–	–
1:1		13.38 (±1.59%)	0.96 (±6.10%)	–	–
4:1	72	–	10.82 (±1.25%)	2.46 (±1.50%)	–
2:1		–	10.45 (±0.92%)	2.26 (±0.53%)	–
1:1		–	9.50 (±2.54%)	1.97 (±1.54%)	–
4:1	107	–	–	5.34 (±2.10%)	0.43 (±1.10%)
2:1		–	–	5.04 (±1.43%)	0.36 (±3.82%)
1:1		–	–	4.69 (±1.59%)	0.25 (±2.41%)

TABLE IV

GAS CHROMATOGRAPHIC RESPONSE OF MIXTURES OF PURE HYDROCARBONS AT 43, 72 AND 107°C

Mixture type	*Temp. (°C)*	*V/L*	*GC Response (× 10^2), average (± relative S.D., n = 3)*			
			Hexane	*Decane*	*Dodecane*	*Hexadecane*
Binary*	43	4:1	87.58 (±2.42%)	9.76 (±5.53%)	–	–
		2:1	82.87 (±7.22%)	9.73 (±2.27%)	–	–
		1:1	86.82 (±6.08%)	8.92 (±5.71%)	–	–
Ternary*		4:1	138.38 (±1.85%)	8.39 (±2.45%)	1.72 (±6.42%)	–
		2:1	138.38 (±0.08%)	7.22 (±17.32%)	1.33 (±9.34%)	–
		1:1	140.64 (±0.54%)	6.37 (±1.78%)	1.07 (±2.93%)	–
Quaternary**		4:1	129.31 (±0.11%)	6.01 (±7.67%)	0.95 (±8.55%)	–
		2:1	129.46 (±0.003%)	6.05 (±6.41%)	0.96 (±6.06%)	–
		1:1	125.81 (±2.67%)	5.62 (±1.71%)	0.80 (±6.74%)	–
Binary*	72	4:1	382.20 (±7.86%)	45.00 (±3.86%)	–	–
		2:1	403.60 (±0.74%)	42.10 (±2.98%)	–	–
		1:1	395.50 (±3.39%)	45.20 (±3.07%)	–	–
Ternary*		4:1	359.97 (±4.84%)	28.70 (±1.26%)	9.07 (±7.69%)	–
		2:1	340.15 (±1.27%)	29.12 (±4.87%)	8.10 (±9.71%)	–
		1:1	345.14 (±0.90%)	28.90 (±1.92%)	9.28 (±5.93%)	–
Quaternary**		4:1	143.20 (±0.72%)	14.90 (±3.29%)	4.82 (±2.84%)	–
		2:1	144.98 (±0.43%)	15.28 (±2.83%)	4.91 (±1.65%)	–
		1:1	146.55 (±0.55%)	14.45 (±0.76%)	4.72 (±3.00%)	–
Quaternary**	107	4:1	328.81 (±0.94%)	65.24 (±3.39%)	28.97 (±3.53%)	6.96 (±1.66%)
		2:1	337.41 (±1.29%)	68.92 (±1.68%)	30.66 (±0.95%)	6.56 (±2.73%)
		1:1	340.99 (±1.55%)	65.54 (±8.29%)	29.45 (±7.10%)	5.49 (±14.61%)

* Equimolar.

** Hexane at 0.1 mole fraction, all other components (decane, dodecane and hexadecane) at 0.3 mole fraction. Response for hexadecane was below the detection limit at 43 and 72°C.

complex mixtures, such as fuels and crude oils, would not present a problem since their retention times would place them in regions of mixture chromatograms that would represent small fractions of the total equilibrated vapor for fuels and crude oils. Precision of triplicate determinations varied from ±0.53 to ±6.10%, with an average of ±2.27% for 18 sets of triplicate determinations.

Simple mixtures

For the mixtures of the *n*-alkane hydrocarbons at 43, 72, and 107°C, average precision was ±4.66, ±3.18, and ±3.98% for 24, 24, and 12 determinations, respectively (Table IV). Relative responses at V/L = 4:1 and 1:1 were significantly different in only 5 cases out of 20 listed. In some of the cases where differences were significant, percent difference was small (2–4%). Variability in precision from sample to sample can be due to inconsistency in instrument operation and/or to some problem in not always making a good seal with the Teflon-lined septa. The effects of variability on the quality of the data may be minimized by adequate replication. We used

TABLE V

VAPOR PRESSURES OF MIXTURES OF PURE HYDROCARBONS

Temp. (°C)	Type	V/L	Partial pressure (kPa)				Total pressure (kPa)	
			Hexane	Decane	Dodecane	Hexadecane	Experimental	Calculated*
43	Binary	4:1	18.52	0.29	–	–	18.81	20.95
		2:1	19.79	0.29	–	–	20.08	
		1:1	18.11	0.26	–	–	18.37	
	Ternary	4:1	13.03	0.25	0.04	–	13.32	14.10
		2:1	13.03	0.22	0.03	–	13.28	
		1:1	13.31	0.19	0.02	–	13.52	
	Quaternary**	4:1	3.86	0.18	0.02	–	4.06	4.34
		2:1	3.86	0.18	0.02	–	4.06	
		1:1	3.75	0.17	0.01	–	3.93	
72	Binary	4:1	47.90	1.19	–	–	49.09	56.90
		2:1	54.14	1.11	–	–	55.25	
		1:1	51.77	1.20	–	–	52.97	
	Ternary	4:1	41.48	0.75	0.25	–	42.48	38.37
		2:1	35.74	0.76	0.22	–	36.72	
		1:1	37.19	0.76	0.26	–	38.21	
	Quaternary**	4:1	10.50	0.50	0.13	–	11.13	12.11
		2:1	10.65	0.51	0.13	–	11.29	
		1:1	10.78	0.48	0.13	–	11.39	
107	Quaternary***	4:1	28.29	2.64	0.82	0.12	31.87	33.76
		2:1	29.06	2.81	0.88	0.12	32.87	
		1:1	29.38	2.66	0.83	0.10	32.97	

* Activity coefficient assumed to be unity.

** Hexadecane response below the detection limit.

*** Temperature too high for binary and ternary mixtures.

a minimum of three replicates per sample type; when outliers occurred in a data set, we repeated the analyses.

Accuracy depends on having reliable reference data. As a first approximation, we assumed that the mixtures of the pure n-alkanes were essentially ideal (*i.e.*, component activity coefficient equal to unity). This approximation was supported by the Scatchard–Hildebrand solution theory[18] and the UNIFAC method[16], both of which allow one to calculate component activity coefficient after making certain assumptions. In either case, component activity coefficients for the simple mixtures were calculated to be near unity. This allowed us then to determine component vapor density from standard injections of the hydrocarbons used to make up the mixtures. Assuming ideal behavior, average difference between experimental total mixture vapor pressure and calculated total vapor pressure was about 6% (Table V). Average precision for vapor pressure determinations was ±3%. For the mixture where component mole fraction was less than 0.1, difference between predicted and experimental total vapor pressures was about 5% (Table VI). Furthermore, average

TABLE VI

COMPONENT PARTIAL PRESSURES OF PURE HYDROCARBONS IN A SEVEN-COMPONENT MIX AT 72°C

The hydrocarbons were blended in a matrix of hexadecane.

V/L	*Partial pressure (kPa)**							*Total pressure (kPa)*
	Hexane	*Heptane*	*Octane*	*Nonane*	*Decane*	*Undecane*	*Dodecane*	
4:1	9.43	3.33	1.38	0.38	0.16	0.08	0.03	14.79
2:1	9.42	3.34	1.45	0.40	0.19	0.08	0.03	14.91
1:1	9.46	3.04	1.18	0.38	0.21	0.08	0.03	14.38

* Predicted component partial pressures were as follows (all values in kPa): hexane: 10.03; heptane: 3.47; octane 1.24; nonane: 0.45; decane: 0.17; undecane: 0.06; dodecane: 0.02. Total vapor pressure = 15.44 kPa.

precision was about ±2%. These differences between predicted and experimental vapor pressures reflected not only instrument operation, but also variability in the preparation of the mixtures; the latter were prepared in bulk and aliquots were pipetted into the headspace vials.

Complex mixtures

Aliquots of diesel fuel were pipetted into the headspace vials at various *V/L* ratios and chromatograms at sample temperatures of 38 and 70°C were developed. The GC trace was divided into 6 and 7 subsections (38 and 70°C, respectively), each approximately centered about the retention time of a pure hydrocarbon standard. This is illustrated in Fig. 2 which shows a gas chromatogram of a vapor sample of diesel fuel at 38°C and retention times (from injection) for a series of *n*-alkane reference standards (pentane through decane), each of which represents one of the six subsections (1–6).

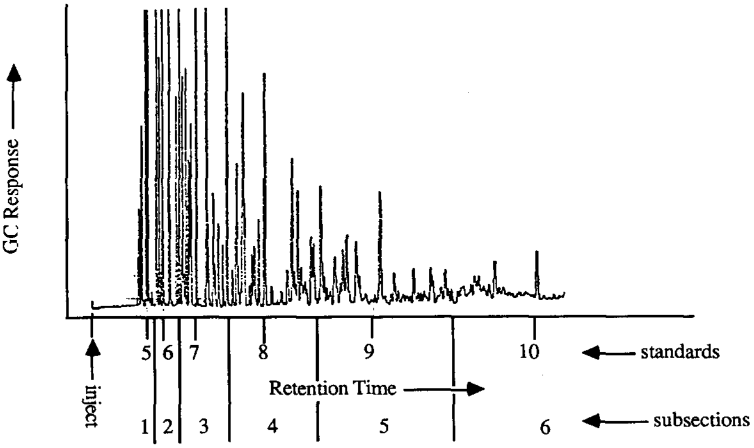

Fig. 2. Gas chromatogram of diesel fuel with standard retentions (C_5–C_{10}). Column: 40°C (5 min), 2°C/min to 80°C.

TABLE VII

VAPOR PRESSURE OF DIESEL FUEL BY HEADSPACE GAS CHROMATOGRAPHY AT TWO TEMPERATURES

Temperature (°C)	*V/L*	*Vapor pressure (kPa) (average ± S.D., n = 3)**
38	4:1	1.13 ± 0.03
	1:1	1.14 ± 0.01
70	4:1	3.83 ± 0.08
	1:1	3.92 ± 0.03

* Typical values at 38°C fall in the range 1.03–1.38 kPa, depending on the season.

Standard curves were generated for each hydrocarbon reference by injecting into sealed headspace vials increasing μl amounts, giving vapor densities below saturation. Then, each standard curve was used to calculate the vapor density for each subsection of the complex chromatogram, yielding subsection partial pressures.

Table VII lists the average total vapor pressures for diesel fuel at the two test temperatures. Vapor pressure was determined from the summed subsection partial pressures, which were derived from the ideal gas law using the subsection vapor density based on the calibration curve of each subsection hydrocarbon standard. The values for V/L = 4:1 and 1:1 had precisions of ±2 and ±1%, respectively. Agreement between the values at V/L = 4:1 and 1:1 were within 1–2% (38°C) and 2–3% (70°C). However, the differences were not significant at the 95% confidence level.

Further evaluation of the method using light fuels and crude oils is currently in progress. Table VIII lists a few preliminary results for gasoline, light, medium-light and heavy crude oils at 38°C and V/L = 4:1. Included are results obtained using the Reid method[1], which measures vapor pressures of petroleum mixtures equilibrated in sealed metal cylinders, equipped with mechanical pressure gauges, at V/L = 4:1. Compared to the average Reid vapor pressures, gasoline and light and medium-light crudes differed by −2.2, −6, and −19%, respectively. Average precision for these mixtures using headspace GC was about ±1%, while the Reid values exhibited precisions of ±1% (gasoline), ±5% (light crude), and ±38% (medium-light crude). Results for the heavy crude indicate that the headspace GC method is capable of measuring vapor pressures of low-volatility mixtures; the Reid method is not able to do this.

TABLE VIII

VAPOR PRESSURE OF GASOLINE AND THREE CRUDE OILS AT 38°C

Mixture (at V/L = 4:1)	*Vapor pressure (kPa) (average ± S.D., n = 3)*	
	Headspace GC	*Reid method*
Gasoline	58.86 ± 0.76	60.17 ± 0.41
Light crude	26.05 ± 0.14	26.91 ± 1.38
Medium-light crude	2.96 ± 0.07	3.65 ± 1.38
Heavy crude	0.04 ± 0.01	–

CONCLUSIONS

With headspace GC, it is possible to measure relatively quickly equilibrium (saturation) vapor pressures of pure *n*-alkanes and of simple and complex mixtures. In the latter case, it is not necessary to know the precise composition of the mixture, but the mixture can be approximated with reference standards the GC retention times of which span the chromatogram of the mixture. A significant aspect of the headspace GC technique is microprocessor control of the critical steps in the analysis, promising precise and accurate measurements: (1) sample thermostating; (2) vial pressurization; and (3) headspace sampling and injection. Furthermore, microprocessor control would allow around-the-clock operation for high sample through-put (*ca.* 50–100/day)

The method, as presented here, had good precision and accuracy at all experimental temperatures. Furthermore, increasing the number of components in the synthetic mixtures seemed to give better behaved solutions, where all component partial pressures were close to the predicted values. This implies that the method would work well with complex petroleum mixtures, which was demonstrated to be the case in this study using diesel fuel as a model petroleum mixture and for some samples of gasoline and crude oil. In a current study, the method is being used to measure vapor pressures of fuels (*e.g.*, gasoline and jet fuel), syncrude, and light, medium and heavy crude oils at several temperatures and V/L ratios for further evaluation. These applications will be the subject of a separate report.

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