

EVALUATION OF A METHOD FOR DETERMINING VAPOR PRESSURES
OF PETROLEUM MIXTURES BY HEADSPACE GAS CHROMATOGRAPHY

Final Report

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ABSTRACT

Headspace gas chromatography (HS-GC) was used to measure the vapor pressures of Chevron light, Texaco medium, and Santa Fe heavy crude oil samples at various temperatures in the range 43°C-97°C. The method was validated with single n-alkane hydrocarbons and their binary, ternary, and quaternary mixtures. The microprocessor-controlled HS-GC instrument automatically thermostated the crude oil samples contained in septum-sealed glass vials to equilibrate the vapor and liquid for 60 min, pressurized the vials to a pre-set pressure (15-30 psig) by inserting a hollow needle through the septum, and sampled the vapor for 0.01 min by allowing the pressure in the vial to drive an aliquot of the vapor through the needle and onto the analytical column. Using this technique, vapor pressures for the crudes were determined by simulating the composition of the mixtures with a series of n-alkane hydrocarbon standards whose GC retention times spanned the GC envelopes of the mixtures. Only for the Santa Fe heavy crude was it possible to determine vapor pressures at 43°C (0.73 ± 0.18 torr), 72°C (1.84 ± 0.14 torr), and 97°C (4.64 ± 0.63 torr). For Texaco medium and Chevron light crudes, vapor pressure determinations were made at 43°C (40.88 ± 2.23 torr) and 72°C (99.79 ± 12.29 torr) and at 43°C (134.39 ± 13.03 torr) only, respectively. Determinations at 72°C (light crude) and 97°C (light and medium crudes) were not made because of the inability of the instrument to handle the greater vapor densities and/or possible unsafe pressures at the higher temperatures. The HS-GC method measures only the volatile organic constituents of hydrocarbon mixtures, and is, therefore, preferred over methods that rely on measurement of total pressure within a sealed container, since the latter may also include contributions from dissolved air and water.

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DISCLAIMER

The statements and conclusions in this report are those of the contractor and not necessarily those of the California Air Resources Board. The mention of commercial products, their source or their use in connection with material reported herein is not to be construed as either an actual or implied endorsement of such products.

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INTRODUCTION

Evaporation of constituents of petroleum mixtures contribute reactive hydrocarbons to the atmosphere. In order to assess the potential for evaporation from 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. The Reid vapor pressure method (1), which relies on measurement of total pressure within a sealed container, is applicable to gasoline, but is incapable of measuring vapor pressures of low-volatility heavy crudes. Therefore, an approach is needed whereby the organic constituents of heavy crudes are measured with sensitive detectors and the results combined to calculate total vapor pressure for the crudes.

Vapor density determination through headspace sampling and gas chromatographic analysis affords the best approach for complex hydrocarbon mixtures (2-7). Analysis using headspace sampling and gas chromatography 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 gas chromatographic analysis (8-13). 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

$$A_r = a_r + b_r(n_r/V), \quad (r=\text{reference})$$

where the constants "a_r" and "b_r" are the intercept and slope, respectively. 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, or subsection, of GC responses for a series of components and this subsection is represented by a single n-alkane reference standard which is used to generate a standard curve for the subsection. 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, or (n_i/V)=A_i/(b_rM_r) where M_r=the molecular weight of the reference standard if the reference standard curve uses wt/vol rather than mole/vol for the vapor density. The total pressure (P_t) of the mixture is then derived from

$$P_t = \sum P_i.$$

The technique of headspace sampling 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 crude oil mixtures. The procedure was validated using single n-alkanes and their simple mixtures.

DEVELOPMENT OF THE TEST METHOD

The following is a description of how a test method for field sampling and vapor pressure determination of mixtures was developed. The final method, consisting of field sampling, sample transfer, and headspace gas chromatographic vapor pressure determination, for heavy crudes is described in Appendices B and C.

Field Sampling and Sample Transfer

Equipment. The sample container pipe (TP304N stainless steel, 1.90 cm nominal pipe size, schedule 40 (0.287 cm wall thickness), 30.5 cm long with standard threads at either end) was obtained from a local supplier. The stainless steel bar stock ball valves, 1.90 cm, were obtained from Gemini (Raymond, NH). The valves were rated to minimum pressures of 0.02 torr vacuum to 37,224 torr water, oil, and gas and 7,755 torr saturated steam. The valves were also rated to a minimum temperature range of -45°C to 230°C. Stainless steel two-way valves (SS4P4T; 0.64 cm) were supplied by the Nupro Co. (Willoughby, OH). Tygon tubing (1.27 cm ID) was obtained from a local hardware supplier. An assortment of hose connectors, including the sizes 0.95-1.90 cm, 0.95-2.54 cm, 0.95-3.18 cm, 0.95-3.49 cm, 0.95-3.81 cm, and 0.95-5.08 cm, and hose clamps (1.27 cm) were obtained from a local hardware supplier. The glass headspace vials (22 mL), Teflon[®]-coated butyl rubber septa, aluminum caps, and vial cap crimping tool were supplied by Perkin-Elmer Corp. (Norwalk, CT). The crimping tool was lubricated with flouro-Glide (Chemplast, Inc., Wayne, NJ) film bonding lubricant. Glass gas-tight syringes (μ L) were obtained from Hamilton (Reno, NV).

Reagents. Freon-12 and naphtha solvents were used as received from J.T. Baker (Phillipsburg, NJ). The crude oil samples (Chevron light, Texaco medium, and Santa Fe heavy) were obtained from the McKittrick oil field near Bakersfield, California, and diesel

fuel was obtained from local sources. Squalane ($C_{30}H_{62}$, 99%) was used as received from the Aldrich Chemical Co. (Milwaukee, WI) and a lecture bottle of at least 99% butane was obtained from Liquid Carbonic (Chicago, ILL).

Procedures. The stainless steel sample container (Figure 1A) was rinsed with a volatile naphtha solvent, then washed with a strong soap solution, rinsed thoroughly with tap water, and finally with distilled water. Drying was achieved by passing a current of clean, warm air through the container. A 0.95-1.90 cm hose connector was attached to the inlet and outlet valves of the clean and dry sampling container. The inside diameter of the tank sampling line was measured and a connector selected from the ones assembled so that the connector could be fitted to the tank sampling line and Tygon tubing connected between the tank sampling line and the sample inlet valve. Also, Tygon tubing was connected to the sample outlet valve and secured with tubing clamps.

For each type of crude oil sampled (light, medium, heavy) a tank sampling line corresponding to the tank level (top, upper, middle, or lower) was selected. The sampling system as described above was then assembled. The sample outlet valve was opened first, then the sample inlet valve second, and the tank sampling valve last. The sample container was held in an upright vertical position and the crude oil was allowed to flow up through the sampling system long enough to displace any air bubbles (Figure 1B). Then the sample outlet valve of the container was closed first, followed by the sample inlet valve of the container second, and then the tank sampling valve last. All connections were carefully removed to slowly release any pressure buildup between the sample inlet valve and the tank sampling valve. The valve handles were secured closed by taping the handles together with filament tape. Excess crude oil in the connecting tubing was discarded and the outside of the sample container was cleaned with the Freon solvent. The container was labeled and immediately stored in an ice chest for transport to the laboratory where it was stored at -20°C .

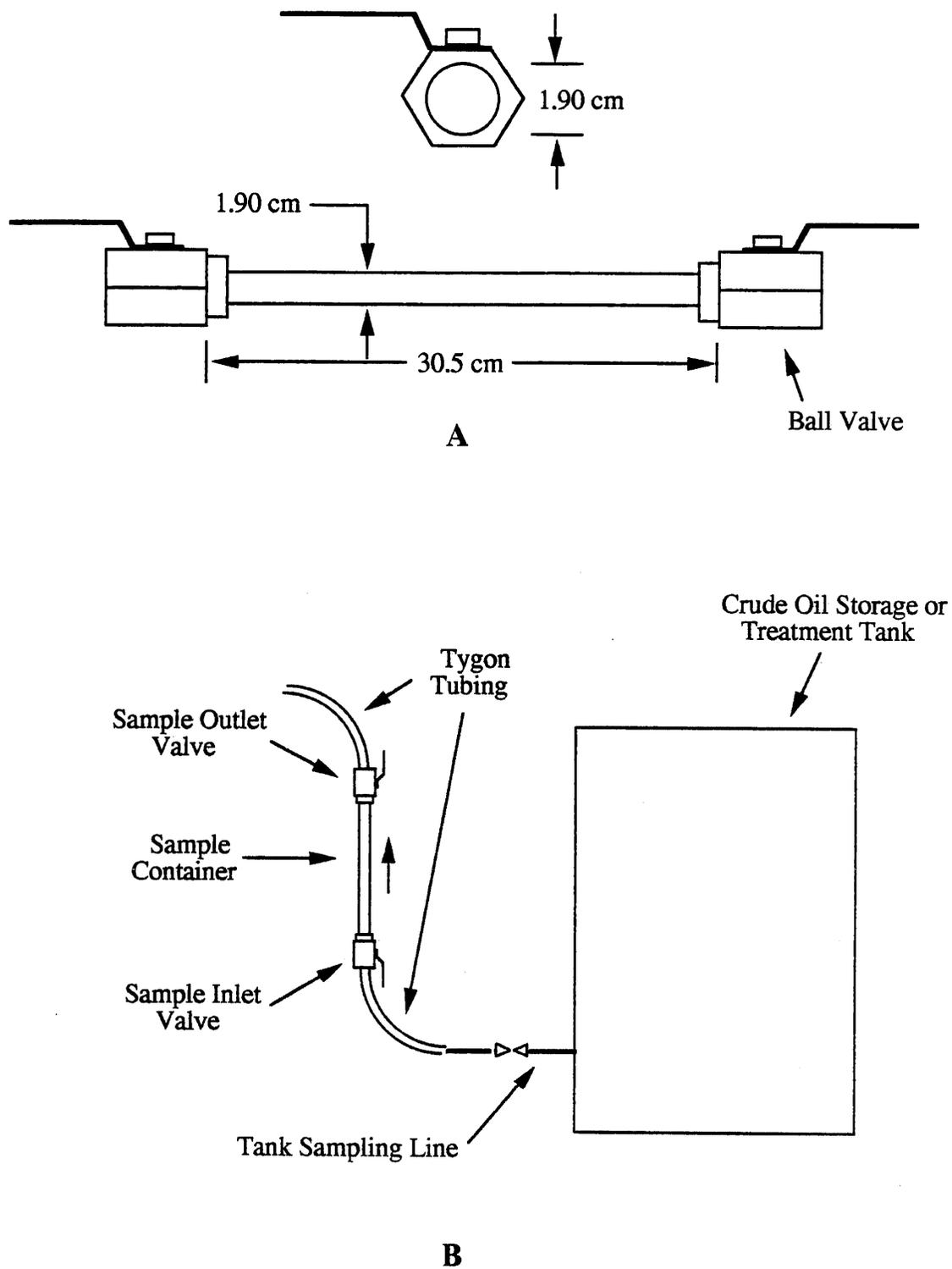


Figure 1. Crude oil sample container (A) and sampling system (B).

In the laboratory, aliquots of diesel fuel, chilled in dry ice for 25-30 min, were spiked with about 4% (v/v) butane, condensed at dry ice temperature, to raise the vapor pressure of the mixture to about 103 torr at room temperature (e.g., 12.5 mL butane was mixed with 287.5 mL diesel fuel). Likewise, aliquots of squalane, chilled in dry ice for 10-15 min, were spiked with about 0.17% (v/v) condensed butane (e.g., 185 μ L butane was mixed with 110 mL squalane) to raise the vapor pressure of the mixture to about 26 torr at room temperature. The mixtures, contained in glass reagent bottles at room temperature, were poured into separate open beakers at room temperature and 11 mL aliquots were decanted into pre-marked headspace vials (room temperature), each of which was immediately sealed with a Teflon-lined septum using the crimping tool. 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 not wrinkled. In other tests, the mixtures were maintained at water ice temperature and 11 mL aliquots were withdrawn using ice-chilled pipettes and transferred to ice-chilled headspace vials, which were immediately sealed. The 11 mL samples were thermostated at 40°C for 60 min prior to headspace sampling. In further tests, an empty stainless steel oil sampling pipe assembly, chilled in water ice for at least 30 min, was filled with the test mixtures by emptying them through bottom spigots attached to their storage containers, also chilled in water ice, a water reservoir was attached to bottom end of the pipe, which was placed in a vertical position, and 5 x 11 mL aliquots were dispensed into chilled headspace vials using nitrogen-pressurized (~1-2 psig) water displacement. An additional 5 mL was dispensed and discarded and the contents of the pipe were allowed to drain out the bottom back into the water reservoir until the mixture just passed the septum (some nitrogen pressure was applied to the top of the pipe) (Figure 2). Aliquots of 5 x 10 μ L were withdrawn through the septum using a chilled gas-tight

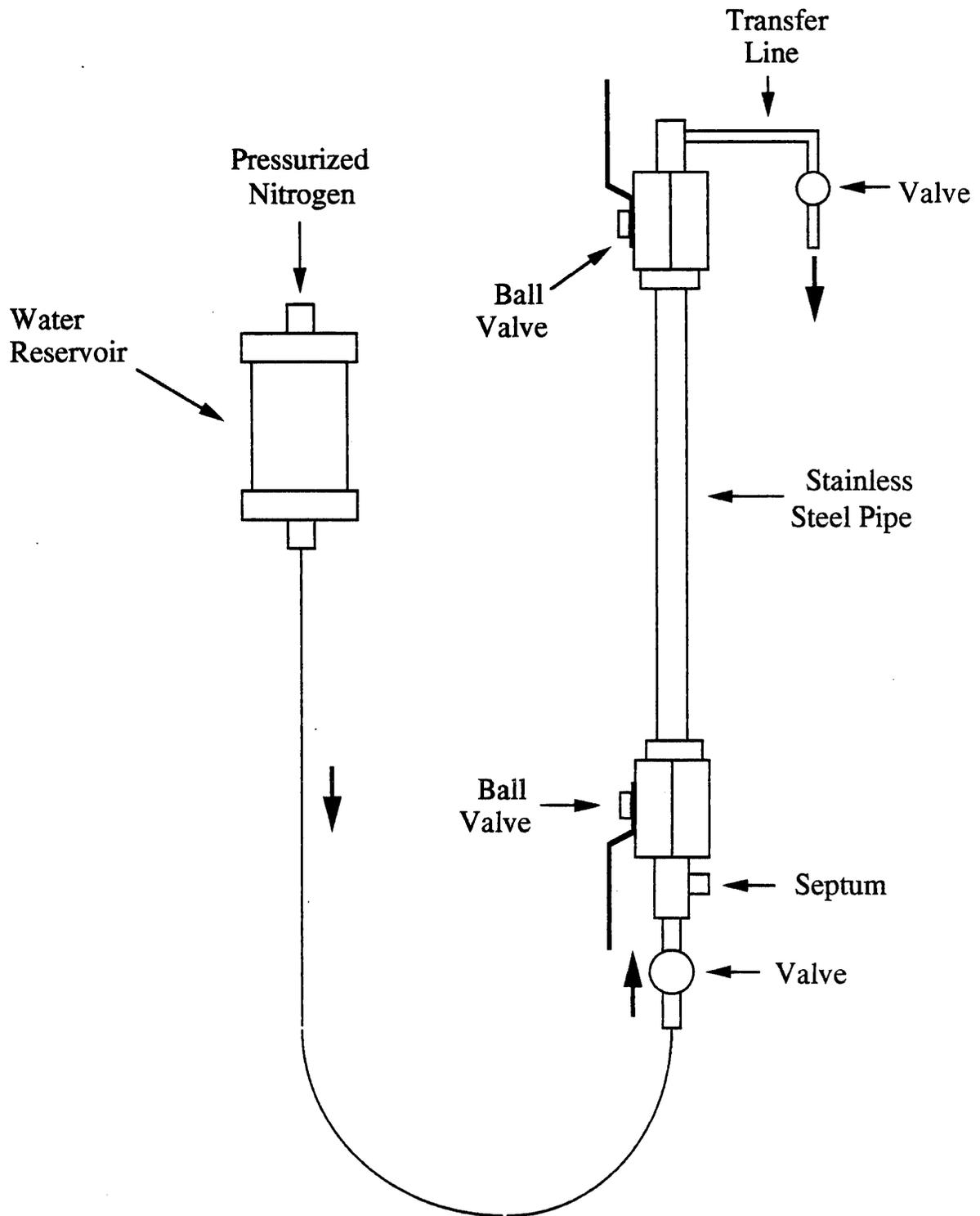


Figure 2. Sample transfer assembly for pressurized nitrogen subsampling of model mixtures and medium and light crudes.

syringe and injected into five sealed headspace vials. Using the same chilled gas-tight syringe, 5 x 10 μ L aliquots were withdrawn from the vials containing the 11 mL aliquots and injected into five sealed headspace vials. The 10 μ L samples were thermostated at 40°C for 30 min prior to headspace sampling and gas chromatography.

Headspace Gas Chromatography

Equipment. Gas chromatography was accomplished using the Perkin-Elmer Corp. (Norwalk, CT) Model HS-100 headspace sampler coupled to the Model Sigma 2000 gas chromatograph (flame ionization detector) and Model LCI-100 laboratory integrator (see Appendix A for detailed description of equipment). The gas chromatograph was equipped with a 30m x 0.25mm (ID) and a 60 m x 0.25mm (ID) fused silica open tubular (FSOT) columns coated with phase-bonded silicone oil (DB-1; J&W Scientific, Rancho Cordova, CA) and the transfer line connecting the HS-100 headspace sampler to the gas chromatograph was filled with a section of wide-bore (0.32mm) FSOT column either uncoated or coated with phase-bonded silicone oil (DB-1; J&W Scientific). 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, Inc., Wayne, NJ) film bonding lubricant. Glass syringes (μ L), with fixed and removable needles and syringe valve, were obtained from Hamilton (Reno, NV).

Reagents. Pure (at least 99+%) n-alkane hydrocarbons, pentane through hexadecane, were used as received from the Aldrich Chemical Co. (Milwaukee, WI), lecture bottles of at least 99% pure methane, ethane, propane, and butane were obtained from Liquid Carbonic (Chicago, ILL), and diesel fuel was obtained from local sources. All bottled gases (hydrogen, helium, nitrogen), except compressed air, were at least 99.995% pure (Liquid Carbonic, Chicago, ILL).

Procedures. One of the FSOT columns 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 the wide-bore FSOT column. Into a series of separate, sealed vials were injected, using fixed-needle syringes at ambient temperature, increasing μL amounts (well below vapor saturation) of the hydrocarbon series pentane through hexadecane. The samples were thermostated at various temperatures in the range 38°C - 107°C for 15 min prior to headspace sampling. In some cases, low hydrocarbon vapor densities (~ 0.1 mg/L) were achieved for the liquid hydrocarbons by injecting 0.05 μL liquid into sealed headspace vials, withdrawing 2 mL of the resulting vapor with a gas-tight syringe, and injecting the aliquot into an empty sealed vial. For the gaseous hydrocarbons methane through butane, headspace vials were purged with the hydrocarbons, the vials were sealed, and 50 - 200 μL aliquots were withdrawn with gas-tight syringes and injected into empty sealed headspace vials. 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 22 mL vials were filled to different extents to give vapor volume-to-liquid volume (V/L) ratios of $4/1$ (4.4 mL liquid), $2/1$ (7.3 mL liquid), and $1/1$ (11.0 mL liquid). The mixtures were thermostated at temperatures in the range 38°C - 107°C for 60 min prior to headspace sampling. The binary and ternary mixtures consisted of approximately equimolar amounts of the constituents, the quaternary mixture consisted of about 10 mole percent hexane and 30 mole percent each of the other constituents, and the seven-component mixture consisted of less than 10 mole percent of each of the components in a matrix of hexadecane at greater than 50 mole percent.

Syncrude was made up of diesel fuel ($\sim 98\%$, v/v) and a mixture ($\sim 2\%$, v/v) consisting of (% v/v) n-propane (1), n-butane (5.6), iso-pentane (6.5), n-pentane (6.6), n-hexane (26.8), and n-heptane (53.5). All hydrocarbons were transferred as liquids to the diesel fuel using syringes, except for n-propane which was transferred as a gas sampled from a pressurized cylinder using a gas-tight syringe equipped with a syringe valve. n-

Butane was condensed at dry ice temperature prior to sampling with a dry ice chilled syringe. The vials were filled to different extents to give vapor volume-to-liquid volume (V/L) ratios of 4/1 (4.4 mL liquid), 2/1 (7.3 mL liquid), and 1/1 (11.0 mL liquid). The mixtures were allowed to reach equilibrium at set temperatures of 40°C and 70°C for 60 min prior to headspace sampling.

Aliquots of the crude oil samples were transferred to the vials from the stainless steel pipes using either gravity feed or nitrogen-pressurized water displacement. The stainless steel pipes were removed from cold storage (-20°C) about 24 hours prior to sampling and allowed to warm to room temperature (22-23°C). Aliquots of Santa Fe heavy crude were removed from the pipes both by gravity feed at room temperature (Figure 3) and by nitrogen-pressurized (~1-2 psig) water displacement (Figure 2) after the pipe had been chilled in water ice for about an hour. The vials were chilled in water ice in both cases and were sealed immediately after receiving the aliquots and returned to water ice storage before analysis; the vials were also pre-marked to expedite oil volume measurement. Pipes containing Chevron light and Texaco medium crudes were chilled in water ice for at least an hour, after which time the pipes were quickly connected to a water reservoir and oil aliquots were quickly transferred to pre-marked vials by applying nitrogen pressure (~1-2 psig) to the water reservoir. The vials were immediately sealed and returned to water ice storage before analysis. The vials were filled to different extents to give vapor volume-to-liquid volume (V/L) ratios of 4/1 (4.4 mL liquid), 2/1 (7.3 mL liquid), and 1/1 (11.0 mL liquid). Vial filling followed the sequence V/L=4/1, 2/1, 1/1, 4/1, 2/1, 1/1, etc., until the sample in the pipe was exhausted (12-15 subsamples, depending on oil viscosity). The oil samples were thermostated at 40°C, 70°C, and 95°C (instead of 107°C because of the presence of water) for 60 min prior to headspace sampling.

After the samples reached equilibrium, the vial septa were punctured by the instrument using a hollow sampling needle, the internal pressure of each vial was raised to at least 15 psig with helium (at least 25 psig column head pressure), and the vapor sampled

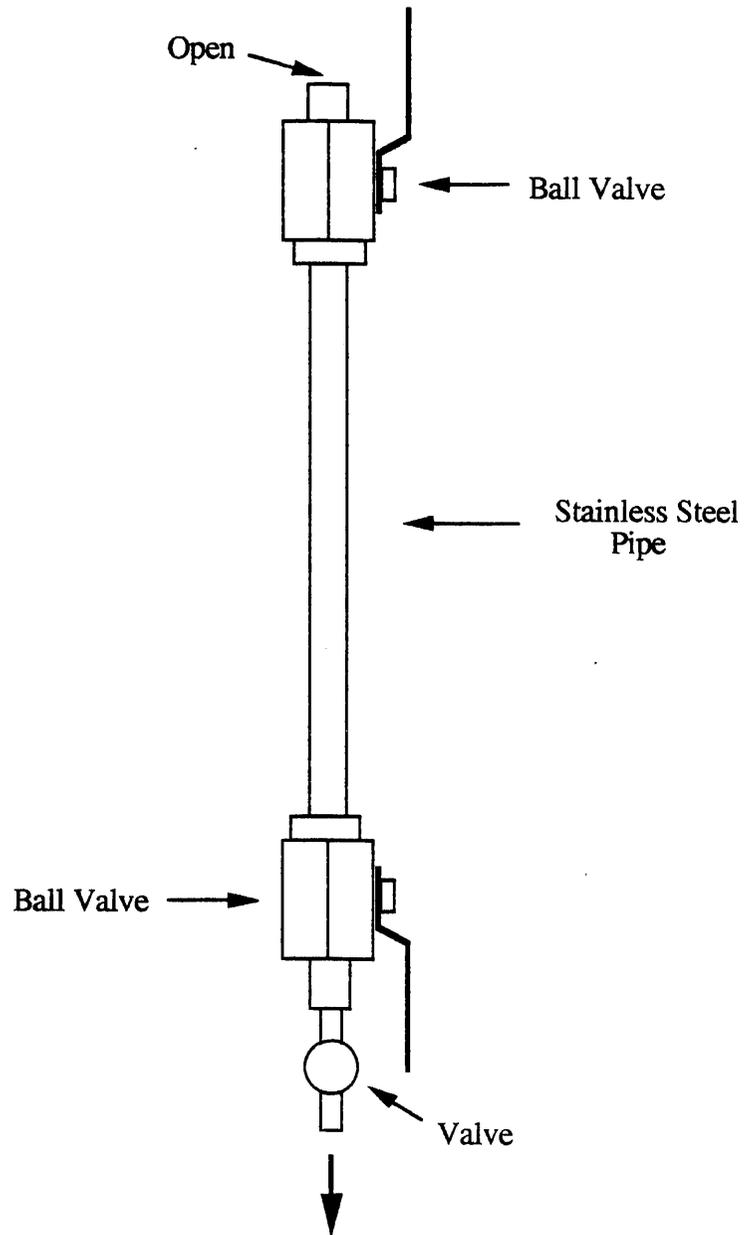


Figure 3. Sample transfer assembly for gravity feed subsampling of heavy crudes.

for 0.01 min. In all cases, the transfer line temperature was set at 150°C, and the column oven was operated isothermally at 40°C, 50°C, 80°C, 110°C, or 130°C and was also temperature programmed (2°/min, 5°/min) beginning at 40°C and ending in the range 80°C-130°C, depending on the type of sample.

For a given gas chromatogram of the headspace of an equilibrated complex mixture, gas chromatographic retention times for a series of pure hydrocarbons spanning the mixture chromatogram were determined by injecting μL amounts of a mixture of the pure standard hydrocarbons into a sealed headspace vial. Then into each of a series of sealed, empty vials was injected a single volume of a pure hydrocarbon of known density. For example, a series of three vials could contain 1, 2, and 4 μL n-pentane; another series of three vials could contain 0.2, 0.4, and 0.8 μL n-heptane, and so on, by direct injection of the liquid hydrocarbons into the sealed vials. However for the hydrocarbon series methane through butane, headspace vials were first purged with the gaseous hydrocarbons at room temperature, the vials were immediately sealed, and aliquots of the gases were then removed with a gas-tight syringe and injected into empty sealed headspace vials. Gas chromatograms for each series of hydrocarbons were then developed using headspace sampling and peak area was related to vapor density (mg/L) for each series of hydrocarbons. The complex mixture chromatogram was then divided into subsections, each of which was associated with a particular hydrocarbon standard curve. Each complex mixture subsection total area was used in its hydrocarbon standard linear regression equation to calculate a vapor density (mg/L) associated with each subsection:

$$(\text{mg/L}) = (\text{subsection area} - \text{intercept}) / \text{slope}$$

Each subsection vapor density result was then used in the ideal gas law to calculate each subsection partial pressure (P_i):

$$P_i = \left[(\text{mg/L}) / (1000 * \text{MW}) \right] * R * T * 760$$

where $R=0.08206 \text{ L}\cdot\text{atm}\cdot\text{K}^{-1}\cdot\text{mole}^{-1}$, $T=\text{K}$, $MW=\text{molecular weight}$, and 760 was used to convert from atmospheres to torr. The total vapor pressure (P_t) of the complex mixture was obtained by summing the subsection partial pressures:

$$P_t = \sum P_i$$

RESULTS AND DISCUSSION

Objectives of the study included (1) the development of a method for headspace sampling and gas chromatographic analysis of the vapor phase of equilibrated hydrocarbon mixtures, using individual pure hydrocarbons and their simple mixtures to validate the method; (2) calculation of vapor pressure of the individual compounds and simple mixtures using the analytical results; (3) applying the resulting methodology to the determination of vapor pressures of crude oils; and (4) developing a technique for field sampling of crude oils and their transfer to the laboratory analytical instrumentation without altering crude oil composition. 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 (Appendix A). 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.

Instrument calibration. The number of standard hydrocarbons necessary to encompass the gas chromatogram of a complex mixture varied depending upon the volatility of the mixture. In general, the number of standards necessary to represent the complex mixture was determined by comparing the area of the first subsection with the areas of subsequent subsections; the comparison ended when a subsection was found whose area was at the most 10% that of the first subsection. For example, if the area of the sixth subsection was $\leq 10\%$ the first, then the complex mixture would be represented by six standards (Figure 4). The standard hydrocarbon volumes injected into sealed headspace vials were well below vapor saturation at a given temperature so that complete vaporization was assured and the standard curves would be linear. While the standard curves for the liquid hydrocarbons (pentane and higher) were derived from their liquid densities, standard curves for the hydrocarbons methane through butane were derived from the molar density of an ideal gas (e.g., 24.45 L/mole at 25°C). For both cases, plots of vapor density (wt/L) vs GC response were generated. However, we found that, with the possible exception of methane, all of the gaseous hydrocarbon standard curves could be replaced with the standard curve for pentane (Figure 5; combining ethane, propane, butane, and pentane data into one linear regression equation gave a correlation coefficient (r^2) of 0.996). The pentane standard curve could be used to calculate partial pressures for the subsections that eluted earlier than the pentane subsection as long as the molecular weights of the particular subsection hydrocarbons were used. We took this approach only because standard curves for the hydrocarbons more volatile than pentane were not generated at the time the oil samples were evaluated. In routine use of the method, however, the hydrocarbons lighter than pentane would be used to generate standard curves for their subsections. Furthermore, instead of purging vials with these hydrocarbons prior to removing aliquots for instrument calibration, an alternative approach would use aliquots taken from gas flows through glass tubing. In this way, all air would be swept from the glass tubing giving constant hydrocarbon vapor densities.

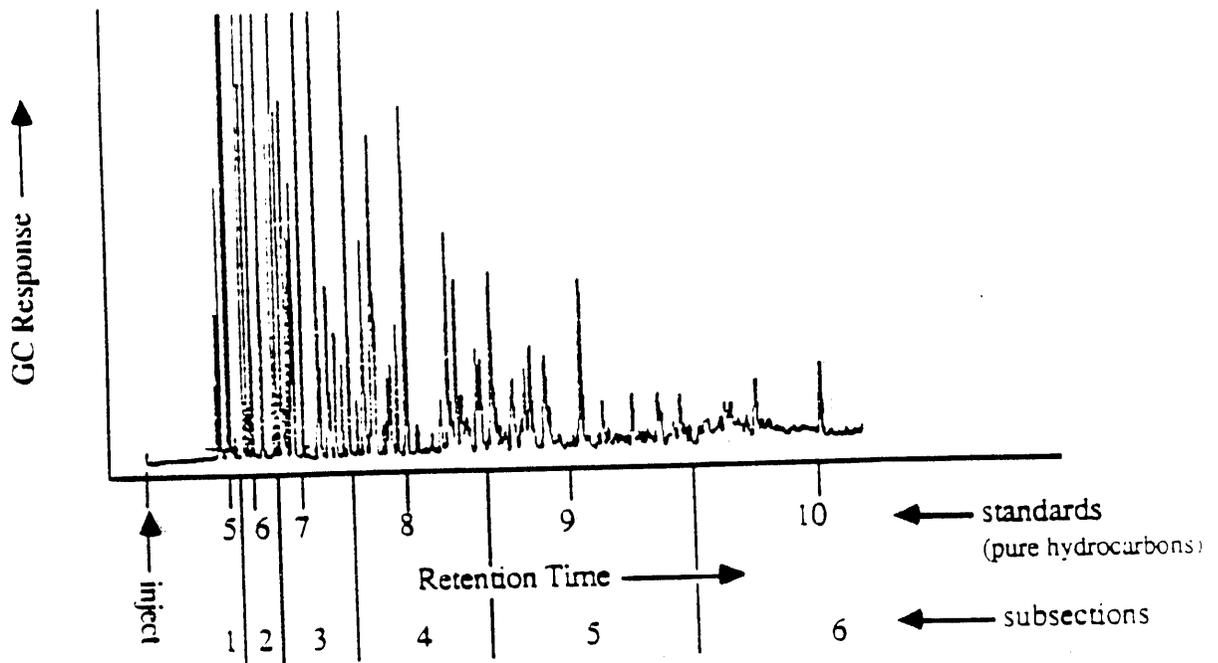


Figure 4. Gas chromatogram of complex mixture with standard retentions.

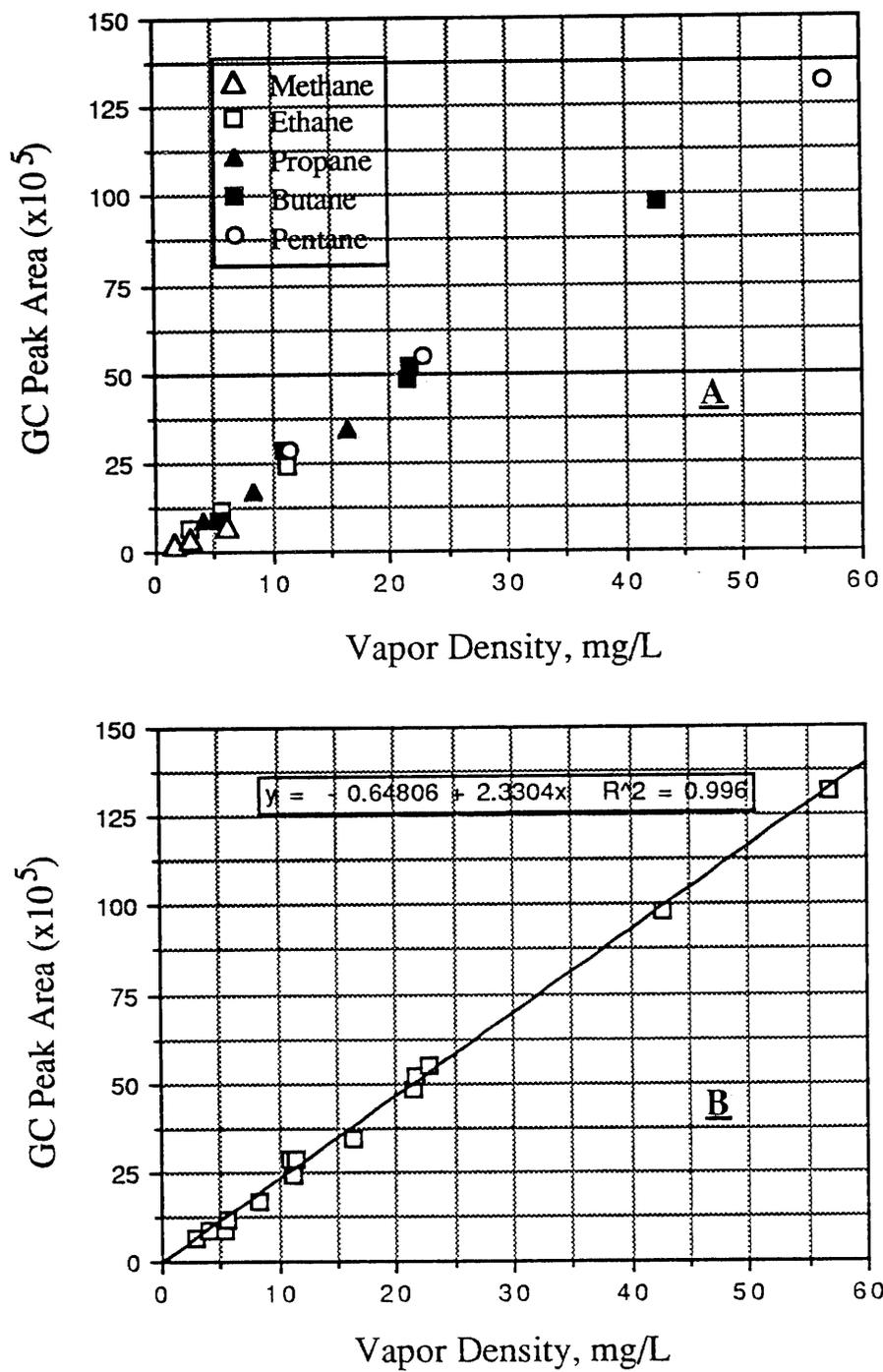


Figure 5. Standard curves for methane through pentane (A) and for the combined data set without methane (B).

The use of a DB-1 (methyl silicone bonded liquid phase) FSOT column for vapor pressure determination of hydrocarbons was based on earlier work which indicated that of the columns commercially available, the methyl silicone column comes closest to being a true boiling point column (7). Table 1 shows that hydrocarbon GC retention time was essentially determined by vapor pressure, regardless of whether the hydrocarbon was aliphatic or aromatic. The GC of a mixture of hexane, benzene, heptane, toluene, octane, and m-xylene gave the expected elution order based on vapor pressure. Furthermore, slopes of the plots of $\ln(1/t_r)$ vs $\ln(\text{vapor pressure})$ for each hydrocarbon in Table 1 (aromatics and aliphatics) fell in the range 0.86-0.90 (4.5%), indicating that change in GC retention time was determined for the most part by change in vapor pressure. Response of the flame ionization detector is proportional to the number of moles of oxidizable carbon. Relative response is illustrated in Figure 6 which shows, as an example, that both hexane and benzene have essentially the same response for a given vapor density (mmole/L); the slopes of their linear regression curves differed by only about 6%. This result is important since hexane is the standard for the subsection containing benzene and implies that all C₆ hydrocarbons should have similar responses.

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 (Figure 7A). This shape was less pronounced for heptane and octane (Figure 7C, 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 (Figure 7B). 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. All vapor pressure determinations were made with a wide-bore insert in the transfer line.

Another important consideration was the transfer line temperature. Instrument default temperature was 30 degrees above the sample temperature. However, for best results all vapor pressure determinations were made with the transfer line temperature set at

Table 1. GC retention times and vapor pressures for a series of aliphatic and aromatic hydrocarbons.

<u>Hydrocarbon</u>	<u>Vapor Pressure, torr^a</u>			<u>Retention Time (t_r), min^b</u>		
	<u>40° C</u>	<u>50° C</u>	<u>60° C</u>	<u>40° C</u>	<u>50° C</u>	<u>60° C</u>
Hexane	277.25	402.39	568.81	1.63	1.17	0.86
Benzene	182.37	270.12	389.26	2.61	1.87	1.36
Heptane	91.92	140.68	208.82	4.21	2.88	2.02
Toluene	58.48	91.18	137.77	6.85	4.64	3.23
Octane	30.80	49.86	77.94	10.86	7.07	4.72
m-Xylene	19.30	31.47	49.60	17.42	11.22	7.46

a Hydrocarbon saturation vapor pressures at the indicated GC column temperatures.

b Adjusted retention time (t_r - t_r(hydrocarbon) - t_r(methane)).

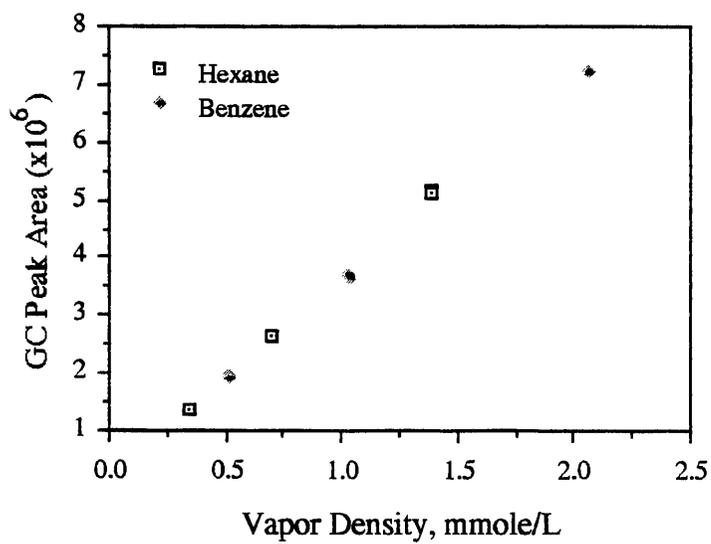


Figure 6. Correlation of gas chromatographic response with vapor density for hexane and benzene.

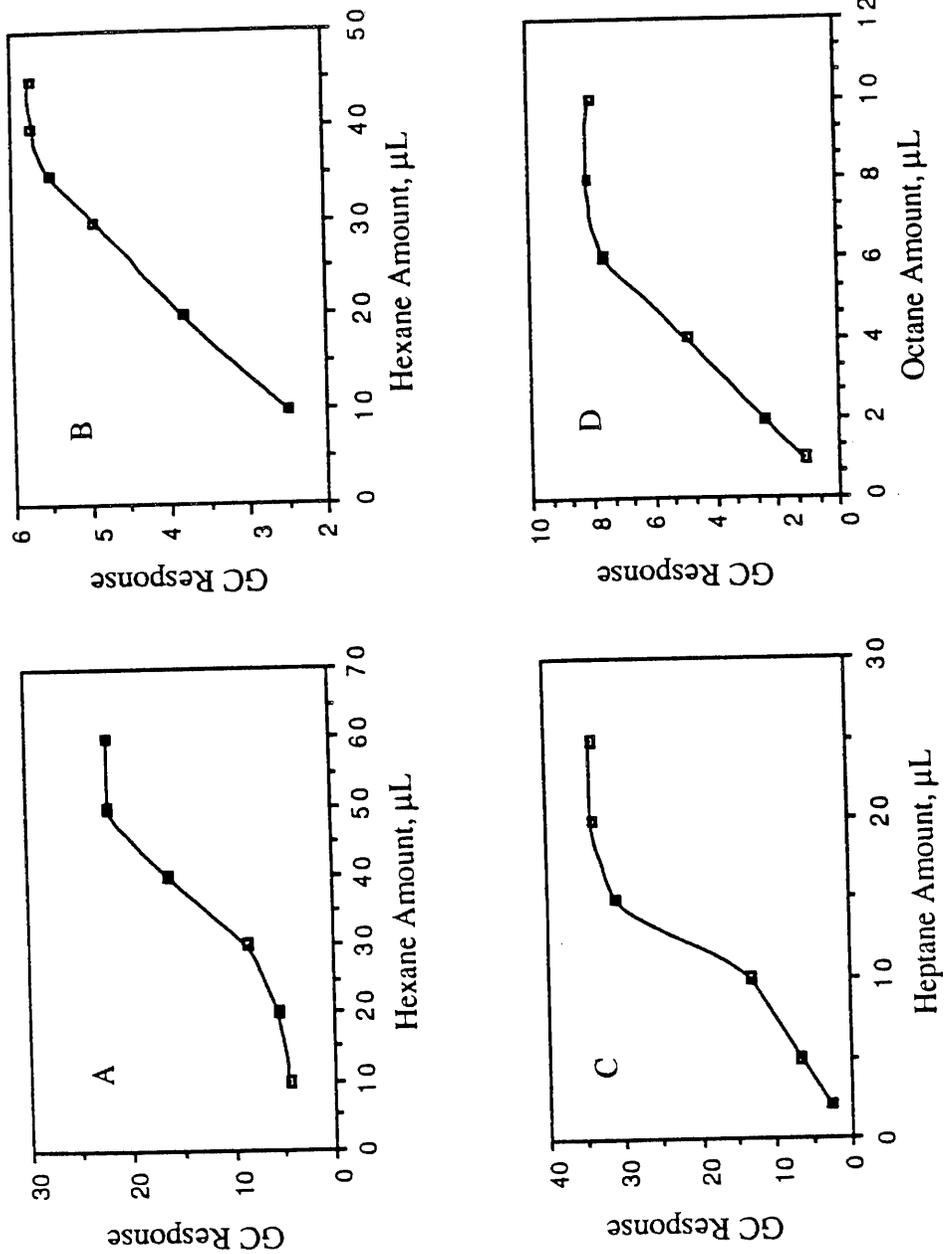


Figure 7. Isothermal (50°C) gas chromatographic responses of hexane (A, B), heptane (C), and octane (D). Only hexane (B) had transfer line insert.

150°C, which was above the boiling points of most of the hydrocarbon components that contributed significantly to the vapor pressures of the mixtures. It was possible to set the temperature at a higher value; however, the time 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/simple mixtures. The capabilities of the method 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) and their simple mixtures (including heptane, octane, nonane, and undecane in one case) at 38°C-107°C using the 30 m FSOT column. The results are summarized in Tables 2-6. Overall, measured vapor pressures differed from those calculated using the Harlacher equation (16) by 0.2-6% (Tables 2, 5, and 6). The Harlacher equation was used to calculate partial pressures of mixture components using mole fraction only, assuming that the mixtures were ideal (component activity coefficients were essentially unity) (17). The comparable results for the measured and calculated mixture vapor pressures indicated that the assumed ideality of the mixtures was a good approximation. This assumed ideality was further supported by the Scatchard-Hildebrand solution theory (18) and the UNIFAC method (16), both of which gave activity coefficients near unity for these mixtures. Average precision for the GC responses and measured vapor pressures fell in the range 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 (e.g., Table 4: ternary, decane, V/L=2/1, 43°C). The effects of variability on the quality of the data may be minimized by adequate replica-

Table 2. Vapor Pressures of Pure Hydrocarbons at Three Temperatures.

Hydrocarbons	Vapor Pressure, Torr ^a					
	38°C		70°C		107°C	
	Exp'tal	Calc'd ^b	Exp'tal	Calc'd ^b	Exp'tal	Calc'd ^b
Hexane	255.04±4.75	256.47	779.43±3.99	785.24	ND ^c	2186
Decane	3.20±0.05	3.21	18.77±0.38	18.88	93.38±0.90	93.62
Dodecane	ND	0.38	3.16±0.04	3.13	20.61±0.05	20.86
Hexadecane	ND	0.007	ND	0.10	1.14±0.11	1.19

^a Values with ±SD are averages of at least three determinations.

^b Calculated using the Harlacher equation:

$$\ln(P) = A + B/T + C \ln T + D(P)/T^2, \text{ where } A, B, C, \text{ and } D \text{ are constants taken from reference 16.}$$

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

Table 3. Gas Chromatographic Response of Pure Hydrocarbons.

<u>V/L</u> ^b	<u>Temp., °C</u>	<u>GC Response (E03)^a</u>			
		<u>Hexane</u>	<u>Decane</u>	<u>Dodecane</u>	<u>Hexadecane</u>
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%)

^a Average (±%SD) of three determinations.

^b Vapor volume-to-liquid volume ratio.

Table 4. Gas Chromatographic Response of Mixtures of Pure Hydrocarbons at 43°C, 72°C, and 107°C.

Mixture Type	Temp., °C	V/L ^a	GC Response (E02)			
			Hexane	Decane	Dodecane	Hexadecane
Binary ^b	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 ^b	43	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 ^c	43	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 ^b	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 ^b	72	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 ^c	72	4/1	143.20(±0.72%)	14.90(±3.29%)	4.82(±2.84%)	--

Table 4, cont.

		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 ^c	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%)

^a Vapor volume-to-liquid volume ratio.

^b Equimolar.

^c 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°C and 72°C.

Table 5. Vapor Pressures of Mixtures of Pure Hydrocarbons.

Temp., °C	Type	V/L ^a	Partial Pressure, Torr				Total Pressure, Torr	
			Hexane	Decane	Dodecane	Hexadecane	Exptl	Calc'd ^b
43	Binary	4/1	138.91	2.18	--	--	141.09	157.14
		2/1	148.44	2.18	--	--	150.62	
		1/1	135.84	1.95	--	--	137.79	
	Ternary	4/1	97.73	1.88	0.30	--	99.91	105.76
		2/1	97.73	1.65	0.22	--	99.60	
		1/1	99.83	1.42	0.15	--	101.40	
Quaternary ^c	4/1	28.95	1.35	0.15	--	30.45	32.55	
	2/1	28.95	1.35	0.15	--	30.45		
	1/1	28.13	1.28	0.08	--	29.49		
72	Binary	4/1	359.28	8.92	--	--	368.20	426.79
		2/1	406.09	8.32	--	--	414.41	
		1/1	388.31	9.00	--	--	397.31	
	Ternary	4/1	311.13	5.62	1.88	--	318.63	287.80
		2/1	268.08	5.70	1.65	--	275.43	
		1/1	278.95	5.70	1.95	--	286.60	
Quaternary ^c	4/1	78.76	3.75	0.98	--	83.49	90.83	

Table 5, cont.

		2/1	79.88	3.82	0.98	--	84.68
		1/1	80.86	3.60	0.98	--	85.44
107	Quaternary ^d	4/1	212.20	19.80	6.15	0.90	239.05
		2/1	217.97	21.08	6.60	0.90	246.55
		1/1	220.37	19.95	6.22	0.75	247.29

^a Vapor volume-to-liquid volume ratio.

^b Activity coefficient assumed to be unity.

^c Hexadecane response below the detection limit.

^d Temperature too high for binary and ternary mixtures.

Table 6. Component Partial Pressures of Pure Hydrocarbons in a Seven Component Mix at 72°C^a.

V/L ^c	Partial Pressure, Torr ^b							Total Pressure, Torr
	Hexane	Heptane	Octane	Nonane	Decane	Undecane	Dodecane	
4/1	70.73	24.98	10.35	2.85	1.20	0.60	0.22	110.93
2/1	70.66	25.05	10.88	3.00	1.42	0.60	0.22	111.83
1/1	70.96	22.80	8.85	2.85	1.58	0.60	0.22	107.86

^a The hydrocarbons were blended in a matrix of hexadecane.

^b Predicted component partial pressures were as follows (all values in Torr): Hexane-75.23; heptane-26.03; octane-9.30; nonane-3.38; decane-1.28; undecane-0.45; dodecane-0.15. Total vapor pressure=115.82 Torr.

^c Vapor volume-to-liquid volume ratio.

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

In most cases, varying vial V/L did not significantly affect instrument response. The few cases where it did included the neat hydrocarbons dodecane and hexadecane (Table 3), but the effect may have been partly due to the fact that their boiling points were about 76°C (dodecane) and 137°C (hexadecane) greater than the transfer line temperature. In those few cases where an effect was also observed for the mixtures, variability was only 2-4% (Table 4).

Complex Mixtures--Syncrude. The primary purposes for evaluating syncrude were to optimize the instrument conditions for the field samples of crude oil and to assess any possible effect that added water might have on instrument response to the equilibrated hydrocarbon headspace. The latter was of some concern since crudes typically contain some water from wash tanks (light) or from secondary steam recovery (heavy). The mixture was formulated to have a vapor pressure of at least 26 torr at room temperature (comparable to a medium crude). Syncrude samples were thermostated at set temperatures of 40°C and 70°C (actual temperatures were 43°C and 72°C) for 60 min prior to headspace sampling and analysis using both the 30 m and 60 m FSOT columns. Mixture vapor pressures at 43°C were 42.9±2.1 torr and 43.4±2.6 torr with no water and 3% (v/v) added water, respectively. The difference between these two values was only 1.2% and was not significant at the 95% confidence limit. At 72°C, the mixture vapor pressures were 82.7±4.6 torr and 86.3±6.2 torr with 3% (v/v) added water and no water, respectively. The difference between these values was only about 4% and was not significant at the 95% confidence limit. Syncrude was not evaluated at 95°C because of saturation of the detector by the volatile mixture.

Sample transfer. Prior to analysis of the crude oil samples, the process of transferring complex mixtures from candidate field containers to the laboratory headspace vials was examined to assess any possible effect on the composition of the mixtures. The

goal was to devise a sample transfer method that would prevent or at least minimize losses of volatile components from the crudes. Diesel fuel and squalane were spiked with enough butane to simulate light (103 torr) and medium (26 torr) crudes, respectively, at room temperature. The diesel fuel/butane results for room temperature transfer, ice temperature transfer, and transfer from a chilled stainless steel pipe (Figure 2) are summarized in Table 7. It is obvious, and not surprising, that for the ice transfer procedure less butane was lost, if any, compared to the room temperature transfer. Average responses for the two procedures were significantly different at the 95% confidence limit. Furthermore, the ice transfer and chilled pipe transfer appeared to be equivalent (averages were not significantly different). This suggests that temperature was the most important variable affecting mixture composition, assuming that mixture composition remained essentially unchanged during chilled pipe transfer. The latter was supported by the fact that the composition of the 10 μL aliquots taken from the sealed headspace vial was not significantly different from that for the 10 μL aliquots taken directly through the pipe septum. The squalane/butane results for the same tests are summarized in Table 8. Comparing the results for room temperature and ice temperature transfer indicated that the averages were significantly different; however, the difference was less than 5%, compared with a difference of about 47% for the diesel fuel/butane mixture under the same conditions (Table 7). The slight, though significant, difference in the squalane/butane results may have been partly due to some difficulty in measuring small volumes ($\sim 100 \mu\text{L}$) of cold liquid butane. As was expected because of the relatively low volatility of the mixture, averages of gas chromatographic responses for the two sets of 10 μL samples were not significantly different (Table 8). While these results have some bearing on possible future field sample container design (a simple and inexpensive sealable container would probably work well), the crude oil samples evaluated for this report were all stored in the stainless steel pipe container (Appendix B). Therefore, chilled pipe transfer with nitrogen-pressurized water displacement was the technique used in most cases.

Table 7. Gas chromatographic response of diesel fuel/butane mixtures.

Samples	Gas Chromatographic Peak Height Counts						
	Room Temp. Transfer ^a	Ice Temp. Transfer ^a	Vial ^b	Septum ^c	Vial ^d	Room Temp. Transfer ^a	Ice Temp. Transfer ^a
DF/B-1	10095	17152	18690	447.87	485.71	10066±544	16197±1200
DF/B-2	10430	17205	12644	442.60	430.39		
DF/B-3	10023	14986	13404	423.70	461.50		
DF/B-4	8959	14800	16783	426.93	399.27		
DF/B-5	10484	16840	16462	448.86	--		
DF/B-6	10541	--	--	--	--		
DF/B-7	9931	--	--	--	--		
						15597±2512	437.99±11.87
							444.22±37.56

^a V/L=1/1 (11 mL); mixtures consisted of 115 mL diesel fuel/5 mL butane.

^b 11 mL aliquots withdrawn from the pipe; mixtures consisted of 287.5 mL diesel fuel/12.5 mL butane.

^c 10 μ L aliquots withdrawn through pipe septum (Figure 2).

^d 10 μ L aliquots withdrawn from sealed headspace vials containing 11 mL aliquots from the pipe.

Table 8. Gas chromatographic response of squalane/butane mixtures.

<u>Samples</u>	<u>Gas Chromatographic Peak Height Counts</u>				
	<u>Room Temp. Transfer^a</u>	<u>Ice Temp. Transfer^a</u>	<u>Septum^b</u>	<u>Pipe Transfer</u>	
				<u>Vial^c</u>	
S/B-1	3654.6	3668.4	19.56	18.02	
S/B-2	3582.5	3770.3	20.60	18.17	
S/B-3	3610.0	3706.6	17.36	17.66	
S/B-4	3590.7	3729.4	17.16	19.67	
<u>S/B-5</u>	<u>3370.6</u>	<u>3749.6</u>	<u>18.31</u>	<u>16.71</u>	
	3561.7±110.4	3724.9±39.4	18.60±1.47	18.05±1.07	

a V/L=1/1 (11 mL); mixtures consisted of 60 mL squalane/100 μ L butane.

b 10 μ L aliquots withdrawn through pipe septum (Figure 2).

c 10 μ L aliquots withdrawn from sealed headspace vials containing 11 mL aliquots from the pipe.

Crude Oil. The stainless steel pipes containing the crude oil samples (Appendix B) were removed from cold storage (-20°C) about 24 hrs prior to subsampling and analysis and were allowed to warm to room temperature to allow the oil samples to remix after some possible separation during cold storage. Gravity feed sampling (Figure 3) at room temperature was the only technique that worked well enough with the heavy crude to allow aliquots to be taken smoothly and quickly with a minimum of oil loss. Nitrogen-pressurized water displacement (Figure 2) resulted in channeling and water breakthrough (especially if the oil was chilled), rendering the transfer process tedious and time consuming. The pipes containing the medium and light crudes were chilled in water ice for at least one hour, after which time aliquots were rapidly taken using nitrogen-pressurized water displacement. The heavy crude samples were thermostated at 40°C, 70°C, and 95°C (actual temperatures were 43°C, 72°C, and 97°C) for 60 minutes prior to headspace sampling and analysis using the 30 m FSOT column. The medium and light crudes were also thermostated for 60 minutes but only at 40°C and 70°C prior to headspace sampling and analysis using the 60 m FSOT column; these crudes were not evaluated at 95°C because of some concern over the possible generation of high pressures and saturation of the detector. The vial pressure (VP, psig)/column pressure (CP, psig) combinations used for the vapor pressure determinations of Santa Fe heavy, Texaco medium, and Chevron light crudes were 15 (VP)/25 (CP), 30 (VP)/30 (CP), and 30 (VP)/30 (CP), respectively. These vial pressure/column pressure combinations were used to avoid pre-injection of the sample during vial pressurization. It was necessary to maintain the column pressure at values equal to or greater than those of the vial pressure, as recommended by the manufacturer.

Crude oil vapor pressures were determined using the technique described earlier where the gas chromatographic envelope of each oil sample was divided into subsections, each approximately centered about the retention time of a pure hydrocarbon standard. Standard curves, generated for each hydrocarbon reference by injecting into sealed head-

space vials varying amounts yielding linear regression equations of the form $y=mx+b$, were used to calculate the vapor density for each subsection of the complex chromatogram, giving subsection partial pressures. As discussed above, partial pressures for those subsections with GC elution times less than that for pentane were determined using the pentane regression equation, but with the molecular weights of the appropriate hydrocarbon references (i.e., methane, ethane, propane, and butane). The methane subsection, however, could be represented only approximately by the pentane regression equation, but its occurrence in the crude oil samples was noted in only two cases (Santa Fe heavy crude at 43°C and 97°C, based on GC retention time). Tables 9-14 list the subsections, regression equations, and subsection partial pressures for the crudes at the various test temperatures and V/L.

Table 15 lists the average total vapor pressures for the three crude oils at the various 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 (see pp 1-2), as illustrated in Tables 9-14. Ranges of precision for the values in Table 15 were 6-30% (ave=14%), 1-12% (ave=5%), and 3-5% (ave=4%) for heavy, medium, and light crudes, respectively. The poorest precision for the heavy crude ($\pm 30\%$) occurred at 43°C and V/L=4/1 (4.4 mL), conditions unlikely to be used for measuring vapor pressures of this crude. While there was marked variability in the precision with temperature at V/L=4/1 and 1/1 for the heavy crude, essentially the same precision (6-7%) was observed regardless of the temperature at V/L=2/1 (7.3 mL). Furthermore, the overall greater average range for the heavy crude may have reflected some variability in composition of the samples taken from the stainless steel sampling pipes. For example at 97°C, some of the heavy crude aliquots not included in Table 12 had GC responses that were less than half of those for the samples reported (Table 16). Warming slowly to room temperature from -20°C over a 24 hr period was probably not adequate for remixing the oil after some separation occurred

Table 9. Subsection areas and partial pressures for Santa Fe heavy crude^a at 43°C.

Subsection Areas:		Gas Chromatographic Response, Area Counts								
V/Lb	Methane	Ethane	Propane	Butane	Pentane	Hexane	Heptane	Octane	Nonane	
4/1-1	60431	11124	--	282	11987	13848	12863	28257	46627	
-2	91394	11315	--	345	10908	14643	14047	29301	43202	
-3	40635	11046	--	222	12253	14100	13503	27512	44961	
2/1-1	94363	13469	891	919	11731	15112	13763	25904	44639	
-2	106257	13049	1152	1000	11364	15739	13767	29000	44957	
-3	105297	13530	1128	1096	11763	15956	13500	26890	46243	
1/1-1	110843	18004	1109	978	13692	16724	14014	28274	44423	
-2	73221	22765	2386	2817	13849	14768	12871	27000	40368	
-3	48634	23411	1847	2297	13601	14219	12363	26870	40785	

Subsection Regression Equations:

Standards

Pentane: Area= -93 + 182768(mg/L)

Hexane: Area= 1454 + 123289(mg/L)

Heptane: Area= -89 + 173649(mg/L)

Octane: Area= -926 + 200634(mg/L)

Table 9, cont.

Nonane: Area= -1394 + 162462(mg/L)

Subsection Partial Pressures:

V/Lb	Vapor Pressure, Torr										Total
	Methane	Ethane	Propane ^c	Butane ^c	Pentane	Hexane	Heptane	Octane	Nonane		
4/1-1	0.41	0.04	--	--	0.02	0.02	0.02	0.02	0.03	0.05	0.59
-2	0.61	0.04	--	--	0.02	0.02	0.02	0.02	0.03	0.04	0.78
-3	0.27	0.04	--	--	0.02	0.02	0.02	0.02	0.02	0.04	0.43
2/1-1	0.63	0.05	--	--	0.02	0.02	0.02	0.02	0.02	0.04	0.80
-2	0.71	0.05	--	--	0.02	0.03	0.02	0.02	0.03	0.04	0.90
-3	0.71	0.05	--	--	0.02	0.03	0.02	0.02	0.02	0.04	0.89
1/1-1	0.74	0.06	--	--	0.02	0.03	0.02	0.02	0.02	0.04	0.93
-2	0.49	0.08	0.01	--	0.02	0.02	0.02	0.02	0.02	0.04	0.70
-3	0.33	0.08	--	--	0.02	0.02	0.01	0.02	0.02	0.04	0.52

a #1527 shipping tank, lower level; sample #2.

b Vapor volume-to-liquid volume ratio.

c Most subsection vapor pressures were not significant.

Table 10. Subsection areas and partial pressures for Santa Fe heavy crude^a at 72°C.

Gas Chromatographic Response, Area Counts										
Subsection Areas:	V/L ^b	Ethane	Butane	Pentane	Hexane	Heptane	Octane	Nonane	Decane	
	4/1-1	560720	5360	41435	47052	56889	102085	198629	128012	
	-2	488339	5158	44496	48959	57084	102364	194805	121647	
	-3	482345	5160	42211	46531	59921	107346	213537	139702	
	2/1-1	439908	5084	44001	47812	58916	96311	189202	120394	
	-2	553928	850	46586	49046	54152	95221	184770	118938	
	1/1-1	532404	379	37149	45216	53163	95853	189277	125059	
	-2	384270	1260	43517	48330	55619	97429	189970	116735	

Subsection Regression Equations:

Standards

Pentane: Area= 4219 + 322600(mg/L)

Hexane: Area= -320590 + 591700(mg/L)

Heptane: Area= -229360 + 445800(mg/L)

Octane: Area= -104870 + 363900(mg/L)

Nonane: Area= -129080 + 304100(mg/L)

Decane: Area= -118000 + 250200(mg/L)

Table 10, cont.

Subsection Partial Pressures:

V/L ^b	Vapor Pressure, Torr									
	Ethane	Butane ^c	Pentane	Hexane	Heptane	Octane	Nonane	Decane	Total	
4/1-1	1.23	--	0.03	0.16	0.14	0.11	0.18	0.15	2.00	
-2	1.07	--	0.04	0.16	0.14	0.11	0.18	0.14	1.84	
-3	1.06	--	0.04	0.15	0.14	0.11	0.19	0.16	1.85	
2/1-1	0.97	--	0.04	0.16	0.14	0.10	0.18	0.14	1.73	
-2	1.22	--	0.04	0.16	0.14	0.10	0.17	0.14	1.97	
1/1-1	1.17	--	0.03	0.15	0.14	0.10	0.18	0.15	1.92	
-2	0.84	--	0.04	0.16	0.14	0.10	0.18	0.14	1.60	

a #1527 shipping tank, lower level; sample #4.

b Vapor volume-to-liquid volume ratio.

c Vapor pressure for this subsection was not significant.

Table 11. Subsection areas and partial pressures for Santa Fe heavy crude^a at 97°C.

Subsection Areas:		Gas Chromatographic Response, Area Counts											
		Methane	Propane	Butane	Pentane	Hexane	Heptane	Octane	Nonane	Decane	Undecane	Dodecane	Tridecane
V/Lb													
4/1-1	599950	--	40734	87621	123770	285908							
-2	792130	--	63738	148100	138118	333858							
-3	440425	--	30556	111291	120813	330536							
2/1-1	733756	--	57051	100231	124272	311682							
-2	453689	11188	64632	159009	121505	328219							
-3	373865	81285	55344	144437	119333	324466							
1/1-1	807500	--	56632	151170	118148	289178							
-2	347711	23030	40613	103495	87457	203069							
-3	578431	--	52902	132713	106129	301815							
V/Lb													
4/1-1	425844	904243	544657	528319	388282	163469							
-2	557153	1156668	766450	711105	482606	206808							
-3	670314	1442469	1065384	921229	630738	216669							
2/1-1	494460	1028156	670153	595387	421660	190661							
-2	539340	1118812	776993	675871	477266	213683							

Table 11, cont.

-3	543522	1132647	799611	706443	525306	204874
1/1-1	503331	1081906	784367	674017	474518	191300
-2	365520	760538	530032	470236	334606	143508
-3	526150	1120287	828926	722277	483650	210993

Subsection Regression Equations:

Standard

Pentane: Area= -79866 + 490570(mg/L)

Hexane: Area= -1014 + 277250(mg/L)

Heptane: Area= -314 + 280430(mg/L)

Octane: Area= -60758 + 356870(mg/L)

Nonane: Area= -76832 + 351520(mg/L)

Decane: Area= -30847 + 317770(mg/L)

Undecane: Area= -38283 + 258170(mg/L)

Dodecane: Area= -43167 + 264000(mg/L)

Tridecane: Area= -37383 + 252710(mg/L)

Subsection Partial Pressures:

V/Lb	Vapor Pressure, Torr						
	Methane	Propane ^c	Butane	Pentane	Hexane	Heptane	Octane
4/1-1	1.99	--	0.10	0.11	0.12	0.24	0.28

Table 11, cont.

-2	2.56	--	0.12	0.15	0.13	0.27	0.35
-3	1.52	--	0.09	0.12	0.12	0.27	0.41
2/1-1	2.38	--	0.11	0.12	0.12	0.26	0.31
-2	1.56	0.10	0.12	0.16	0.12	0.27	0.34
-3	1.33	0.17	0.11	0.15	0.12	0.27	0.34
1/1-1	2.60	--	0.11	0.15	0.12	0.24	0.32
-2	1.25	0.11	0.10	0.12	0.08	0.17	0.24
-3	1.93	--	0.11	0.14	0.10	0.25	0.33
V/Lb	Nonane	Decane	Undecane	Dodecane	Tridecane	Total	
4/1-1	0.50	0.29	0.32	0.22	0.10	4.27	
-2	0.63	0.41	0.43	0.27	0.12	5.44	
-3	0.78	0.56	0.55	0.34	0.12	4.88	
2/1-1	0.56	0.36	0.36	0.24	0.11	4.93	
-2	0.61	0.41	0.41	0.27	0.12	4.49	
-3	0.62	0.42	0.42	0.29	0.12	4.36	
1/1-1	0.59	0.42	0.41	0.26	0.11	5.33	
-2	0.43	0.29	0.29	0.19	0.09	3.36	
-3	0.61	0.44	0.43	0.27	0.12	4.73	

a #1527 shipping tank, lower level; sample #1. b Vapor volume-to-liquid volume ratio. c Missing values were either non-existent or insign

Table 12. Subsection areas and partial pressures for Texaco medium crude^a at 43°C.**Subsection Areas:**

V/L ^b	Gas Chromatographic Response, Area Counts					
	Propane	Butane	Pentane	Hexane	Heptane	Octane
4/1-1	5915836	7839880	7398953	3836860	1108521	72009
-2	3889422	8143622	7684808	4000156	1182833	64698
-3	7087352	7713068	7224636	3957363	1183384	67719
2/1-1	7597578	8571125	7879717	3455520	1010689	57040
-2	4290746	8174946	7304119	3499128	1042820	46744
-3	4736457	8707609	7478283	3541817	1082573	55426
1/1-1	6841788	11646062	5985789	2317812	670110	38261
-2	7666885	12118066	6191838	2434641	692438	38490
-3	7396934	11665046	5731144	2194745	595541	35394

Subsection Regression Equations:Standard

Pentane: Area= 55000 + 259580(mg/L)

Hexane: Area= 61333 + 141680(mg/L)

Heptane: Area= 209520 + 31065(mg/L)

Octane: Area= -12625 + 10875(mg/L)

Subsection Partial Pressures:

V/L ^b	Vapor Pressure, Torr						
	Propane	Butane	Pentane	Hexane	Heptane	Octane	Total
4/1-1	10.09	10.17	7.73	6.09	5.69	1.34	41.11
-2	6.60	10.56	8.03	6.36	6.16	1.23	38.94
-3	12.11	10.00	7.54	6.29	6.17	1.27	43.38
2/1-1	12.98	11.12	8.23	5.48	5.07	1.10	43.98

-2	7.29	10.61	7.63	5.55	5.28	0.94	37.30
-3	8.06	11.30	7.81	5.62	5.53	1.08	39.40
1/1-1	11.68	15.14	6.24	3.64	2.92	0.81	40.43
-2	13.10	15.76	6.46	3.83	3.06	0.81	43.02
-3	12.64	15.16	5.97	3.44	2.44	0.76	40.41

a Antelope Shell light; tank 1GF59, bottom; sample #6.

b Vapor volume-to-liquid volume ratio.

Table 13. Subsection areas and partial pressures for Texaco medium crude^a at 72°C.**Subsection Areas:**

V/L ^b	Gas Chromatographic Response, Area Counts				
	Propane	Butane	Pentane	Hexane	Heptane
4/1-1	8044761	12941742	15318300	8157495	2447642
-2	8896318	13084439	15469340	8406903	2396280
-3	8665871	13237902	15614949	8496769	2526034
2/1-1	12832493	15167168	15520779	7542898	2492159
-2	13008645	14788247	15573516	7508618	2240585
-3	13067482	14696579	15509374	7581030	2619317
1/1-1	11318848	12138744	12130806	5699458	1607777
-2	13978764	12703226	13041092	6199085	3287026
-3	14278099	12561815	13307623	6273722	4083635

Subsection Regression Equations:Standard

Pentane: Area= 255100 + 201200(mg/L)

Hexane: Area= 92205 + 122800(mg/L)

Heptane: Area= -18744 + 42600(mg/L)

Subsection Partial Pressures:

V/L ^b	Vapor Pressure, Torr					
	Propane	Butane	Pentane	Hexane	Heptane	Total
4/1-1	18.89	23.34	22.33	16.40	12.44	93.40
-2	20.96	23.60	22.55	16.91	12.18	96.20
-3	20.40	23.89	22.76	17.09	12.83	96.97
2/1-1	30.50	27.44	22.63	15.15	12.66	108.38
-2	30.93	26.74	22.70	15.08	11.39	106.84

-3	31.07	26.57	22.61	15.23	13.30	108.78
1/1-1	26.83	21.86	17.60	11.40	8.20	85.89
-2	33.28	22.90	18.95	12.42	16.67	104.22
-3	34.01	22.64	19.34	12.57	20.69	109.25

a Antelope Shell light; tank #1GF59, bottom; sample #4.

b Vapor volume-to-liquid volume ratio.

Table 14. Subsection areas and partial pressures for Chevron light crude^a at 43°C.**Subsection Areas:**

V/L ^b	Gas Chromatographic Response, Area Counts					
	Propane	Butane	Pentane	Hexane	Heptane	Octane
4/1-1	17339268	18757429	15061640	6733210	1700660	75032
-2	17498027	16148869	13700048	6270756	1561099	65513
-3	16186293	16327740	13859944	6727773	1668990	74412
2/1-1	23611863	18244648	14183611	6097360	1408246	65809
-2	27531076	18247092	13428627	5532783	1281600	54466
-3	28867446	18625747	14103170	5895684	1318029	53577
1/1-1	31434563	16568763	10961706	4073533	871509	45661
-2	35433877	15747117	10225681	3792924	828617	40523
-3	35068417	13896722	8769682	3951326	825525	45458

Subsection Regression Equations:Standard

Pentane: Area= 632090 + 170900(mg/L)

Hexane: Area= 207000 + 136500(mg/L)

Heptane: Area= 143020 + 32200(mg/L)

Octane: Area= -4974 + 10938(mg/L)

Subsection Partial Pressures:

V/L ^b	Vapor Pressure, Torr						
	Propane	Butane	Pentane	Hexane	Heptane	Octane	Total
4/1-1	43.69	35.96	23.06	10.93	9.52	1.26	124.42
-2	44.10	30.78	20.89	10.16	8.67	1.11	115.71
-3	40.68	31.14	21.14	10.92	9.33	1.25	114.46
2/1-1	60.09	34.94	21.66	9.86	7.74	1.12	135.41

-2	70.34	34.95	20.45	8.92	6.96	0.94	142.56
-3	73.84	35.70	21.53	9.53	7.18	0.92	148.70
1/1-1	80.55	31.62	16.51	6.48	4.46	0.80	140.42
-2	91.01	29.99	15.33	6.01	4.19	0.72	147.25
-3	90.05	26.32	13.00	6.27	4.17	0.80	140.61

^a Shipping tank, lower level; sample #1.

^b Vapor volume-to-liquid volume ratio.

Table 15. Vapor pressures of heavy, medium, and light crudes at three temperatures.

Crude	V/L ^b	Vapor Pressure, torr ^a		
		43°C	72°C	97°C
Santa Fe heavy	4/1	0.60±0.18	1.90±0.09	4.86±0.58
	2/1	0.86±0.06	1.85±0.12	4.59±0.30
	1/1	0.72±0.20	1.76±0.16	4.47±1.01
	Grand Ave: ^c	0.73±0.18	1.84±0.14	4.64±0.63
Texaco medium	4/1	41.14±2.22	95.52±1.88	--d
	2/1	40.23±3.42	108.07±1.02	--d
	1/1	41.29±1.50	99.79±12.29	--d
	Grand Ave: ^e	40.88±2.23	101.10±8.31	
Chevron light	4/1	118.20±5.42	--f	--d
	2/1	142.22±6.65	--f	--d
	1/1	142.76±3.89	--f	--d
	Grand Ave: ^g	134.39±13.03		

a Average (±SD) of three determinations in all cases (except at 72°C and V/L=2/1 and 1/1 for Santa Fe heavy crude, for which duplicate determinations were made). Actual vial temperatures shown (set points were 40°C, 70°C, and 95°C).

b Vapor volume-to-liquid volume ratio.

c Averages of values from Tables 9-11

d No measurement was made.

e Averages of values from Tables 12 and 13.

f Measurements varied widely (see text).

g Average of values from Table 14.

Table 16. Total vapor pressures of Santa Fe heavy crude at 97°C.

Total Vapor Pressure, Torr			
V/L	Gravity feed ^a	V/L	Water displacement ^b
4/1-1	4.27	4/1-1	3.84
-2	1.71	-2	2.22
-3	5.44	-3	2.29
-4	4.88	-4	2.17
2/1-1	4.93	-5	2.77
-2	4.49	2/1-1	3.36
-3	2.56	-2	3.78
-4	2.71	-3	2.39
-5	4.36	-4	4.74
1/1-1	5.33	1/1-1	1.83
-2	1.88	-2	3.77
-3	3.36	-3	3.32
-4	4.73	--	--

a Figure 3.

b Figure 2.

during cold storage. Perhaps warming the oil to some point above room temperature for a period of time would promote more thorough mixing. While the heavy crude did not show any clear-cut trends for precision vs temperature, the medium and light crudes showed increasing variability in response with increasing temperature. Variability became dramatic for Chevron light crude when it showed a precision of $\pm 31\%$ at 72°C (vapor pressures were approximately 309 torr, 477 torr, and 588 torr at $V/L=4/1$, $2/1$, and $1/1$, respectively). This result indicates a limitation to the headspace method when dealing with complex mixtures that have vapor pressures much greater than about 300 torr. Furthermore, the variability was more pronounced using the 60 m FSOT column compared to the shorter 30 m column. However with the shorter column, sample pre-injection was a problem with the medium and light crudes, as discussed above. Table 15 also includes grand averages at each temperature for each type of oil. These numbers were included to suggest that, since it was simple to control the volume of the oil aliquots removed from the storage pipes, vapor pressure determination could be done at various V/L and then the data combined to average any variability that may occur with V/L .

Sources of Error. The headspace gas chromatographic instrument (gas chromatograph plus headspace auto-sampler and injector) has a typical reproducibility of about $\pm 1\%$, according to the manufacturer. Glass μL syringes, used in the vapor pressure method to generate standard curves for instrument calibration, all have accuracy errors and mechanical reproducibilities of $\pm 1\%$ (manufacturer's claim). However, gas chromatographic responses of pure hydrocarbons and their simple mixtures using the above equipment (Tables 2, 3, 4, 7, and 8) had standard deviations ranging from $<\pm 1\%$ to $\pm 16\%$ (ave= $\pm 4\%$, $n=102$). These results were probably related to at least three potential sources of error: 1) The operator's ability to handle volatile compounds and mixtures; 2) how well the Teflon-lined septum made a seal with the glass headspace vial and the integrity of the septum itself; and 3) the ability of the two-stage regulator to control the pressure of the vial pressurization gas. The high value in the above range ($\pm 16\%$; the next

highest value was $\pm 8\%$) was the result of one test, where 11 mL aliquots of the diesel fuel/butane mixture were removed from the stainless steel pipe (Table 7), and was probably due to poor septum seals in two cases. A poor seal can be caused by an improperly seated septum cap; if the cap can be turned after crimping, there is a chance that the vial will leak under pressure. A poor seal can also be caused by a chip in the rim of the vial mouth. The two-stage regulator, which was attached to the cylinder of high pressure ($>2,000$ psig) helium, appeared to regulate well the pressure in the vials if the pressure of the source remained above about 1,000 psig; we routinely replaced the cylinder when its pressure dropped to 1,000 psig. A malfunctioning regulator can introduce appreciable error into the gas chromatographic response of samples if the regulator is unable to control the vial pressure.

CONCLUSIONS AND RECOMMENDATIONS

With headspace gas chromatography, it was possible to measure relatively quickly equilibrium (saturation) vapor pressures of pure n-alkanes and of simple and complex mixtures. In the latter case, it was not necessary to know the precise composition of the mixture, but the mixture could be approximated with reference standards whose GC retention times spanned the chromatogram envelope of the mixture.

The method, as presented here, had good precision and accuracy for the pure hydrocarbons and their synthetic mixtures at all experimental temperatures. This was achieved in part by inserting a section of FSOT column into the transfer line of the headspace instrument, by maintaining the transfer line temperature at a reasonably high value (150°C in this case) (18), and by setting the column head pressure greater than or equal to the vial pressure. Furthermore, best results were also achieved for the light and medium crudes by using the 60 m FSOT column and for the heavy crude by using the 30 m FSOT column. The shorter 30 m FSOT column was preferred for the heavy crude because of the low volatility of this mixture and less variability of its GC response with V/L.

At the various V/L, as well as for the grand averages (Table 15), precision was good for the medium and light crudes. This might have been due in part to possibly little separation during cold storage and/or to good remixing when the samples were warmed to room temperature. The heavy crude, on the other hand, showed some variability in response ($\pm 8-25\%$ for the grand average), and this might have been due to separation and/or chemical change of the crude during cold storage followed by poor remixing when the sample was allowed to warm to room temperature. Remixing of the heavy crude might have been achieved by heating the oil to near its field storage temperature for several hours (perhaps with some shaking or tumbling) and then chilling in water ice prior to taking the aliquots for vapor pressure determination. Since the valves of the storage pipes can take up to over 37,000 torr before leaking and since the pipes were filled in the field with heavy crude near 100°C , warming the samples to near the field temperature shouldn't be a problem. The ability of the stainless steel storage pipes to take very high pressures suggests that it might be possible to avoid having to use cold storage at all for the oil samples, as long as the valves could be secured against accidental opening. A suggested procedure would be to fill the pipes in the field, close and secure the valves, transport the samples to the laboratory under ambient conditions, store at temperatures consistent with field conditions (e.g., $95-100^{\circ}\text{C}$ for heavy crude; $25-30^{\circ}\text{C}$ for medium crude), and then chill the samples in water ice just prior to subsampling for vapor pressure determination.

Transfer of the oil samples from the storage pipes to the headspace vials using nitrogen-pressurized water displacement proved to be a rapid and smooth operation for the medium and light crudes at water ice temperature. Gravity feed subsampling, as opposed to nitrogen-pressurized water displacement (Table 16), worked well for the heavy crude, as long as it was maintained at room temperature (results for room temperature and ice temperature transfers for a low volatility synthetic mixture differed by less than 5%--Table 8). However, if the heavy crude is chilled, it would probably be necessary to apply some nitrogen pressure to the top of the pipe to move the oil in a reasonable amount of time.

For this study, vapor pressure averages and their relative errors were based in most cases on sets of nine samples (three each at $V/L=4/1$, $2/1$, and $1/1$) for each crude oil type under each set of conditions (Tables 9-14), even though in many cases more than nine samples were removed from each sample storage pipe (total volume was about 120 mL). The variable V/L was included in the development of the method to assess any possible effect on vapor pressure determination. Since V/L had a slight, but unimportant, effect on the vapor pressure measurements of the three crudes, any value up to $V/L=1/1$ (11 mL) should give reliable results.

We recommend the headspace method for the vapor pressure determination of heavy crudes. Furthermore, heavy crudes should be evaluated at 97°C and $V/L=2/1$ (~7 mL) using the 30 m capillary column. This temperature is consistent with those values commonly encountered in the field and the results of this study indicated that 7 mL of heavy crude in the headspace vial gave the best precision at 97°C and the most consistent precision with varying sample temperature. Since the heavy crude samples used to develop this method had been stored for some time at -20°C , we recommend verifying the method by obtaining fresh samples, storing them at room temperature, and measuring their vapor pressures within 1-2 weeks.

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APPENDIX A

DESCRIPTION OF HEADSPACE EQUIPMENT

(Condensed from various Perkin-Elmer user manuals)

The headspace equipment consisted of three main components: (1) The Model Sigma 2000 gas chromatograph; (2) the Model HS-100 auto-injector (Figure A-1); and (3) the Model LCI-100 reporting integrator. The gas chromatograph was equipped with both a 30m x 0.25mm (ID) and a 60m x 0.25mm (ID) FSOT columns and a flame ionization detector. All of the functions of the gas chromatograph (e.g., temperature control and oven programming variables, gas flows, timed events, range and attenuation settings) are controlled by the on-board computer, which can contain up to ten methods. The auto-injector operates on the principle of pneumatic, pressure balanced sampling. The unit is able to analyze up to 100 samples, either singly, for different sample conditions, or as a group with constant thermostating time for each sample. In addition, the auto-injector has a progressive extraction mode for determining equilibration time and performing kinetic studies and a multiple headspace extraction mode for determination of mixture composition. Samples can be thermostated between about 40°C and 150°C, in increments of 1°C, with a precision better than $\pm 0.1^\circ\text{C}$, and transfer line temperatures are selectable between 50°C and 180°C in increments of 10°C.

The HS-100 was also equipped with a high pressure sampling accessory which allowed the vial pressure to be set independent of the column head pressure. Figure A-2 shows a schematic diagram of the accessory and the sampling sequence using the accessory. Carrier gas (helium) at pressure P1 is applied to the inlet of valve V4. P1 is the required column head pressure. Auxilliary carrier gas (helium) at pressure P2 is applied to the inlet of valve V5. P2 must be higher than the internal pressure in the headspace vial. When the sample contains water, the vapor pressure in the vial at the selected thermostating temperature can be calculated, or the optimum pressure P2 can be determined empirically

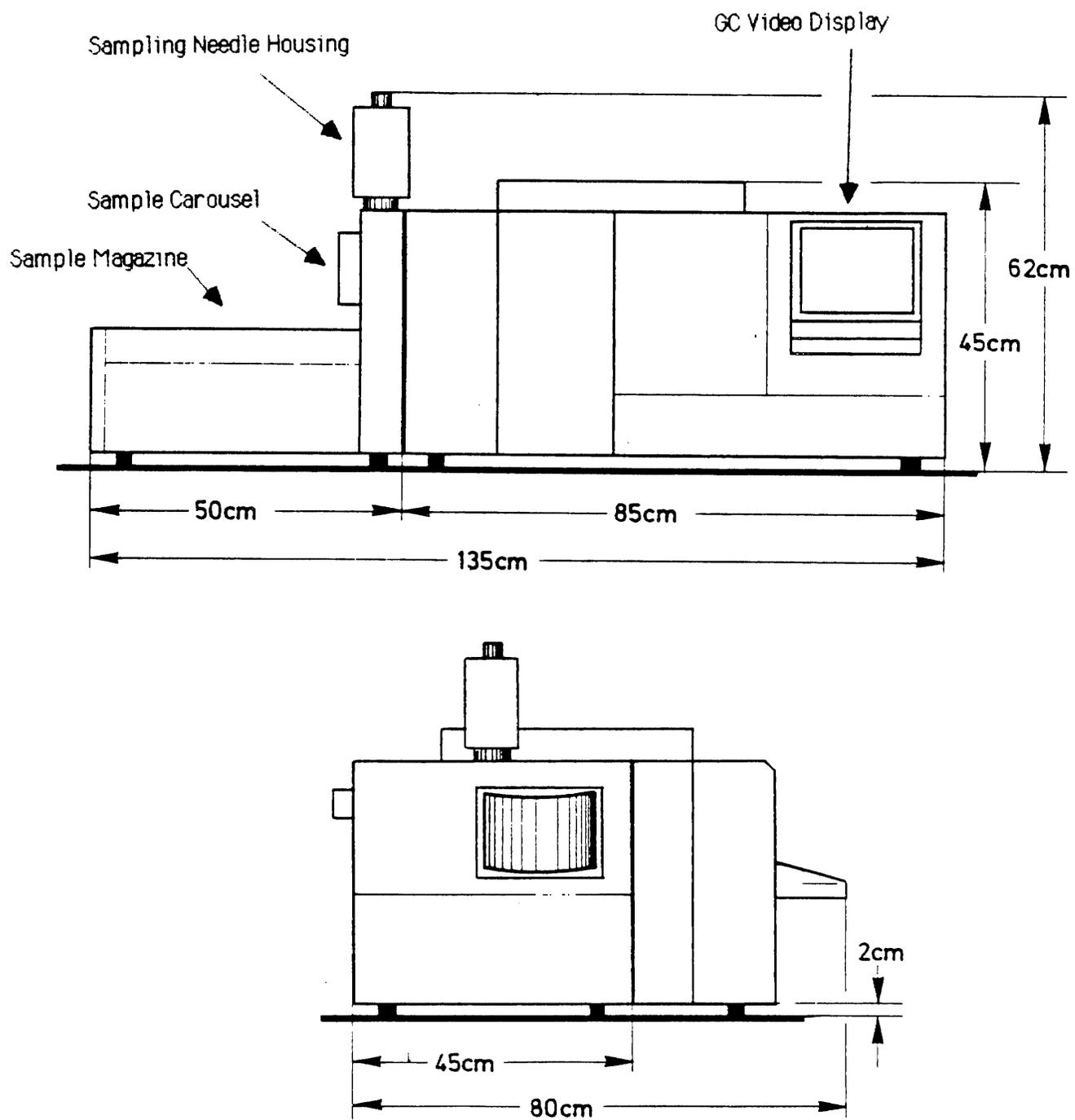


Figure A-1. HS-100 and Sigma 2000 headspace sampling and analysis system.

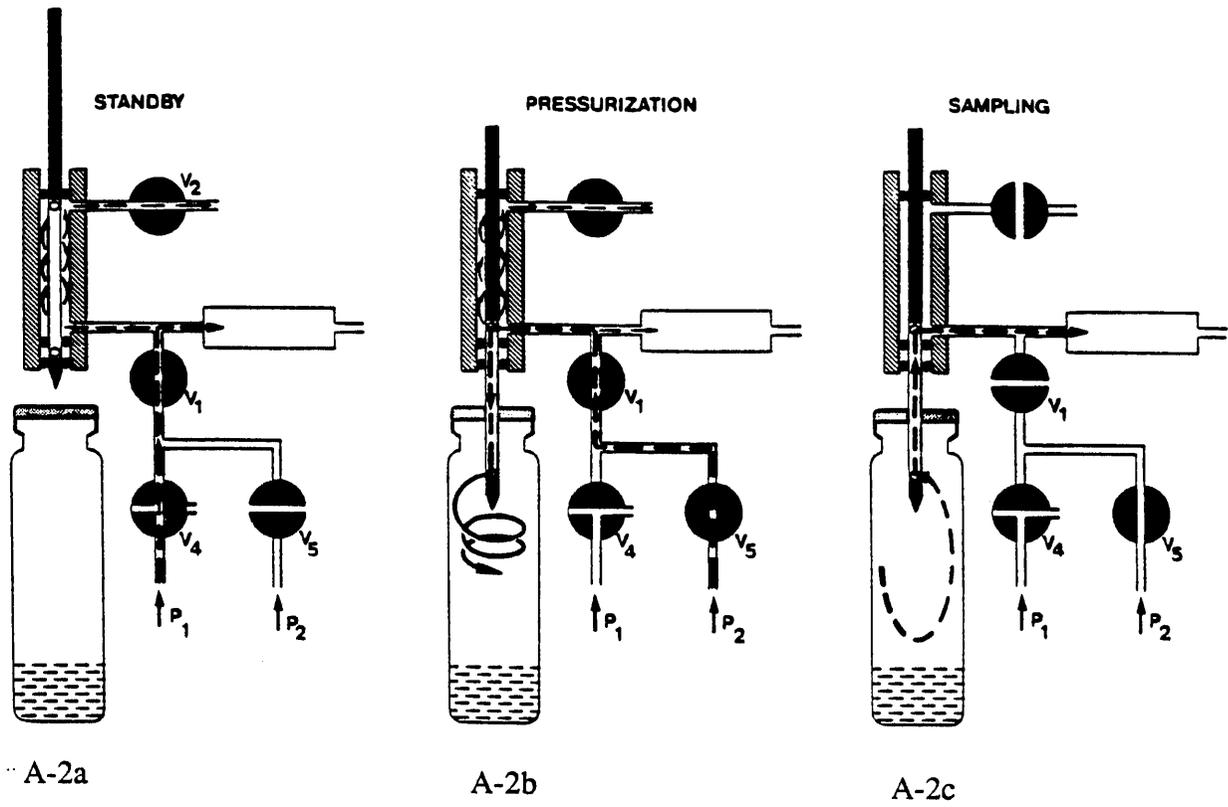


Figure A-2. Headspace sampling sequence.

by running test chromatograms. During sample thermostating, the system is in the standby position (Figure A-2a). Carrier gas streams through valves V4 and V1 to the column. A small cross-flow enters the needle cylinder and vents via valve V2. At the end of the selected thermostating time, the sampling needle descends, pierces the septum cap and enters the vial headspace. Simultaneously, valve V4 closes and valve V5 opens. The sample vial is pressurized with carrier gas at pressure P2 (Figure A-2b). At the end of the selected pressurization time, valves V1 and V2 close (Figure A-2c). Resulting from the pressure drop across the column, vapor from the vial headspace streams to the column. At elapse of the injection time, valves V1, V2, and V4 open and valve V5 closes. Carrier gas streams to the column where separation of the sample constituents takes place. At the end of the withdrawal time, the sampling needle positions to vent the vial and then returns to the standby position.

The LCI-100 laboratory computing integrator is designed to provide high quality data processing of the analog signal from the Sigma 2000 gas chromatograph. This processing includes digitization of the analog signal, plotting of the chromatogram, detection and integration of the peaks, and production of a report. The calculation used to prepare the report can be area percent or normalized percent, internal or external standard, using either area or height to report peak data. The integrator is controlled by a 16 bit microprocessor and has two types of memory. One is a read only memory (ROM) with a capacity of 256K bytes. The ROM contains the chromatography software required to run the system. It is a nonvolatile memory which will not be affected by loss of power. The other memory is random access memory (RAM) with a capacity of 128K bytes. Part of this memory is reserved for system operation but the remainder is available to store user generated data. Stored data types include the following: (a) Methods generated by the user directing the integrator as to how to process the chromatograms, peak files that contain the peak data from a chromatographic run, and the raw data file from the last run. The integrator is capable of storing multiple methods and peak files. It will store the raw data

from the last run automatically, allowing the user to replot and reintegrate this run using a completely new set of parameters, if required, before beginning the next run. The RAM memory is volatile and is completely erased when power is turned off. If power is removed from the integrator, all user entered data will be lost.

APPENDIX B

Method for Collection of Crude Oil Samples from Crude Oil Storage Tanks for Subsequent Determination of the True Vapor Pressure of the Samples

1. Scope

1.1 This method covers the equipment to be used and the process to be followed for collecting a crude oil sample from a crude oil storage or treatment tank. The sample will subsequently be tested by gas chromatography to determine the true vapor pressure (TVP) of the crude oil at the tank temperature.

2. Applicable Documents

2.1 ASTM standards:

A312 Standard Specification for Seamless and Welded Austenitic Stainless Steel pipe¹

D4057 Standard Practice for Manual Sampling of Petroleum and Petroleum Products²

3. Summary of Method

3.1 The sample container is attached to the crude oil tank to be sampled. The sample inlet and outlet valves are opened and crude oil is passed through. All valves are closed and the container is removed and immediately placed in an ice bath.

4. Significance and Use

4.1 This sampling method can be used to collect samples of light, medium and heavy crude oils from its storage or treatment tanks for true vapor pressure determinations.

¹ Annual Book of ASTM Standards, Vol. 01.01.

² Annual Book of ASTM Standards, Vol. 05.03.

5. Apparatus

5.1 The required apparatus is described in Annex A1.

6. Preparation for Sampling

6.1 Before sampling, assemble the equipment listed below:

1) Sampling apparatus (as described in Annex A1) .

2) Tygon tubing (1/2 in. inside diameter).

3) Hose connections, valve to tubing (male)

a) 3/4" - 3/8" (2 needed)

b) 1" - 3/8"

c) 1 1/4" - 3/8"

d) 1 3/8" - 3/8"

e) 1 1/2" - 3/8"

f) 2" - 3 / 8 "

4) Ice bath

5) Tubing clamps

6) Tool Box

7) Plastic bucket

8) Razor Blades

9) Solvent

6.2 Clean the true vapor pressure (TVP) sample container in accordance with the cleaning procedure in Practice D4057. Rinse the TVP sample container with Stoddard solvent or other naphtha of similar volatility. (It may be necessary to use sludge solvents to remove all traces of sediment and sludge from the containers previously used). Then wash the TVP sample container with a strong soap solution, rinse it thoroughly with tap water, and finally with distilled water. Dry by passing a current of clean, warm air through the container.

6.3 Screw on a 3/4" - 3/8" hose connector to the inlet and outlet valves of the TVP sampling container. The inside diameter of the tank sampling line shall be measured and a connector selected from the ones assembled so that the connector may be fitted to the tank sampling line and Tygon tubing connected between the tank sampling line and the sample inlet valve. Also connect Tygon tubing to the sample outlet valve (see Figure B-1B). Secure Tygon tubing with tubing clamps.

7. Procedure

7.1 For each type of crude oil sampled (light, medium, heavy) select a tank sampling line corresponding to the tank level (top, upper, middle, or lower). Assemble the sampling system as described in section 6.3. Open the valves, the sample outlet valve first, the sample inlet valve second, and the tank sampling valve last. Hold the TVP sample container in an upright vertical position as shown in Fig. B-1B. Next, allow crude oil to flow through the sampling system long enough to eliminate any air bubbles that may be present. Then close all valves, allowing the container to fill, close the sample outlet valve of the container first, the sample inlet valve of the container second, and the tank sampling valve last. Remove all connections being careful to slowly release any pressure buildup between the sample inlet valve and the tank sampling valve. Secure valve handles in place with industrial strength tape or spring clamps. Discard any excess crude oil and clean the residual crude oil from the outside of the TVP sample container with the solvent. Promptly label the container as described in section 7.2 and immediately place it in an ice bath.

7.1.1 CAUTION-Crude oil samples may be at temperatures up to 250 F. Gloves should be worn to prevent burning and protective eyewear should be worn to prevent injury from any splashing of crude oil that may occur.

7.2 Label the TVP sample container immediately after the sample is obtained. Use waterproof and oil proof ink or a pencil hard enough to dent the tag.

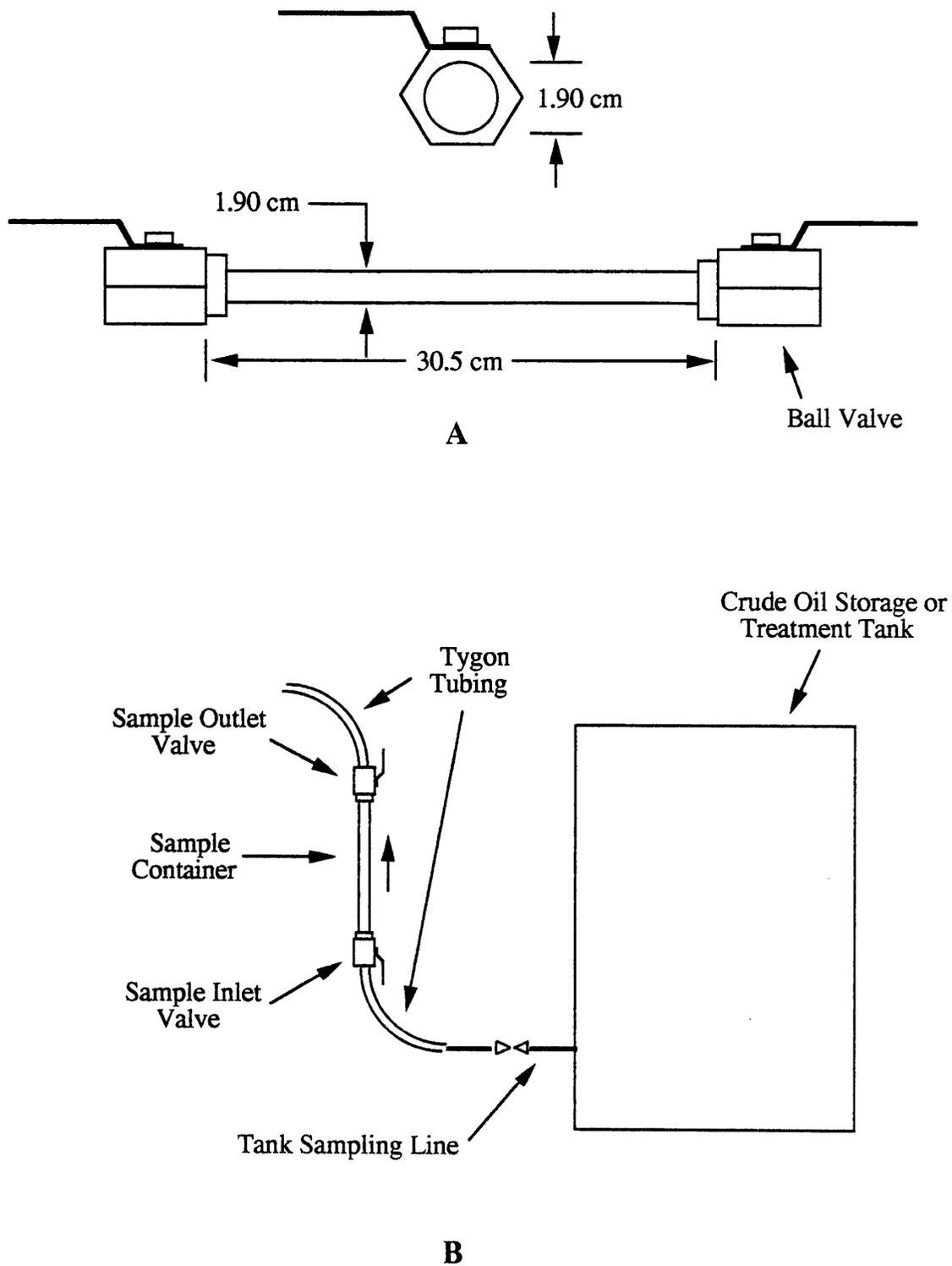


Figure B-1. True vapor pressure (TVP) sample container (A) and sampling system (B).

- 7.2.1 Date and time;
- 7.2.2 Name of the sampler;
- 7.2.3 API gravity of produced crude oil;
- 7.2.4 Reference symbol or identification number;
- 7.2.5 Operator Name;
- 7.2.6 Lease Name;
- 7.2.7 Tank ID;
- 7.2.8 Location of sampling port (tank level);
- 7.2.9 Tank temperature

ANNEX A1

(MANDATORY INFORMATION)

A1. APPARATUS FOR COLLECTION OF CRUDE OIL SAMPLES FROM CRUDE OIL STORAGE TANKS FOR THE TRUE VAPOR PRESSURE DETERMINATIONS

A1.1 True vapor pressure sample container, consisting of stainless steel pipe and two stainless steel valves shall conform to the following requirements.

A1.1.1 Stainless Steel Pipe -The stainless steel pipe as shown in Fig. A1.1 shall be TP304N stainless steel³, 3/4" nominal pipe size, schedule 40 (wall thickness 0.113 in.), 1ft. long with standard male threads at either end. The stainless steel pipe shall be rated for high temperature service and have a bursting pressure of 7533 psi. Stainless steel was selected because it provides the greatest protection to corrosion and attack by chemicals. The dimensions of the pipe are specified so that the total volume of the crude oil contained (5.30 in³) will be sufficient for three laboratory analyses (volume of a laboratory sample vial is 1.34 in³).

³ Refer to ASTM Standard: A312 Standard Specification for Seamless and Welded Austenitic Stainless Steel Pipe for chemical composition and properties of TP304N stainless steel. Stainless steel of a similar or higher grade may also be used.

A1.1.2 Stainless Steel Valves-The stainless steel valves are to be connected to the pipe as shown in Fig. B-1A. The stainless steel bar stock ball valves shall be 3/4" in size. At minimum the valves shall meet CGA⁴-3.16 specifications and be 100% factory tested to ensure bubble tight closure. The valves shall be rated to minimum pressures of 20 microns vacuum to 720 psi WOG⁵; 150 psi saturated steam and to a minimum temperature range of -50 F to 450 F.

⁴ Canadian Gas Association.

⁵ Water, Oil, Gas.

APPENDIX C

Method for Determination of True Vapor Pressure of Heavy Crude Oil Samples from Storage Tanks

1. Scope

1.1 This method covers the determination of true vapor pressures of heavy crude oils. It is assumed that the operator will have a thorough knowledge of gas chromatography.

2. Summary of Method

2.1 Aliquots of the crude oils are dispensed into the headspace vials from the stainless steel storage container (Appendix B) at room temperature or at 0°C using pressurized nitrogen. The sealed vials are thermostated for 60 min in the headspace apparatus at temperatures consistent with those that exist during storage and handling in the field. The equilibrated headspace in each vial is sampled by the headspace apparatus and injected into a gas chromatograph.

3. Significance and Use

3.1 This method can be used to determine true vapor pressure of heavy crude oils taken from storage or treatment tanks. Vapor pressure determination should be done at typical storage/handling temperatures for the crude oils.

4. Apparatus

4.1 The required apparatus is a gas chromatograph (Perkin-Elmer Model Sigma 2000 or equivalent) coupled to a headspace auto sampler and injector (Perkin-Elmer Model HS-100 or equivalent) with a laboratory computer or integrator (Perkin-Elmer Model LCI-100 or equivalent) to interpret the analog signal.

5. Preparation for Sub-sampling

5.1 Before sub-sampling, assemble the following equipment:

- 1) Headspace apparatus.
- 2) Glass headspace vials with closures consisting of (Figure C-1A)

- a) Cap.
 - b) Star spring.
 - c) Teflon-coated septum.
- 3) Crimping tool for sealing headspace vials with closures (Figure C-1B).
 - 4) Brass fittings for the oil sample container:
 - a) 3/4"-1/2" male adaptor (two needed).
 - b) 1/2"-1/4" female adaptor.
 - c) 1/4" (male pipe)-1/4" (Swagelok tubing) elbow.
 - d) 1/2"-3/8" female adaptor.
 - e) 3/8" (male pipe)-1/4" (Swagelok tubing) connector.
 - 5) SS 4P4T Nupro valve.
 - 6) 1/4" Swagelok nuts with ferrules (8 needed).
 - 7) 1/4" copper or stainless steel tubing.
 - 8) Toluene solvent.
 - 9) Plastic bucket.
 - 10) Disposable wipes.
 - 11) Water-proof marking pens.
 - 12) Teflon tape to wrap the threads of all adaptors.
 - 13) Single-stage pressure regulator.

5.2 The following is for heavy crude oil sub-sampling (Figure C-2):

To each end of the sample container, attach one 3/4"-1/2" male adaptor. To the upper end attach the 1/2"-1/4" female adaptor and to that attach the 1/4" (male pipe)-1/4" (Swagelok tubing) elbow. To the lower end attach the 1/2"-3/8" female adaptor and to that attach the 3/8" (male pipe)-1/4" (Swagelok tubing) connector. Finally, attach the SS 4P4T valve through a short piece of metal tubing.

6. Procedure

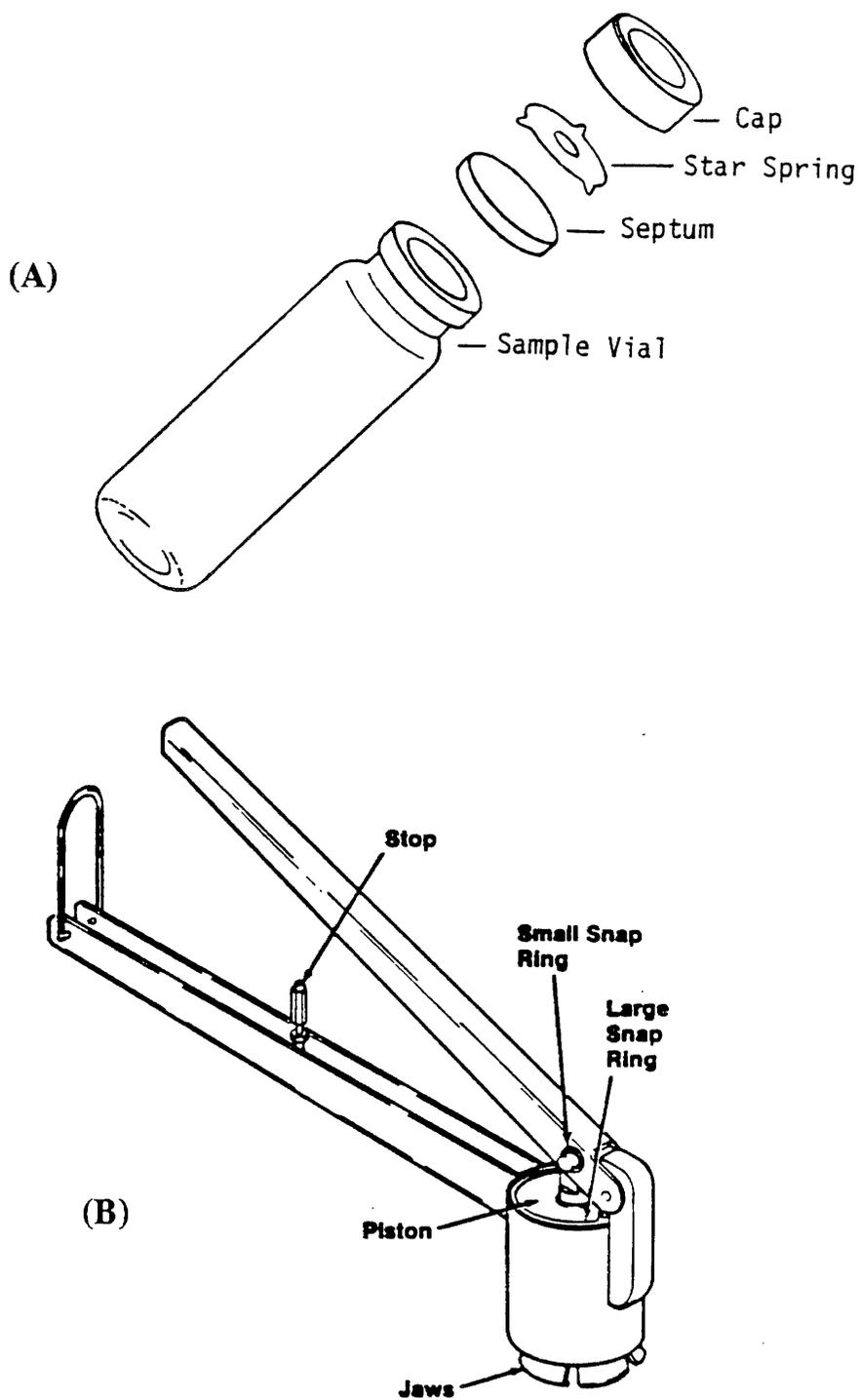


Figure C-1. Headspace vial and closure (A) and vial crimper tool (B).

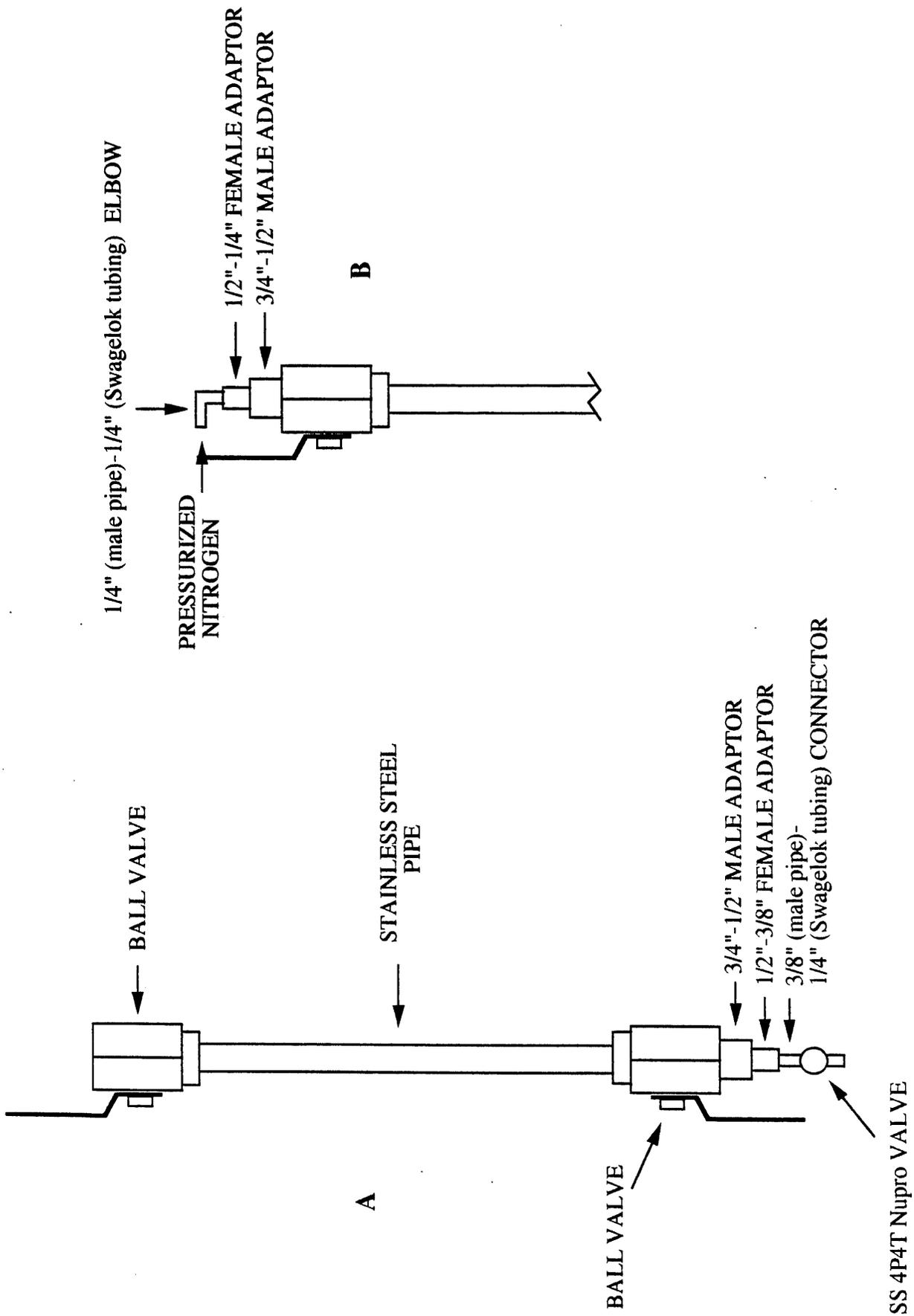


Figure C-2. Diagram of the oil sample container illustrating gravity sub-sampling (A) and pressurized nitrogen sub-sampling (B).

- 6.1 Allow the oil sample container to equilibrate at room temperature for about 24 hours. Set aside 15 clean headspace vials and mark them using a water-proof marking pen to indicate V/L=1/1 (half-filled vial). Then store the vials in water ice, contained in the plastic bucket, to chill them prior to sub-sampling. Attach the fittings to the sample container and place the sample container in a vertical position using a ring stand and clamps. If sub-sampling is to be done with a chilled sample, pack the sample container, with fittings attached, in water ice for at least one hour.
- 6.2 To sub-sample heavy crudes, open the two main valves on the sample container followed by the 4P4T Nupro valve to allow aliquots of oil at room temperature to flow by gravity feed into pre-marked headspace vials (Figure C-2A). After filling and sealing, the vials are returned to water ice storage. If the heavy crude is chilled before sub-sampling, attach a pressurized nitrogen source directly to the upper end of the sample container and slowly apply enough pressure (1-2 psi) using the single-stage pressure regulator to facilitate sample transfer (Figure C-2B).
- 6.3 Before measuring the vapor pressures of the oil aliquots, fill the transfer line of the headspace instrument with a piece of uncoated fused silica open tubular (FSOT) column. Attach a 30 m narrow bore (0.25 mm ID) or wide bore (0.32 mm ID) FSOT column to the end of the transfer line that penetrates the gas chromatograph oven and attach the other end of the FSOT column to the flame detector (Figure C-3).
- 6.4 Place the sub-samples in the sample tray of the auto sampler/injector and set up the headspace instrument by specifying sample temperature, sample thermostating time, sample injection time, transfer line temperature, gas chromatographic oven program, column head pressure, vial pressure, and integrator parameters by following the instructions in the operator manuals.

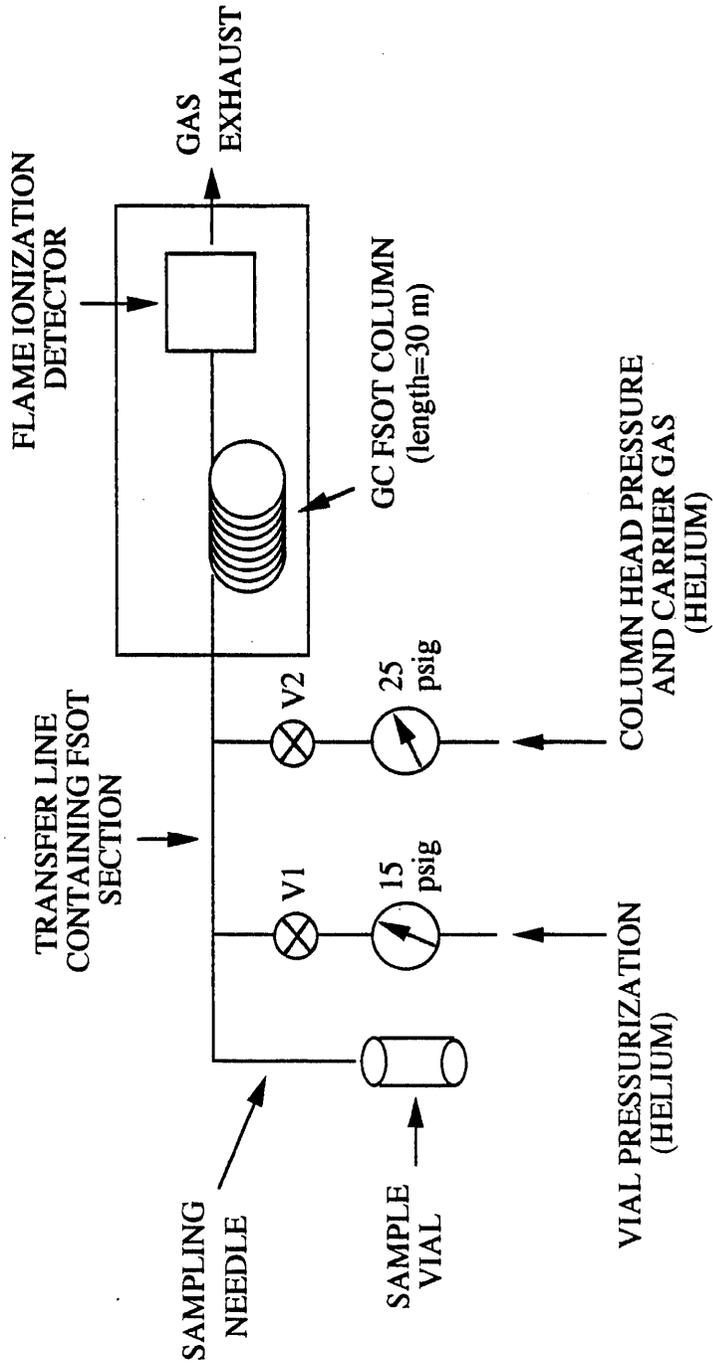


Figure C-3. Schematic of the headspace apparatus for the determination of vapor pressures of heavy crudes.

Maintain the transfer line temperature at 150°C and set the sample temperature at levels consistent with storage/handling temperatures in the field. Set the column head pressure at 25 psig, using the gas chromatograph gas regulator, and the vial pressure at 15 psig, using the gas cylinder regulator. During standby operation, while a sample is thermostating, valve 1 (V1) will remain closed and valve 2 (V2) will remain open (Figure C-3). After the sample has thermostated, the headspace apparatus will simultaneously close valve 2 and open valve 1; after 30 sec, valve 1 will close as well, allowing the pressure in the sample vial to inject an aliquot of sample onto the FSOT column. Valve 2 will then open after 0.01 min, re-establishing carrier gas flow so that the sample gas chromatogram may develop. The gas chromatograph oven program will vary in termination time depending on the sample temperature, but in general a typical program is 40°C (5 min), 2°C/min to termination time (as long as 50 min).

- 6.5 Run the samples, obtaining hard-copy chromatograms. Run a mixture of a series of pure n-alkane hydrocarbons to determine the retention time for each under the same instrument conditions. Subsection the oil sample chromatogram according to the retention times of the pure hydrocarbons by splitting the difference in retention time between adjacent pure hydrocarbons. The result should place each pure hydrocarbon near the mid point of its subsection (Figure C-4). According to the total area of each subsection, generate standard curves (vapor density vs area) for each subsection that will bracket the total subsection area using the pure hydrocarbon for each subsection. This entails running a series of sealed vials into which varying μL amounts of pure liquid hydrocarbons (pentane and above) have been injected, taking care that the amounts injected are well below vapor saturation for the pure hydrocarbons at the particular sample temperature (Figure C-5A). For

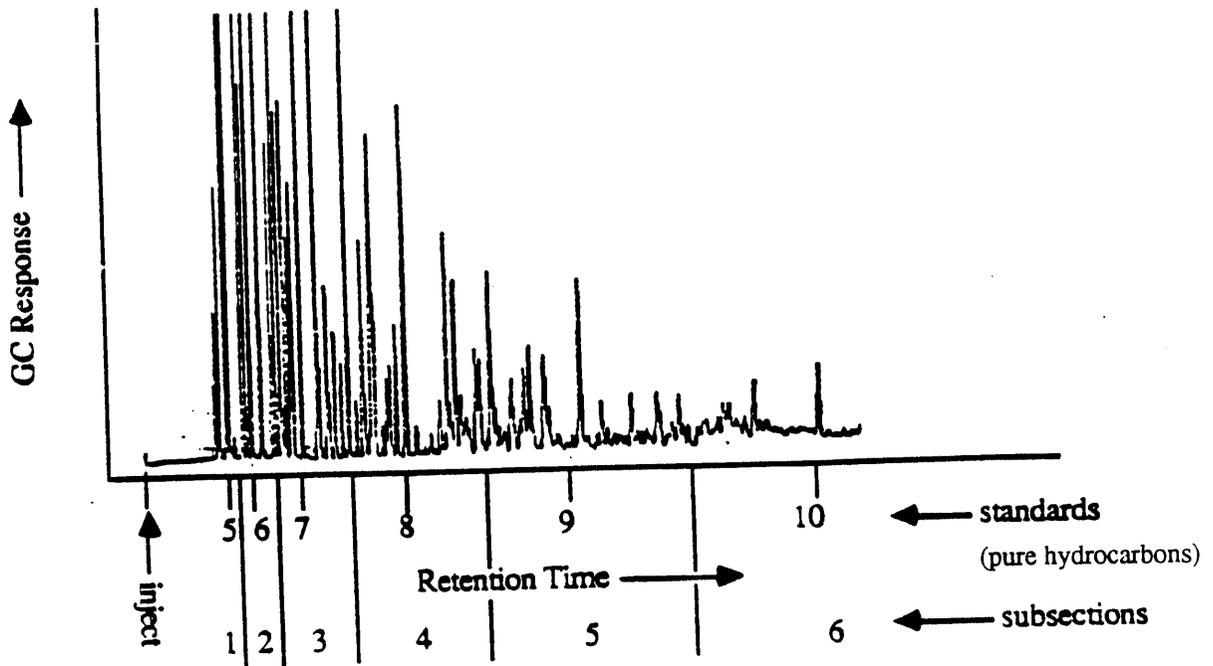


Figure C-4. Gas chromatogram of oil mixture with pure hydrocarbon retention times.

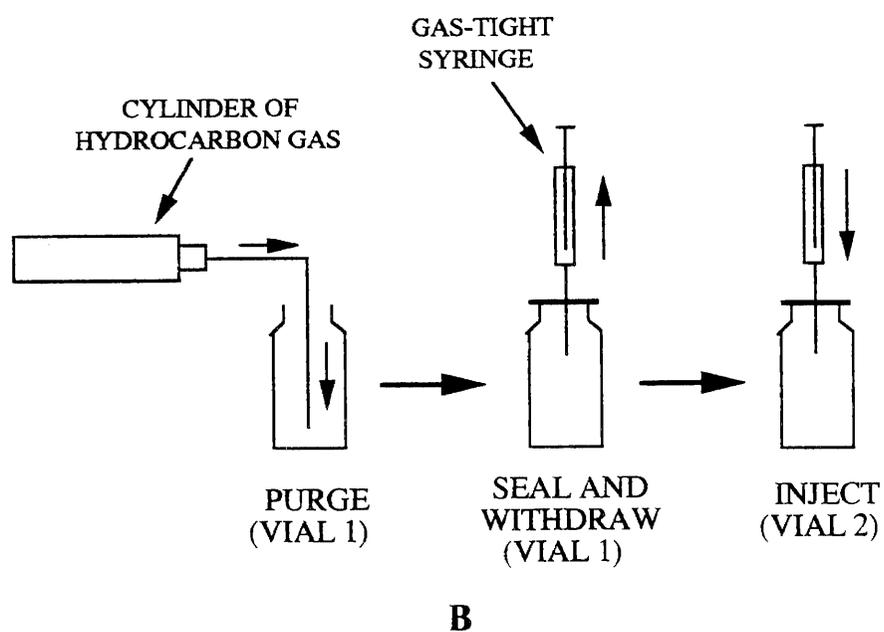
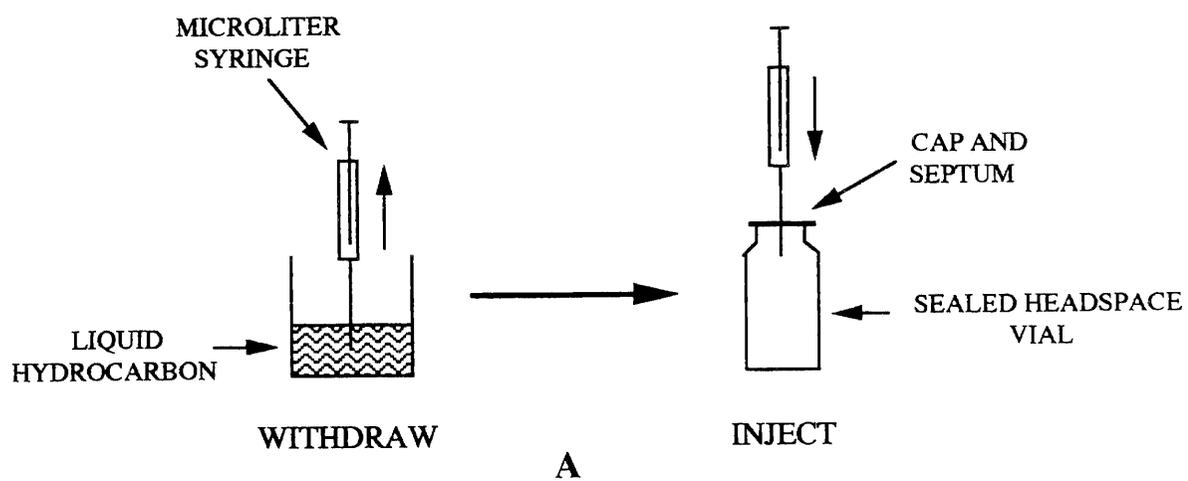


Figure C-5. Preparation of pure liquid (A) and gaseous (B) hydrocarbons for generation of standard curves.

those hydrocarbons that are gases at room temperature (methane through butane), purge headspace vials with the hydrocarbon at known ambient temperature, immediately seal the vial, withdraw μL aliquots with a gas-tight syringe, and inject into sealed empty headspace vials (Figure C-5B). Use the standard curves and the ideal gas law to calculate subsection partial pressures, attributing the properties of each pure hydrocarbon to its subsection. An example calculation follows: Subsection standard curves usually have the form

$$y=mx+b$$

where y =GC area response, x =pure hydrocarbon vapor density (wt/vol), m =slope, and b = y intercept. Vapor density for the pure liquid hydrocarbons is determined from the liquid densities of the hydrocarbons and the μL aliquots used to generate the standard curves; vapor density for the pure gaseous hydrocarbons is determined from the molar volume of an ideal gas at the temperature of the gas (e.g., 0.041 mole/L at 25°C) and the μL aliquots used to generate the standard curves. For a given subsection GC area taken from the crude oil chromatogram, the quantity that is not known and needs to be calculated is the vapor density (x) equivalent to that GC area. Therefore, the above equation is rearranged to

$$x=(y-b)/m$$

where x =subsection vapor density (wt/vol), y =subsection GC area, and the slope (m) and intercept (b) are taken from the pure hydrocarbon standard curve. After the subsection vapor density (x , g/L) is obtained, the subsection partial pressure (P_i , torr) is calculated in the following way:

$$P_i=(x/MW)*R*T*760$$

where MW =molecular weight of the pure hydrocarbon representing the subsection, $R=0.08206 \text{ L}\cdot\text{atm}/\text{K}\cdot\text{mole}$, T =temperature (K), and 760 is included to convert from atm.to torr. After a similar series of calculations is

done for each subsection of the crude oil chromatogram, total vapor pressure (P_t) for the crude oil is obtained from the summed partial pressures:

$$\sum P_i = P_t$$

APPENDIX D

**Reprint: James E. Woodrow and James N. Seiber,
Vapor-pressure measurement of complex hydrocarbon
mixtures by headspace gas chromatography,
J. Chromatogr., 455, (1988), 53**

CHROM. 20 835

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 μ l) through the needle and onto the analytical column. Using this technique, single *n*-alkane hydrocarbon vapor pressures, measured by totally vaporizing μ l 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 method¹) 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

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 —isoteniscope², Knudsen effusion^{3,4}, gas saturation^{5,6}, and gas chromatographic (GC) techniques⁷— 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 reviewed⁸⁻¹³. 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 (μ l), 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-ideal¹⁶.

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 force¹⁰.

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.

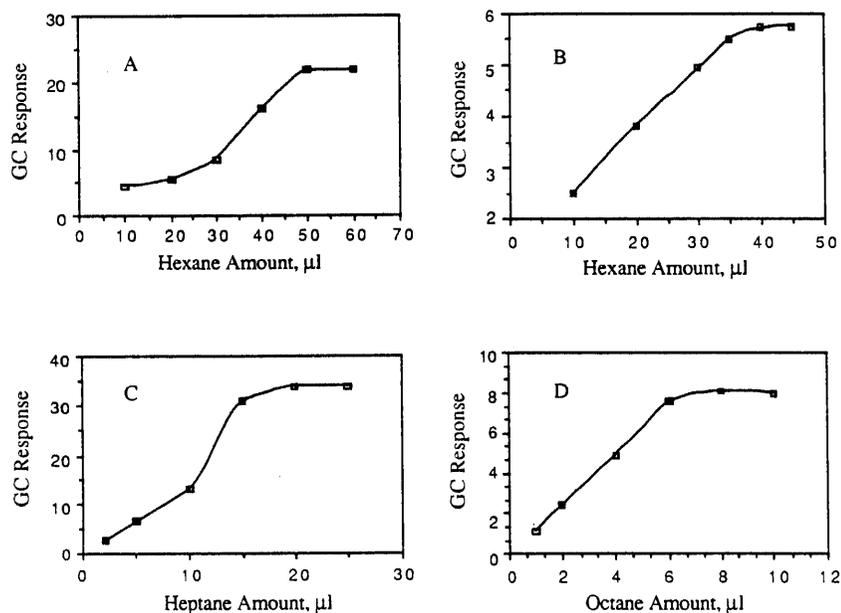


Fig. 1. Isothermal (50 C) gas chromatographic responses of hexane (A, B), heptane (C), and octane (D). Only hexane (B) had transfer line insert.

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 ($\times 10^7$), average (\pm relative S.D., $n = 3$)		
	Transfer line temperature ($^{\circ}$ C)		
	68	100	150
4:1	2.99 ($\pm 2.6\%$)	3.76 ($\pm 0.9\%$)	4.13 ($\pm 1.8\%$)
1:1	2.74 ($\pm 1.3\%$)	3.49 ($\pm 0.6\%$)	4.10 ($\pm 1.9\%$)

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 model¹⁷, 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 \pm S.D. ($n \geq 3$) (kPa)					
	38°C		70°C		107°C	
	Experimental	Calculated*	Experimental	Calculated*	Experimental	Calculated*
Hexane	34.00 \pm 0.63	34.19	103.91 \pm 0.53	104.69	ND	291.44
Decane	0.43 \pm 0.01	0.43	2.50 \pm 0.05	2.52	12.45 \pm 0.12	12.48
Dodecane	ND	0.05	0.42 \pm 0.005	0.42	2.75 \pm 0.01	2.78
Hexadecane	ND	0.0009	ND	0.01	0.15 \pm 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 equation¹⁶. 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 μ l 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 μ l for dodecane and 0.002 μ l for hexadecane at 38°C and 0.03 μ l 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

<i>V/L</i>	Temp. (°C)	GC Response ($\times 10^3$), average (\pm relative S.D., <i>n</i> = 3)			
		Hexane	Decane	Dodecane	Hexadecane
4:1	38	13.36 ($\pm 0.59\%$)	1.04 ($\pm 5.52\%$)	—	—
2:1		13.32 ($\pm 0.79\%$)	0.99 ($\pm 5.56\%$)	—	—
1:1		13.38 ($\pm 1.59\%$)	0.96 ($\pm 6.10\%$)	—	—
4:1	72	—	10.82 ($\pm 1.25\%$)	2.46 ($\pm 1.50\%$)	—
2:1		—	10.45 ($\pm 0.92\%$)	2.26 ($\pm 0.53\%$)	—
1:1		—	9.50 ($\pm 2.54\%$)	1.97 ($\pm 1.54\%$)	—
4:1	107	—	—	5.34 ($\pm 2.10\%$)	0.43 ($\pm 1.10\%$)
2:1		—	—	5.04 ($\pm 1.43\%$)	0.36 ($\pm 3.82\%$)
1:1		—	—	4.69 ($\pm 1.59\%$)	0.25 ($\pm 2.41\%$)

TABLE IV

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

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

* 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 $\pm 6.10\%$, with an average of $\pm 2.27\%$ 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 $\pm 3.98\%$ 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	Experi- mental	Calcu- lated*		
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 theory¹⁸ and the UNIFAC method¹⁶, 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 $\pm 3\%$. 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.

<i>V/L</i>	<i>Partial pressure (kPa)*</i>							<i>Total pressure (kPa)</i>
	<i>Hexane</i>	<i>Heptane</i>	<i>Octane</i>	<i>Nonane</i>	<i>Decane</i>	<i>Undecane</i>	<i>Dodecane</i>	
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 $\pm 2\%$. 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).

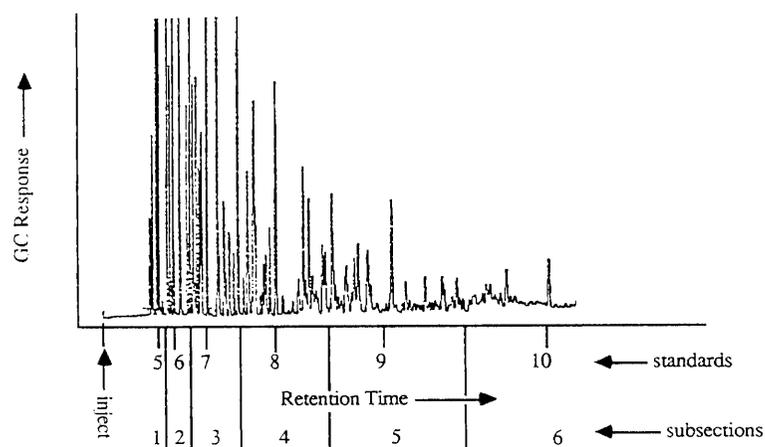


Fig. 2. Gas chromatogram of diesel fuel with standard retentions (C_5 – C_{10}). Column: 40°C (5 min), 2°C/min to 80°C.

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

Temperature ($^{\circ}$ C)	V/L	Vapor pressure (kPa) (average \pm S.D., $n = 3$)*
38	4:1	1.13 \pm 0.03
	1:1	1.14 \pm 0.01
70	4:1	3.83 \pm 0.08
	1:1	3.92 \pm 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 μ l 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 $\pm 1\%$, respectively. Agreement between the values at $V/L = 4:1$ and $1:1$ were within 1–2% (38 $^{\circ}$ C) and 2–3% (70 $^{\circ}$ 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 $^{\circ}$ C and $V/L = 4:1$. Included are results obtained using the Reid method¹, 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 $\pm 1\%$, while the Reid values exhibited precisions of $\pm 1\%$ (gasoline), $\pm 5\%$ (light crude), and $\pm 38\%$ (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 $^{\circ}$ C

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