

# PVT Analysis for Oil Reservoirs

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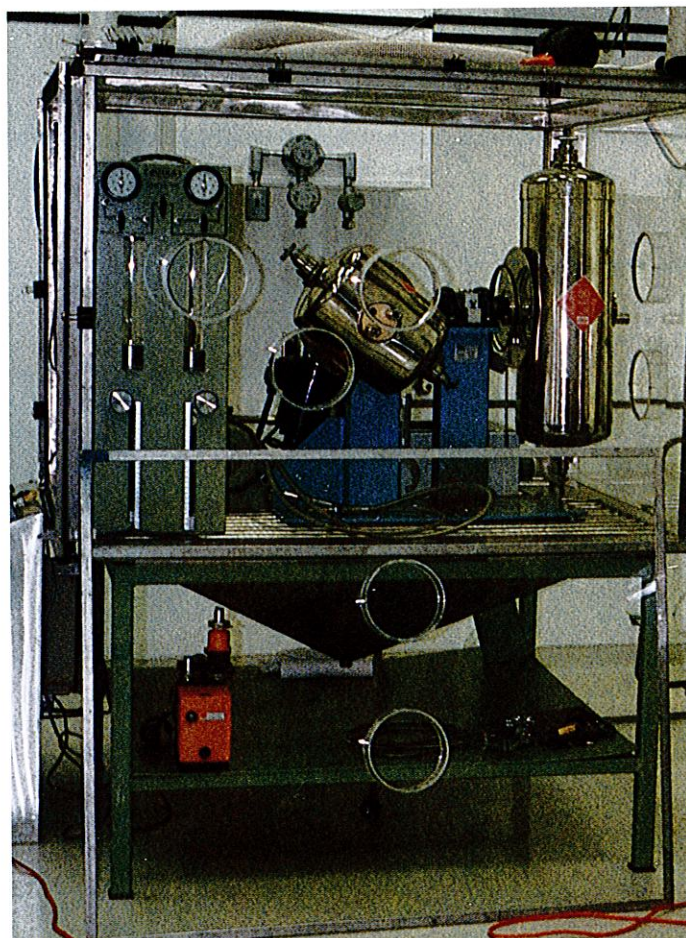
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The challenge for reservoir and production engineers is to maximize hydrocarbon recovery in the minimum amount of time and with the smallest expense. In terms of the engineers' on-the-job concerns, this means asking a variety of questions about what and how the reservoir will produce:

*How large are the reserves?  
What will the primary recovery be?  
What kind of crude will be produced and what will the market pay for it?  
Does the crude contain unwanted compounds that will destroy tubing or plug the well?  
For offshore wells, will the crude solidify at ocean-bottom temperatures, thereby stopping production?  
What separator pressures will maximize liquid hydrocarbon recovery?  
Will gas produced at the surface be reinjected, sold, or burned off?*

Answering these questions requires anticipating the volumetric and phase behavior of produced hydrocarbons as they travel from the reservoir, up the tubing, through surface separators, and finally into pipelines; and of hydrocarbons in place as the reservoir pressure declines with production.<sup>1</sup> Hydrocarbon composition, viscosity, density, compressibility—all these properties change with pressure and temperature (see "Introduction to Hydrocarbon Phase Behavior," page 6).

In a pressure-volume-temperature (PVT) lab, researchers employ an arsenal of instruments to determine reservoir fluid behavior and properties from oil and gas samples. Their goal is to simulate what takes place in the reservoir and at the surface during production. A central aspect of PVT analysis is



□ High-pressure, high-temperature pressure-volume-temperature (PVT) cells. The smaller cell (inclined cylinder) is used for bubblepoint determination, differential liberation tests, and flash liberation tests on oil-reservoir samples. It is rocked back and forth before each flash and differential liberation. The larger cell (vertical cylinder) is used to recombine surface oil and gas samples at reservoir conditions.

how gas evolves from oil when pressure falls below the bubblepoint. Researchers use two processes to describe this—flash liberation and differential liberation (see page 9, middle).

In flash liberation, a sudden pressure drop causes gas to come out of solution, which then remains confined with the oil that is left. In differential liberation, gas comes out of solution as pressure is gradually decreased, but is removed from the oil.

When reservoir pressure drops below the bubblepoint, flash liberation dominates. Gas comes out of solution and initially remains

in the pores in contact with the oil. Meanwhile, single-phase oil continues to flow into the well, although it has a slightly different composition than that of the original reservoir fluid. When enough gas accumulates to reach the critical gas saturation, it begins to flow. Since gas is less viscous and flows faster than oil, the gas liberation now becomes differential.

Gas liberation occurring in the tubing is considered flash liberation because the agitation of the flow keeps the two phases in contact with each other. Flash liberation also dominates in the separator, where a sudden pressure drop releases more gas from the oil while the two remain in contact.

Flash and differential liberation are recreated on a small scale in the lab using high-pressure, high-temperature PVT cells, positive displacement mercury pumps and precision thermometers and pressure gauges (*left*). When introduced to a sample-filled cell, mercury compresses the fluid; when withdrawn from the cell, it allows the sample to expand.

The flash liberation test is used to determine the bubblepoint of the reservoir fluid. Both flash and differential liberation tests establish parameters that relate the surface volumes of produced oil and gas to their reservoir volumes.

### Bubblepoint Determination

The bubblepoint is determined during a flash liberation test on a small amount of reservoir fluid (about 100 cm<sup>3</sup>), sampled downhole or recombined from surface gas and oil samples taken from the separator. After transferring the sample to a high-pressure cell maintained at reservoir temperature and above reservoir pressure, the cell pressure is decrementally decreased by removing mercury from the cell. For each volume change, cell pressure is recorded.

Upon reaching the bubblepoint, gas comes out of solution and any subsequent mercury removal causes small pressure reductions. This transition is well marked on a pressure-volume graph of the data (*below*).

The bubblepoint is crucial for understanding how hydrocarbons behave in the reservoir and indicates the probable drive mechanisms. For example, if the reservoir pressure is initially at the bubblepoint, a gas cap almost certainly exists that will expand, pushing oil toward the well and increasing recovery to 40 percent of the oil in place.

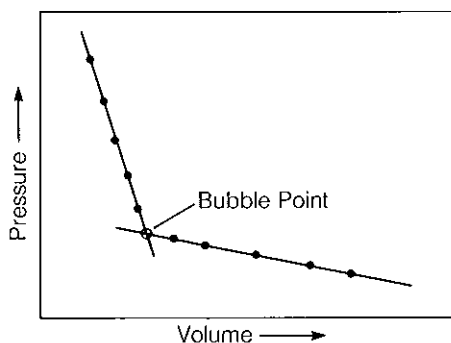
In a reservoir producing below the bubblepoint, gas coming out of solution may either be produced, or if production is slow and vertical permeability is high, it may migrate upward and form a secondary gas cap that helps drive the reservoir. This type of drive,

called gravity segregation, may yield up to 70 percent of the oil in place.

If initial reservoir pressure is much higher than the bubblepoint, meaning the oil is undersaturated (contains little dissolved gas), then the only drive will be monophasic liquid expansion, resulting in poor recovery—only a few percent of the oil in place. An enhanced recovery program may then be implemented. The presence of a natural water drive in this case, however, could lead to a recovery of up to 60 percent of the oil in place.

In the case of a retrograde condensate reservoir, the only drive mechanism is gas expansion, but as pressure declines large amounts of oil, called condensate, may condense from the gas and remain in the reservoir.

*continued on page 8*



□ Bubblepoint determination during a flash liberation test. Starting above the reservoir pressure, pressure on the reservoir sample is decreased in steps by removing mercury from the cell. The initial slope of the pressure-volume curve is very steep until gas begins to come out of solution at the bubblepoint. Then, any subsequent volume increases cause small changes in cell pressure and the slope of the pressure-volume response shows a dramatically reduced slope.

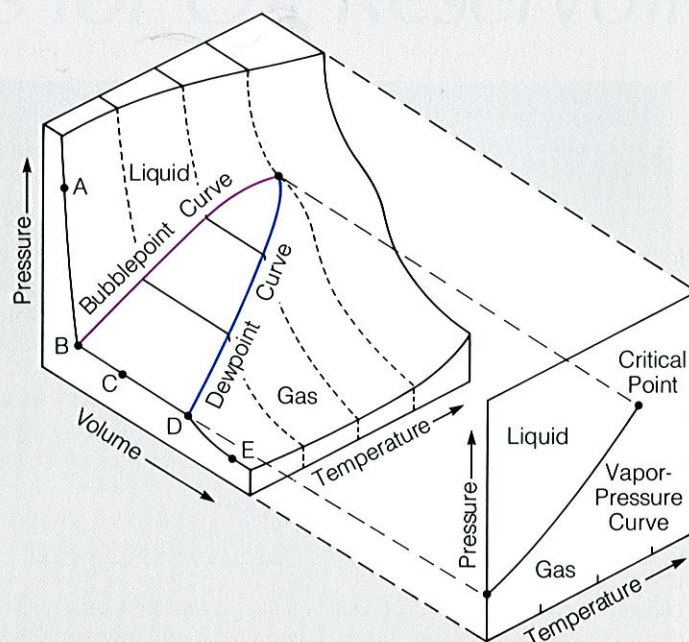
1. Recommended reading and viewing on reservoir engineering:  
Amyx JW, Bass DM Jr and Whiting RL: *Petroleum Reservoir Engineering*. New York: McGraw-Hill Book Company, 1960.  
Dake LP: *Fundamentals of Reservoir Engineering*. Amsterdam: Elsevier Scientific Publishing Company, 1978.  
Lang KR: *Reservoir Fluids: Sampling and Analysis, Module PE406: Petroleum Engineering*. IHRDC Video Library for Exploration and Production Specialists, Boston: International Human Resources Development Corporation, 1985.



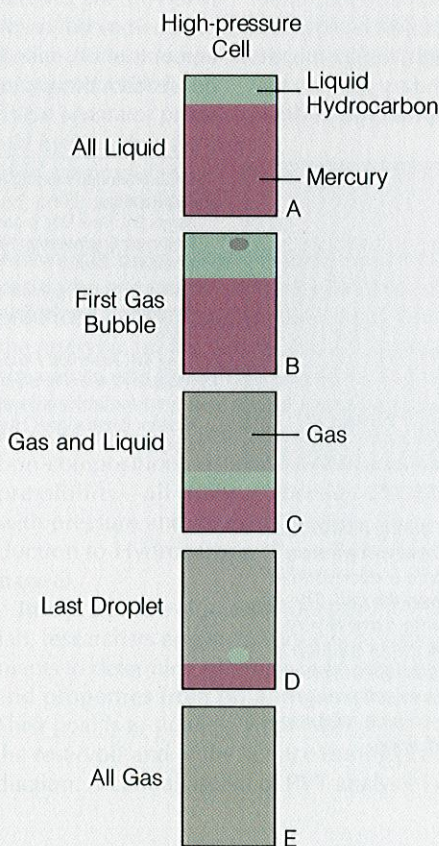
# Introduction to Hydrocarbon Phase Behavior

To understand the complex behavior of a reservoir fluid, let's first follow the case of a single-compound hydrocarbon initially in liquid form in a pressurized cell containing mercury (*below*). As mercury is gradually removed with the temperature held constant, the liquid expands and the pressure in the cell drops. Isothermal conditions simulate a reservoir's generally constant temperature. The pressure continues to drop with additional mercury removal until the first bubble of gas comes out of solution—the bubblepoint. Below the bubblepoint pressure, the gas continues expanding as mercury is removed, but the pressure remains constant. When all the liquid has vaporized—the dewpoint—further gas expansion is again accompanied by decreasing pressure.

This experiment run at different temperatures produces different bubblepoints and



□ The pressure-volume-temperature behavior of a single-compound hydrocarbon showing the temperature and pressure conditions that produce a gas or liquid phase. At the pressure and temperature corresponding to the critical point, the gas and liquid phases are indistinguishable.



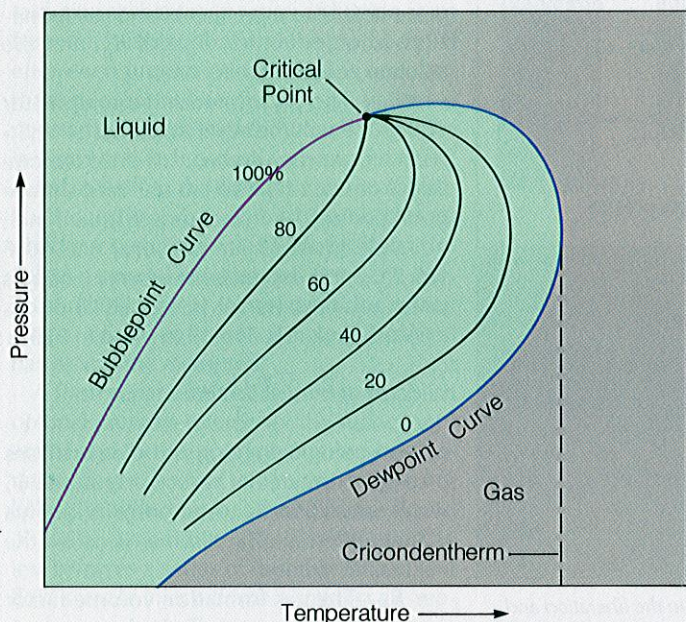
□ Phase behavior of a single-compound hydrocarbon in a constant temperature mercury cell. As mercury is removed, the liquid hydrocarbon expands and the cell pressure drops. This continues to the bubblepoint, when the first gas bubble comes out of solution. Below the bubblepoint, the volume of gas increases rapidly but at constant pressure until all of the liquid has vaporized, at the dewpoint. Below the dewpoint, further gas expansion is accompanied by decreasing pressure.

dewpoints. Projecting the locus of bubblepoints, the bubblepoint curve, and the locus of dewpoints, the dewpoint curve, onto a pressure-temperature graph yields a unique dividing line known as the vapor-pressure curve (*above*). Above this curve, the hydrocarbon exists as a liquid, below as a gas. At the critical point, gas and liquid phases are indistinguishable.

Multicomponent hydrocarbons generate complicated phase diagrams, whose shape depends on the composition of the mixture (*right, above*). The bubblepoint and dewpoint curves projections no longer coincide, but produce an envelope in which gas and liquid coexist. The maximum temperature of the two-phase envelope is called the cricondetherm.

Phase diagrams illustrate the evolution of hydrocarbon phases during production. Pressure depletion is represented as a vertical line because the reservoir temperature generally remains constant (*far right, top*).





□ Phase diagram of a multicomponent hydrocarbon mixture. Within the envelope formed by the bubblepoint and dewpoint curves, the fluid exists as gas and liquid, above the bubblepoint curve as only liquid, and below the dewpoint curve as only gas. Additional curves within the envelope represent a constant percentage of liquid. The maximum temperature of the two-phase system is called the cricondentherm.

In a gas well, if the reservoir temperature exceeds the cricondentherm, only dry gas will exist in the reservoir throughout production. This same gas produced to surface conditions falling within the envelope will become a mixture of gas and liquid.

If the temperature of the gas reservoir is below the cricondentherm, a transition called retrograde condensation occurs: oil condenses with decreasing rather than increasing pressure (right, middle). This type of reservoir is appropriately called a retrograde gas condensate.

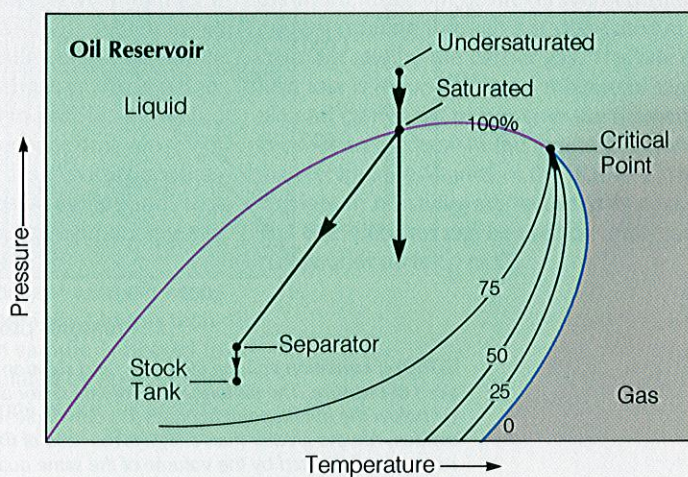
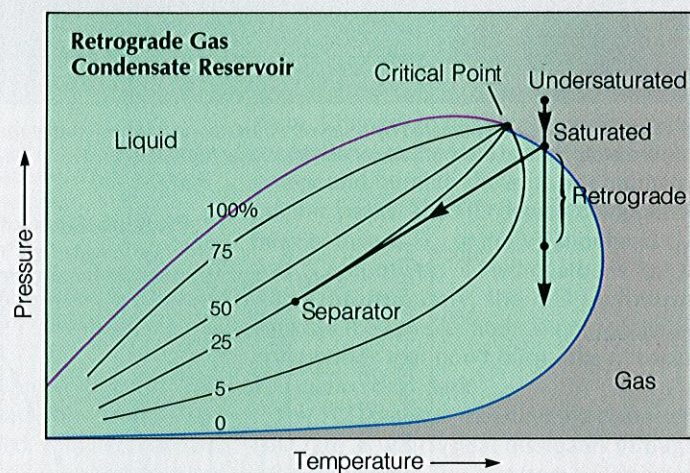
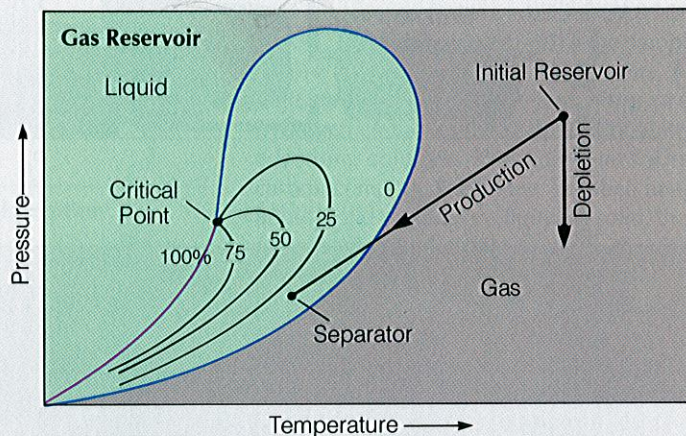
In an oil reservoir at a temperature below the critical point, only liquid oil containing dissolved gas exists above the bubblepoint (right, bottom). When this oil is produced to the surface, gas comes out of solution, the amount depending on surface conditions. Since all the produced gas comes out of solution, surface volumes of gas and oil are easily related to volumes at reservoir conditions.

□ Phase diagrams of gas, gas condensate and oil reservoirs.

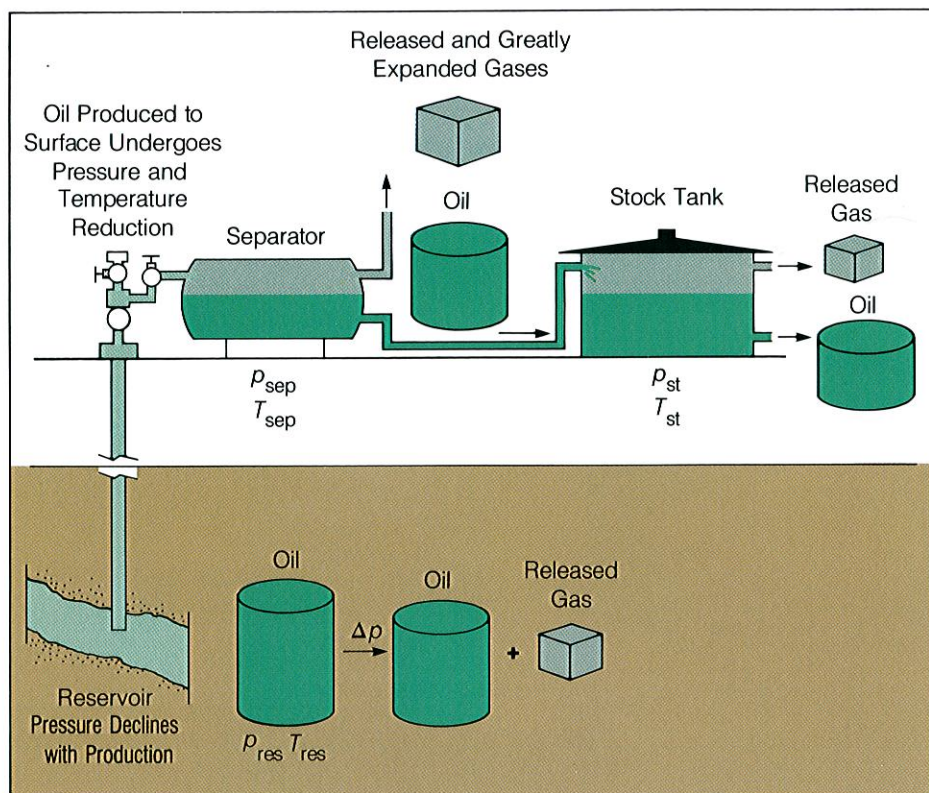
In a gas reservoir (top), only gas exists initially. Producing the gas to separator conditions creates a mixture of gas and condensed oil.

In a retrograde gas condensate reservoir (middle), temperature is below the cricondentherm, causing oil to condense as pressure decreases.

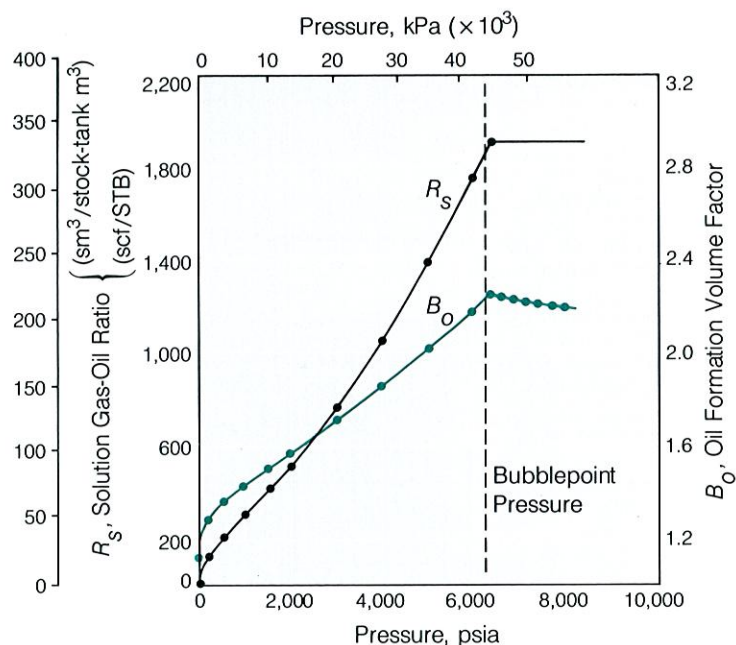
In an oil reservoir above bubble point (bottom), all gas is dissolved in the oil. If pressure falls below bubblepoint, the reservoir contains two phases—oil and free gas, which has come out of solution. When oil is brought to the surface, it liberates gas. The gas at surface comprises any free gas, now expanded, and gas liberated from the oil during production.







□ Pressure changes encountered by reservoir fluids during production that result in the liberation and expansion of gas and the shrinkage of oil. After Lang KR, reference 1.



□ The oil formation volume factor,  $B_o$ , and solution gas-oil ratio  $R_s$ , as functions of pressure. The oil formation volume factor accounts for the fact that oil below the bubblepoint liberates gas downhole resulting in less oil at the surface. Always greater than one, it is the ratio of the volume of a quantity of reservoir oil divided by the volume of the same quantity of oil at standard conditions. The solution gas-oil ratio tells how much gas is dissolved in the reservoir oil.

## Reservoir-to-Surface Volume Relations

Besides the bubblepoint, there are three important parameters derived from flash and differential liberation tests that relate surface volumes to reservoir volumes and thus help determine the amount of hydrocarbons in place (left). These are the oil and gas formation volume factors,  $B_o$  and  $B_g$ , and the solution gas-oil ratio,  $R_s$ .

- $B_o$ —The oil formation volume factor equals the volume of oil that must be withdrawn from the reservoir to produce one barrel of stock-tank oil<sup>2</sup> at standard surface conditions of 14.7 pounds per square inch absolute (psia) [1 atmosphere] and 60°F [15.5°C]. It is expressed as reservoir barrels per stock-tank barrel [res bbl/STB or res m<sup>3</sup>/stock-tank m<sup>3</sup>]. The oil in place in STB is:

$$\frac{V \phi (1-S_w)}{B_o}$$

where geologic, logging and core analyses provide estimates of reservoir volume  $V$ , water saturation  $S_w$ , and porosity  $\phi$ . This manner of estimating reserves is called the volumetric method.

- $B_g$ —The gas formation volume factor equals the volume of gas in the reservoir that will produce one cubic foot at surface under standard conditions. It is expressed as reservoir barrels per standard cubic foot [res bbl/scf or res m<sup>3</sup>/std m<sup>3</sup>]. The standard volume of gas in place is:

$$\frac{V \phi (1-S_w)}{B_g}$$

- $R_s$ —The solution gas-oil ratio is the volume of gas at standard conditions that dissolves into one STB of oil under reservoir conditions expressed as standard cubic feet per stock-tank barrel [scf/STB or sm<sup>3</sup>/stock-tank m<sup>3</sup>]. The amount of gas in scf is:

$$\frac{V \phi (1-S_w) R_s}{B_o}$$

Once production data become available, the formation volume factors and the solution gas-oil ratio may be used in more sophisticated estimations of the hydrocarbons in place using material balance equations. These account for water entry, the expansion of reservoir fluids and the reduction in pore space, all consequences of falling reservoir pressure.

The formation volume factors and the solution gas-oil ratio, all functions of reservoir pressure, are determined by reproducing in the laboratory the sequence of differential and flash liberations that most likely occur during production (left). It is widely



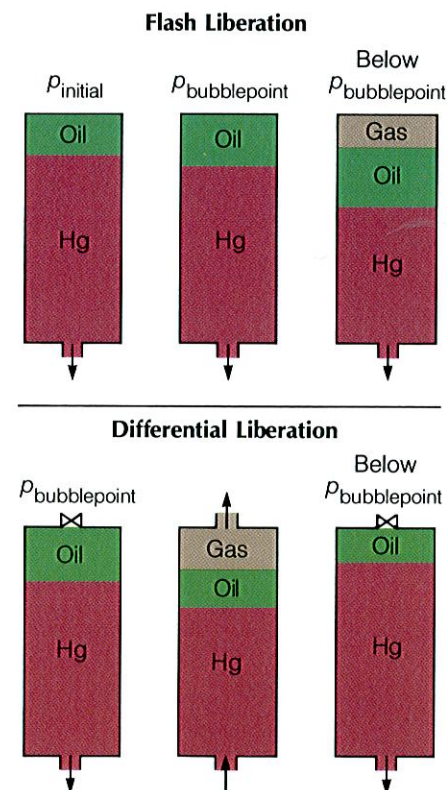
believed that flow in the reservoir is best simulated by differential liberation while flow up the well and through the separator is best simulated by a series of flash liberations called a flash separation.

The laboratory set up for a differential liberation test is identical to the flash liberation test, except that the pressure reduction starts from the bubblepoint, and the gas liberated after each pressure decrement is removed through a port while mercury is injected at constant pressure (*right*). At each stage, the free gas and reduced oil volumes are measured as well as the free gas volume at standard conditions. Eventually, after four to eight pressure reductions down to atmospheric conditions, the cell contains only residual oil at reservoir temperature, which is then cooled to standard temperature and has its volume measured.

A flash separation test is used to establish optimal pressure settings for the surface separator and the appropriate number of separation stages, both of which are designed to keep the light hydrocarbons in the liquid phase and maximize liquid recovery. The test involves a series of flash liberations of a fluid sample injected into a small-scale separation system. The separation pressures and temperatures are altered in steps, and at each stage, the volume of gas liberated and the volume of liquid remaining are measured. Data from these tests are combined to determine  $B_o$ ,  $B_g$ , and  $R_s$  that reflect actual production.

### Compositional Analysis

Compositional analysis of the reservoir sample, a key component of PVT analysis, has several applications in reservoir and production engineering. The most important is to establish how much gasoline, kerosene, fuel oil, heavy oil and bitumen will come from refining a barrel of crude, which determines the crude's market value (see "Com-



□ Comparison between flash liberation and differential liberation. Flash liberation, which portrays the separation stage of production, involves a sudden pressure change that causes the fluid to quickly separate, or "flash" into gas and oil components. In differential liberation, which represents pressure depletion in the reservoir, pressure gradually decreases and any liberated gas is removed from the oil.

position of Hydrocarbons," page 12). The composition also dictates how and where the crude will be refined. A light crude can be refined through distillation, but heavier crudes must be processed at very high temperatures ( $>1,000^{\circ}\text{F}$  [ $540^{\circ}\text{C}$ ]), which break or crack larger molecules of the paraffinic series into smaller, lighter molecules. Refineries configured to process a specific composition of crude economically may not accept all types of crudes. Another application is detecting corrosive compounds that require special noncorrosive producing and transportation equipment.

The main compositional analysis technique is gas chromatography.<sup>3</sup> In this technique, a hydrocarbon sample is heated to vaporization and circulated by an inert carrier gas through columns of porous adsorbing material (*next page, above*). The adsorb-

ing material may be a solid—silica gel, charcoal or a molecular sieve of synthetic zeolites—or more commonly a liquid solvent that coats particles of an inert solid.

The sample is introduced into the injection port of the chromatograph using a syringe or a gas-sampling valve. The port is at a high temperature— $650^{\circ}\text{F}$  to  $850^{\circ}\text{F}$  [ $350^{\circ}\text{C}$  to  $450^{\circ}\text{C}$ —to vaporize the sample before it is injected into the columns. An inert carrier gas such as helium, nitrogen or hydrogen circulates the sample through the adsorbing columns. The individual hydrocarbon compounds alternate between being liquid, solid or gas. As a liquid or solid, they remain adsorbed, while as a gas, they are carried by the inert gas out of the columns. Lighter compounds preferentially remain gaseous and are quickly removed, whereas heavier compounds progress slowly through the column. Each compound is identified by observing how long it takes to exit.

The compounds are usually identified by a flame ionization detector (FID) or a thermal conductivity detector (TCD). In the FID, a flame composed of hydrogen and air burns off the exiting compounds, ionizing them. Changes in the flame's conductivity, proportional to the ions and electrons in the compound burned, show up as chromatographic peaks. The FID detects compounds heavier than  $\text{C}_2\text{H}_6$ , or in PVT shorthand  $\text{C}_{2+}$  (see "Composition of Hydrocarbons," page 12). Unfortunately, the FID technique destroys the sample, and cannot recognize compounds that don't burn, like nitrogen and carbon dioxide.

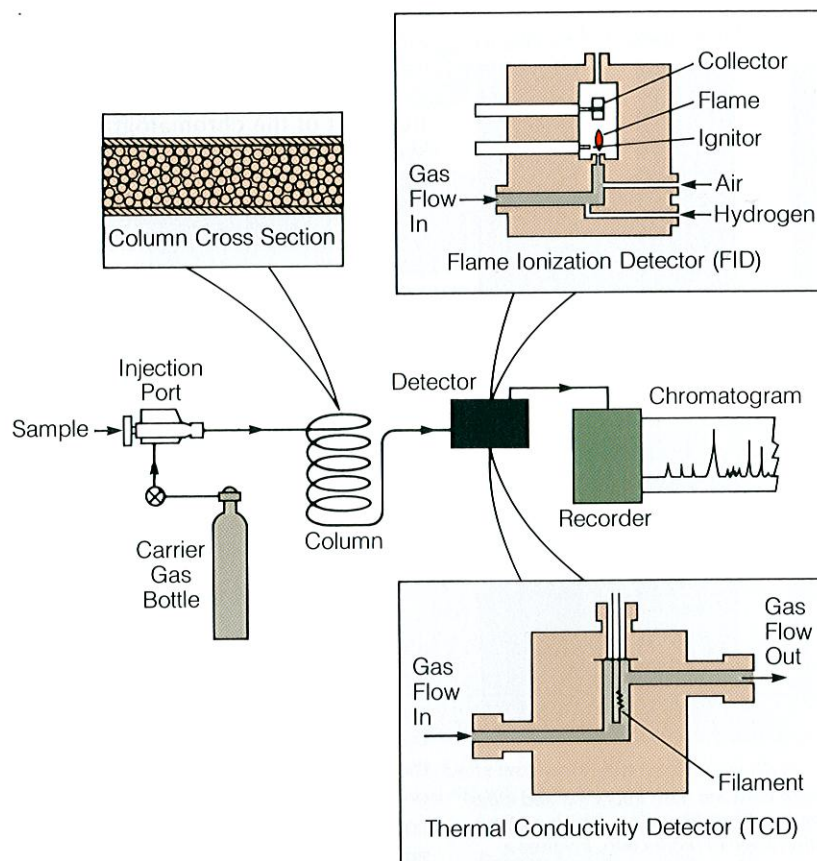
The TCD detector measures the characteristic rate at which heat dissipates through each compound. The heat from a filament of platinum, tungsten or nickel with constant current running through it is dissipated at a constant rate by the carrier gas. The rate of heat loss is reduced when a mixture of sample and carrier gas passes over the filament, causing an increase in the temperature and the electrical resistance of the filament. The changes in resistivity are recorded as peaks. The TCD detector can be used for analyzing compounds up to  $\text{C}_5$  or  $\text{C}_6$ .

2. Stock-tank oil is oil or condensate collected in a surface storage tank at atmospheric pressure after the produced well fluid has been processed through a gas-oil separation system.

3. For a review of gas chromatography: McNair HM and Bonelli EJ: *Basic Gas Chromatography*. Palo Alto, California: Varian Instrument Division Offices, 1969.



## Gas Chromatograph



□ Gas chromatograph for compositional analysis of reservoir fluids. A reservoir sample is injected and vaporized at high temperature, then circulated by an inert gas such as helium through columns filled with adsorbing material. Inside the columns, the compounds in the sample alternate between the carrier phase and the phase of the adsorbing material (either solid or liquid). Eventually, the compounds make their way out of the columns to be detected, with the lighter compounds eluting first. The compounds are detected by either a flame ionization detector (FID) or a thermal conductivity detector (TCD). The resulting output of peaks displayed versus time is called a chromatogram.

The resulting output of peaks from either detector is called a chromatogram (above right). The area under each peak is proportional to the concentration of the corresponding compound. The time it takes each compound to pass through the columns is known as the retention time. Retention times and peak amplitudes are calibrated by injecting the chromatograph with a standard mixture of known composition.

A limitation of gas chromatography is that it cannot make a complete analysis of stock-tank oils that contain heavy alkanes

and asphaltenes, which take unreasonable amounts of time to elute. To analyze these heavy liquids, you can inject the stock-tank oil into the chromatograph while keeping out the heavy hydrocarbons using a selective precolumn. Or, you can distill the stock tank oil into gas and liquid components that go to the chromatograph and a heavy liquid residue that can be measured only for its molecular weight and specific gravity.

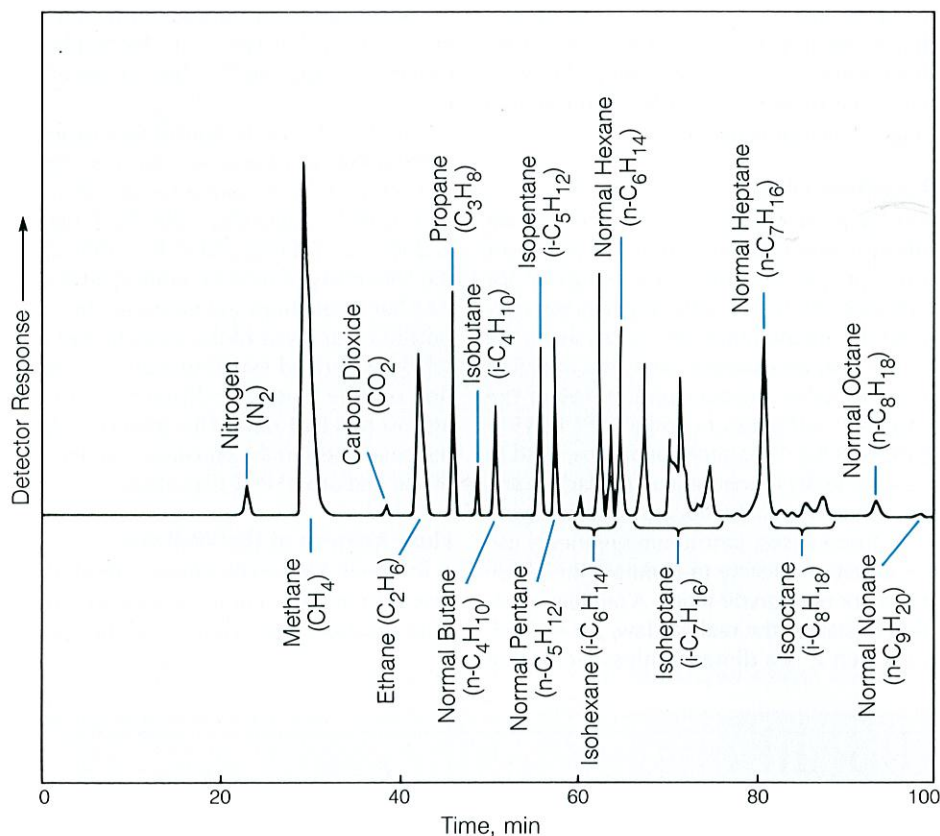
Each method has its drawbacks. Injecting the petroleum liquid into the chromatograph risks polluting the column with heavy elements that won't elute, which causes errors in the measured molecular weight and specific gravity of the liquid residue.

Distillation takes 8 to 12 hours to perform, including the gas chromatography, and requires a minimum sample size of 40 cm<sup>3</sup>. Distillation can lead to inaccurate measurements of intermediate compounds (C<sub>5</sub> to C<sub>11</sub>) that have a boiling point lower than ambient temperature. As the column reaches ambient temperature at the end of the distillation, the intermediate compounds condense and fall back into the heavy liquid residue. The measured properties of the residue will be affected and the reported composition of the light distillation product will not account for the condensed intermediate compounds.

At Schlumberger's PVT lab in Melun, France, researchers Nikos Varotsis and Paul Guieze have developed a fast and fully automated microdistillation process that replaces the standard distillation technique.<sup>4</sup> This process separates more efficiently the heavy residue, resulting in better compositional analysis. It takes one fourth the time to perform and requires only a few microliters (10<sup>-3</sup> cm<sup>3</sup>) of sampling fluid. The molecular composition of a heavy stock-tank oil measured with microdistillation methods compares well with that measured by conventional distillation (right). The percentage concentration of the residue is about three percent greater in distillation than in microdistillation. This difference indicates the presence of intermediate compounds in the residue.

In microdistillation, a small sample is heated to a specific temperature while a continuous inert gas flow removes the vapor produced, which contains light compounds. This continuous removal of vapor induces the heated sample to vaporize faster.

The continuous stream of stripped compounds is carried by the inert gas into a



□ Typical chromatogram used for analyzing hydrocarbon composition. The chromatogram presents detector response versus retention time, the time it took a particular compound to pass through the instrument's adsorbing columns. Chromatograms are calibrated by injecting the chromatograph with a standard mixture of known compounds.

Comparison of Microdistillation and Standard Distillation		
Component	Concentration %	
	Microdistillation	Distillation
C <sub>2</sub>	0.0	0.01
C <sub>3</sub>	0.04	0.12
i-C <sub>4</sub>	0.06	0.09
n-C <sub>4</sub>	0.17	0.31
i-C <sub>5</sub>	0.29	0.30
n-C <sub>5</sub>	0.44	0.50
C <sub>6</sub>	1.98	2.05
C <sub>7</sub>	5.75	5.44
C <sub>8</sub>	10.10	9.27
C <sub>9</sub>	9.99	9.01
C <sub>10</sub>	9.37	8.45
C <sub>11</sub>	6.66	6.31
C <sub>12+</sub>	55.16	58.10
C <sub>12+</sub> spec. gravity	0.883	0.882

low-temperature (less than  $-148^{\circ}\text{F}$  [ $-100^{\circ}\text{C}$ ]) trap filled with adsorbent that captures even the intermediate compounds. When the separation is complete, the trap is heated rapidly to desorb the trapped compounds and then flow them into the gas chromatograph where they are identified with an FID.

Measuring the molecular mass of the residue and the liquid sample mass before and after the microdistillation yields the stock-tank liquid composition. The molecular mass of the residue is measured using a gel permeation chromatograph (GPC), a type of chromatograph that uses a liquid solvent carrier, carbon tetrachloride, rather than a gas carrier.<sup>5</sup>

4. Varotsis N and Guieze P: "Microdistillation: A Method Combining Gas and Liquid Chromatography to Characterize Petroleum Liquids," *Journal of Chromatography* 403 (1987): 159-170.

5. Guieze P and Williams JM: "Determination of the Molar Mass of Petroleum Distillation Residues Using Gel Permeation Chromatography," *Journal of Chromatography* 312 (1984): 261-272.



## Reservoir Fingerprints

Compositional analysis techniques such as GPC allow a "fingerprint" analysis of both residues and lighter petroleum products. Crudes from the same origin have nearly identical chemical fingerprints. Dissimilar fingerprints at different depths in the same well suggest noncommunicating production zones (*opposite, right*). Dissimilar fingerprints from wells in the same field suggest that the wells produce from the different accumulations (*opposite, below right*).

When a mixture is injected into the GPC, molecules carried into the gel-filled columns are separated according to size. Smaller molecules representing the lighter compounds follow the most tortuous paths through the gel and emerge last. Heavy compounds, which are too large to fit through the tiny interstices between gel particles, emerge first. An ultraviolet detector responds to the unsaturated bonds of arenes and an infrared detector responds to the

alkyl fragments of alkanes (see "Composition of Hydrocarbons," *below*). The resulting distributions are plotted with a horizontal molar mass scale, rather than the time scale of a chromatogram.

## Equations of State

During production the petroleum engineer often needs information about reservoir fluid properties and phase behavior for pressure and temperature regimes not covered during the initial PVT analysis. In the North Sea, for example, seawater injection used to drive production can lower the reservoir temperature some 10°F to 15°F [5°C to 8°C]. Separator conditions, used to determine the formation volume factors and the solution gas-oil ratio, may also change.

In these cases, petroleum engineers use an equation of state to simulate the phase behavior of reservoir fluids. A familiar equation of state is the real gas law,  $pV = ZnRT$ , in which  $Z$  is a dimensionless factor that

accounts for the difference between real and ideal gas behavior,  $n$  is the number of moles of a gas, and  $R$  is the universal gas constant.

Much more complicated equations of state have been developed that simulate the attractive and repulsive forces between hydrocarbon molecules—the most popular is due to D-Y. Peng and D.B. Robinson of the University of Alberta, Edmonton, Canada.<sup>6</sup> Such equations are based on the compositional analysis of the mixture and PVT relations derived experimentally. An equation of state must be calibrated, or tuned, against real PVT data. This involves adjusting parameters in the equation until the predicted and actual PVT data agree.

## Fluid Analysis at the Well Site

A thorough PVT analysis takes about three weeks to process and in the case of remote field locations, expedition and transporta-

*continued on page 14*

# Composition of Hydrocarbons

As the term suggests, hydrocarbons consist primarily of hydrogen, 11 to 14 percent by weight, and carbon, 84 to 87 percent by weight (*right*). Oxygen, sulfur, nitrogen, helium and metals exist as trace impurities in crude. The molecular structures of hydrocarbons differ greatly, however, and these structures are classified into 18 different series, depending on whether carbon atom and hydrogen atoms are connected by open chains or cyclic chains, and whether carbon-carbon bonds are single (saturated) or multiple (unsaturated). The amount of each series in the crude determines its properties.

Alkanes, cycloalkanes and arenes are the most common hydrocarbon constituents in crude oils. Alkanes, or paraffins, are saturated hydrocarbons with carbon atoms arranged in open chains and single bonds (*far right*). The general formula is  $C_nH_{2n+2}$ , giving the first member of the series as  $CH_4$ —methane. Two fragments of the alkane molecules,  $CH_2$  or  $CH_3$ , are called alkyls. Alkanes are characteristically stable. At standard temperature and pressure, the first four members of the series—methane, ethane, propane and butane—are gases; the next 13 members— $C_5H_{12}$  to  $C_{17}H_{36}$ —are liquid; and those from  $C_{18}H_{38}$  and above are solids forming paraffin.<sup>2</sup>

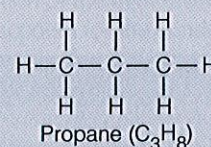
Elemental Composition of Crude Oils <sup>1</sup>	
Element	Weight %
Carbon	84–87
Hydrogen	11–14
Sulfur	0.06–8.00
Nitrogen	0.02–1.70
Oxygen	0.08–1.82
Metals	0.00–0.14

Cycloalkanes are saturated hydrocarbons that form closed rings rather than chains (*right, middle*). These follow the formula  $C_nH_{2n}$ , the first in the series being  $C_3H_6$ —cyclopropane. Like alkanes, they are very stable compounds.

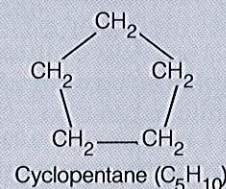
The arenes,  $C_nH_{2n-6}$ , also called aromatics for their fragrant odor, are an unsaturated series forming rings with double carbon bonds (*right*). These compounds are less stable than alkanes, but are not considered highly reactive.

PVT analysts use a shorthand for describing groups of chemical compounds. For example, the term  $C_{3-}$  refers to all compounds with less than three carbon atoms;  $C_{4+}$  stands for all hydrocarbons with four or more carbon atoms. Unless otherwise requested, a compositional analysis provides the mole fraction and percent weight of the lighter compounds up to  $C_{11}$ , and the mole fraction and percent weight of the remaining heavy compounds, collectively referred to as  $C_{12+}$ .

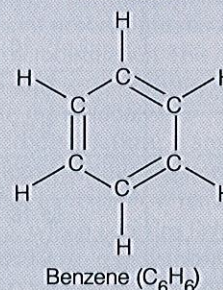
## Alkane Series



## Cycloalkane Series



## Arene Series

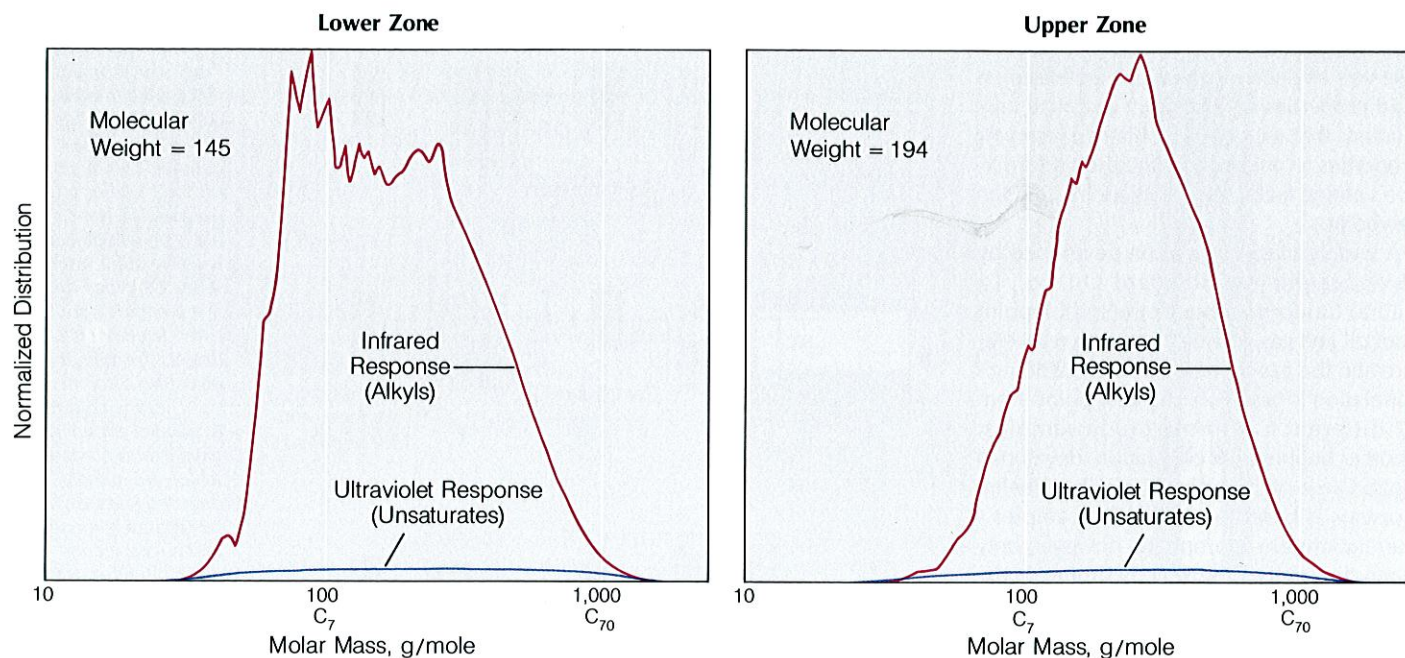


□ Structure of representative members of the three most common constituents of crude oils—the alkane, cycloalkane, and arene series. Propane ( $C_3H_8$ ) represents the alkane series, which are straight chain or branched chain arrangements of hydrogen and carbon atoms. Cyclopentane ( $C_5H_{10}$ ) represents the cycloalkane series, which are saturated hydrocarbons forming closed rings. Benzene ( $C_6H_6$ ) represents the arene series, unsaturated hydrocarbons that contain a double carbon bond.

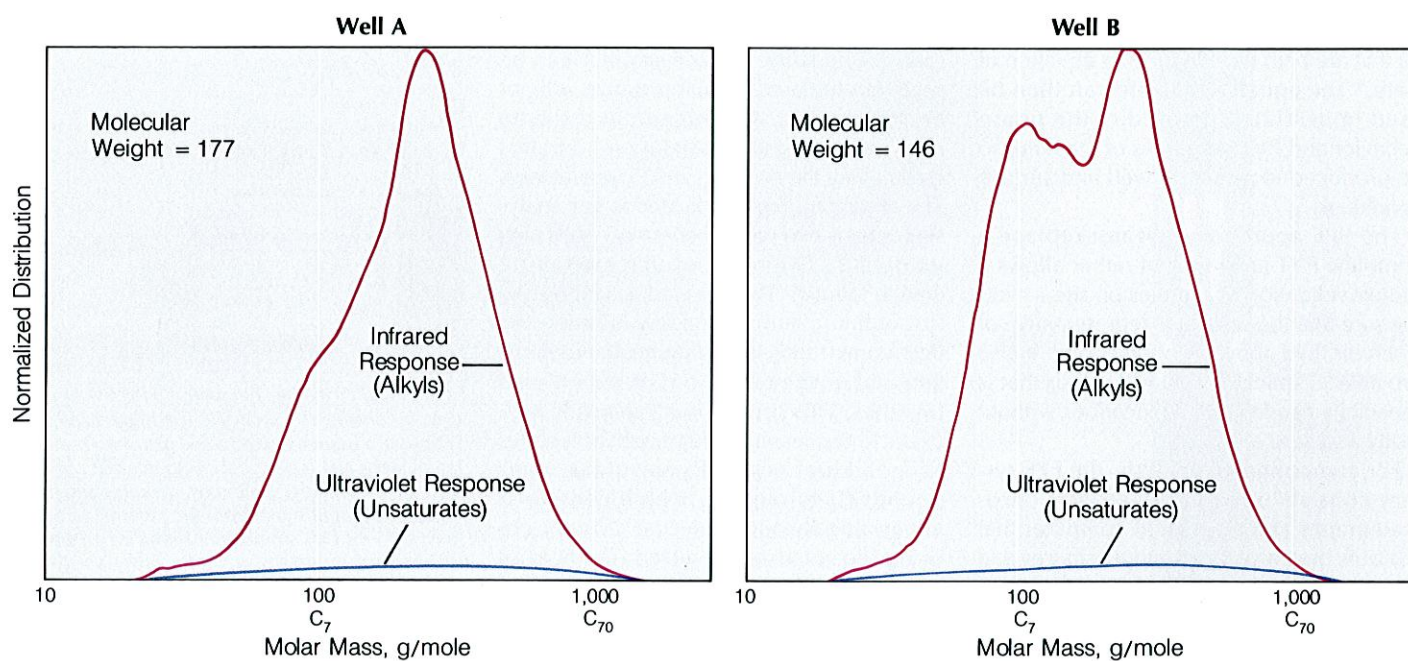
1. Banks RE and King PJ: *Modern Petroleum Technology: Part I*, 5th ed. New York: John Wiley & Sons, 1984.

2. Burcik EJ: "Properties of Naturally Occurring Petroleum Deposits," in *Properties of Petroleum Reservoir Fluids*. Boston: International Human Resources Development Corporation, 1979.





□ Gel permeation chromatography (GPC) fingerprints taken 15 feet [5 meters] apart in depth in a US Gulf Coast well. The dissimilar alkyl responses indicate that these fluids originate from noncommunicating production zones.



□ Gel permeation chromatography (GPC) fingerprints taken from two wells in the same field. The dissimilar alkyl responses reveal that the wells produce from separate reservoirs.

6. Peng D-Y and Robinson DB: "A New Two-Constant Equation of State" *Industrial Engineering Chemistry, Fundamentals* 15 (1976): 59-64.

For a historical review of the evolution of equations of state from Van der Waal's to the present:  
Tsonopoulos C and Heidman JL: "From Redlich-Kwong to the Present," *Fluid Phase Equilibria* 24 (1985): 1-23.



tion problems can sometimes delay the results for months. In the meantime, crucial reservoir engineering decisions are based on fluid properties derived from empirical correlations that relate easily obtained reservoir properties to parameters like the oil formation volume factor, the bubblepoint, and the dewpoint.

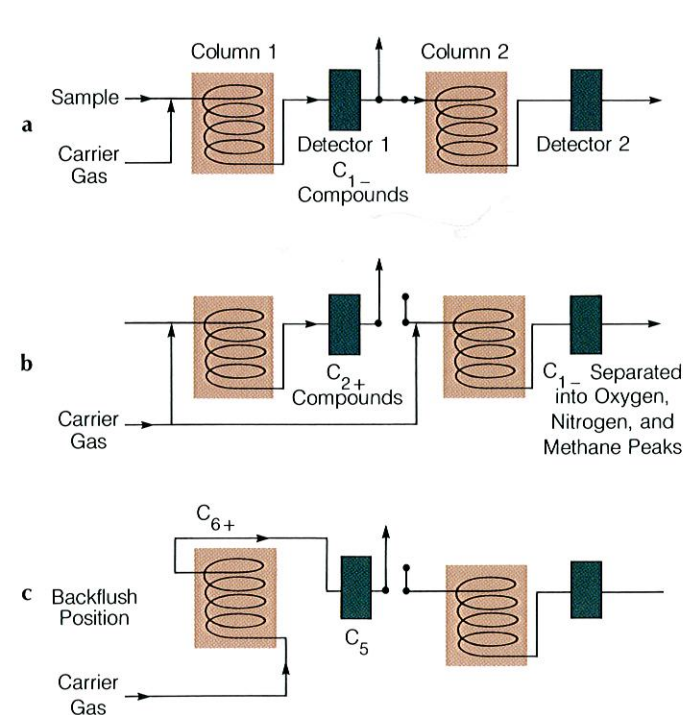
A widely used correlation developed by M.W. Standing of Standard Oil Co., La Habra, California obtains the bubblepoint from oil and gas gravities, reservoir temperature and the gas-oil ratio (GOR).<sup>7</sup> Standing's correlation is based on 105 data points from 22 different California crude samples. Another bubblepoint correlation, developed by Ø. Glasø of the University of Trondheim, Norway, is based on North Sea samples.<sup>8</sup> Correlations are appropriate, however, only when the reservoir sample is similar to the samples that generated the correlation.

A new Flopetrol-Schlumberger service called the Fluid Properties Estimation (FPE\*) system, also developed by Varotsis and Guieze, reduces the need for correlations in the field by providing on-site measurements of fluid properties and compositional analysis that are both used to tune an equation of state.<sup>9</sup> The equation of state can then be used immediately to predict the phase behavior and PVT properties of the fluids to be produced at reservoir, well and surface conditions.

The FPE approach does not replace a complete PVT analysis, but rather allows a proper validation of samples on site—making sure that the sample is representative of reservoir fluid above its bubblepoint. It also provides a "quicklook" fluid analysis that is especially needed in field locations without ready access to a PVT lab.

For compositional analysis, the FPE system consists of two portable gas chromatographs and a personal computer that controls the chromatography, acquires and processes the output signal from the chromatograph and performs the PVT simulation of the oil with the equation of state (*far right*). Other measurements performed on the samples include the bubblepoint, specific gravity, viscosity and refractive index.

Currently, the analysis works best with bottomhole samples (see "Sampling Sum-

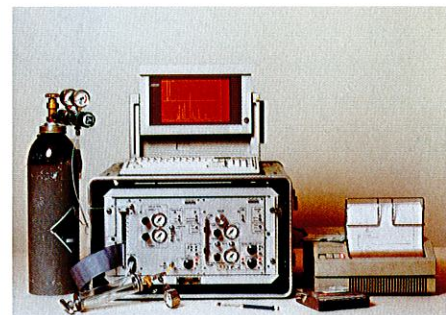


□The gas chromatograph of the Fluid Properties Estimation (FPE\*) system dedicated to analysis of gas samples. Its two columns can be connected in series or in parallel. (a) The sample is initially injected with the columns in series. (b) When the first thermal conductivity detector (TCD) detects the methane peak, the computer switches the columns to parallel allowing oxygen and nitrogen, which are initially detected together, to be separately identified by the second TCD. (c) When the first TCD detects C<sub>5</sub>, the computer reverses the carrier flow to backflush the C<sub>6</sub>+ compounds out of the first column directly into the first TCD.

mary," *opposite*). Surface samples can be used, but the bubblepoint pressure will not be measurable. A bubblepoint estimate must be made using correlations, and this could affect the accuracy of FPE predictions. The chromatograph dedicated to gas analysis contains two packed columns, each with its own TCD and a column switching device (*above*). The injected gas enters the first column, and, after a few minutes, the light compounds including methane, nitrogen and oxygen elute out of the column together. This group of compounds proceeds to the second column where it elutes as individual peaks. By this time, compounds C<sub>2</sub> through C<sub>5</sub> which continued advancing through the first column are being separated and detected. The heavier compounds (C<sub>6</sub>+) are backflushed out of the first column and detected as one lump peak by the first TCD.

The chromatograph dedicated to liquid analysis contains a packed precolumn, a thin column coated on the inside with an absorbing liquid and a TCD. Stock-tank oil is placed in the injector and partially vaporized. The distillate proceeds to the precolumn where it is split into a light part (C<sub>6</sub>-) and a heavy part (C<sub>6</sub>+). The light part is sent to the column and the heavy part is backflushed out of the precolumn. This prevents contamination of the column with the heavy compounds.

TAL



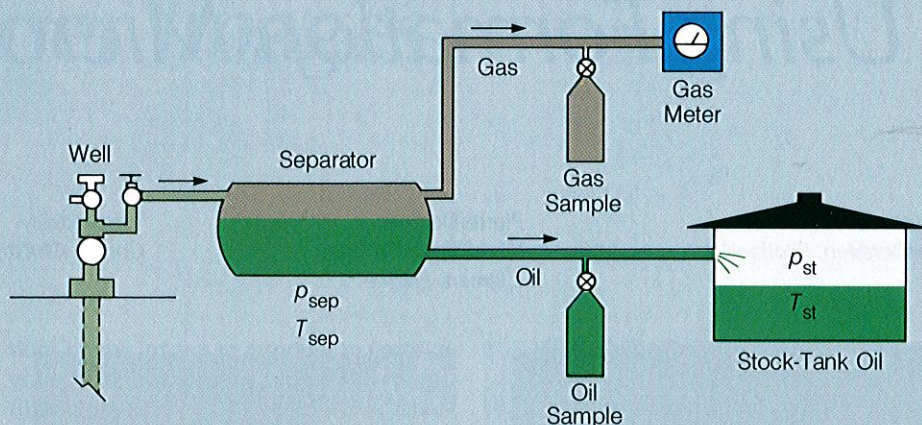
□The Fluid Properties Estimation (FPE) System used for on-site PVT analysis. The ruggedized FPE system houses two portable gas chromatographs and a personal computer that controls the chromatographic runs, acquires and processes the output signal from the chromatograph and performs PVT simulations based on an equation of state.

7. Standing MB: "A Pressure-Volume-Temperature Correlation for Mixtures of California Oils and Gases," *Drilling and Production Practices*. New York: American Petroleum Institute (1947): 275-287.
8. Glasø Ø: "Generalized Pressure-Volume-Temperature Correlations," *Journal of Petroleum Technology* 32 (1980): 785-795.
9. Varotsis N and Guieze P: "Onsite Reservoir Fluid Analysis," paper SPE 18317, presented at the SPE 63rd Annual Technical Conference and Exhibition, Houston, October 2-5, 1988.

\* Mark of Schlumberger



# Sampling Summary



□ Surface sampling of oil and gas. Oil and gas samples are collected simultaneously from the separator to ensure identical sampling conditions and appropriately recombinable fractions. The temperature and pressure of the separator and stock tank are recorded during sampling.

Successful PVT analysis requires that fluid samples represent the original hydrocarbon in the reservoir. Unlike coring and logging programs, which are performed routinely throughout reservoir development, fluid sampling for PVT analysis must occur soon after the exploration wells are drilled in order to characterize the original reservoir fluid. Once the reservoir pressure falls below the bubblepoint, gas comes out of solution and will accumulate to a critical saturation in the rock pores before flowing to the well. Similarly in a gas condensate well, oil begins to condense once the pressure falls below the dewpoint. The oil in a gas condensate, moreover, may never reach a critical saturation and flow. In either case, the composition of the fluid entering the wellbore differs from its original state.

Sampling procedures depend on whether the reservoir is saturated (its pressure equals the bubblepoint) or undersaturated (its pressure is above the bubblepoint).<sup>1</sup> Before sampling the well, reservoir engineers use correlations to estimate the bubblepoint from well test data such as the initial and present reservoir pressures, reservoir temperature, oil and gas gravities, and stabilized production GOR at surface.

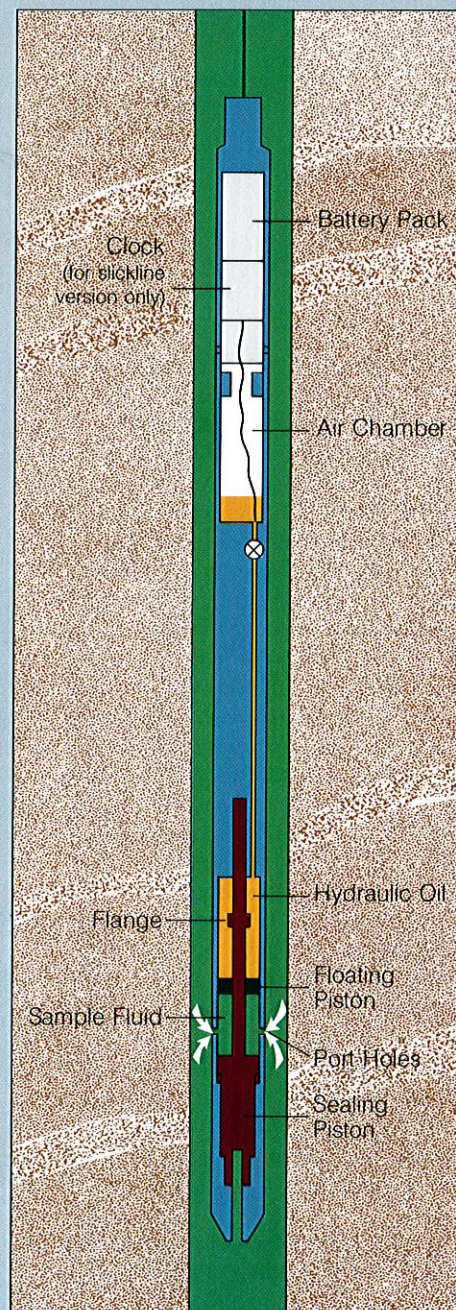
Most wells must be conditioned before sampling because the initial pressure drawdown with production alters the nature of the fluids around the wellbore. The goal of

conditioning is to ensure that fluid entering the wellbore is identical to the original reservoir fluid. This is accomplished by producing the well at successively lower rates until the GOR stabilizes.

Reservoir fluids can be sampled downhole or at the surface. In surface sampling, samples of separator gas and oil are collected simultaneously along with rate measurements and recombined to form a reservoir fluid sample (above). Between two and four 10- or 20-liter samples of gas, depending on the GOR, and 600 cm<sup>3</sup> of oil are collected.

Downhole sampling employs a sampler tool that is run with a pressure gauge on either wireline or slickline (right). After lowering the sampler to the top of the producing zone, the sample chamber is opened by a clock (for slickline tools) or an electric signal from surface (for wireline tools). The oil flows slowly into the tool at constant pressure to avoid gas coming out of solution. A piston seals the chamber and the tool is brought to surface. A minimum of three samples should be collected to ensure that at least one is valid.

The advantage of surface sampling is that it easily provides large fluid samples, but the GOR used to recombine the oil and gas samples must be accurately measured. Downhole samples are validated initially in the field and later in the PVT lab by measuring the sample's bubblepoint and checking that it is less than the sampling pressure. Another check is to compare the bubblepoints of the three or so collected samples—if they agree then the samples are considered representative. If the measured bubblepoint exceeds the downhole sampling pressure, then the sample container has leaked oil or collected free gas.



□ Sampler tool for downhole sampling. After the well has been properly conditioned, the sampler is lowered to the desired depth and activated to collect a sample. Once filled, a piston seals the chamber and the tool is retrieved. At least three bottomhole samples should be collected.

1. *Guidelines for Reservoir Fluid Sampling*. Melun, France: Flopetrol Johnston, 1973.

*API Recommended Practice for Sampling Petroleum Reservoir Fluids*. Dallas: American Petroleum Institute, 1966.