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DOWNHOLE SAMPLING OF GEOPRESSURED GAS WELLS
Final Report for 1982-1984

O. Weres, M. Michel, W. Harnden,
and A. Newton

July 1984

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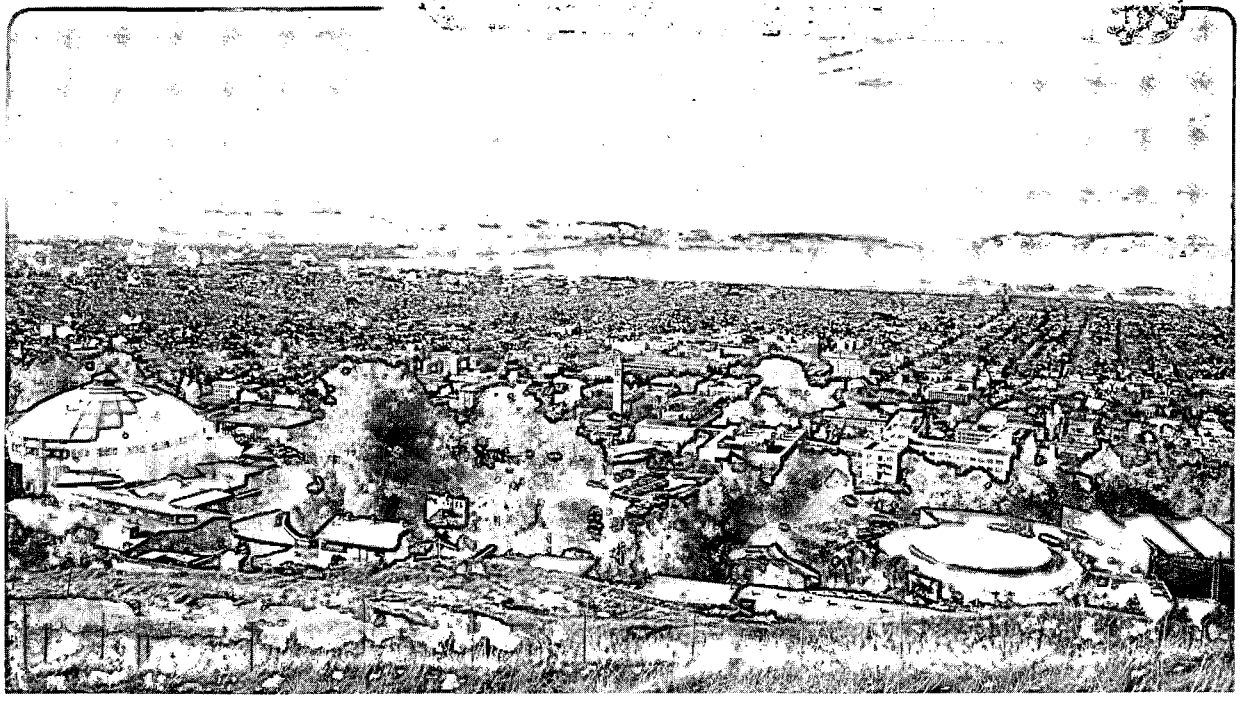

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GRI-83/0028

DOWNHOLE SAMPLING OF GEOPRESSURED GAS WELLS

FINAL REPORT FOR 1982-1984

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For

GAS RESEARCH INSTITUTE

Contract No. 5081-212-0552

GRI Contract Manager
Leo A. Rogers
Co-Production of Gas and Water

July 1984

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16. Abstract (Limit: 200 words)

Under a previous GRI supported project, LBL designed and built a downhole fluid sampler for use in geopressured gas wells. This report describes engineering tests performed on the sampler, and the design and fabrication of auxiliary tools needed to use the sampler effectively.

The fluid inside the sampler exchanges with ambient fluid in a few minutes; therefore, fluid exchange rate is no problem. The sample extraction system allows brine and gas to be removed from the sampler and packaged for shipment, all without exposure to air.

Wellhead samples of gas condensate, oil, and brine from geopressured gas wells were analyzed. The condensates are derived from oil dispersed in the reservoir rock. The unusual aromatic condensates represent the relatively water soluble fraction of the oil. The paraffinic condensates represent production of oil by solution in dense, high pressure gas downhole. Geopressured brines contain carboxylic acid anions, which cause them to have high B.O.D. These anions may be chemical precursors to the gas dissolved in the brine.

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RESEARCH SUMMARY

Title:

Downhole Sampling of Geopressured Gas Wells
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GRI contract number: 5081-212-0552

Contractor:

Lawrence Berkeley Laboratory
University of California
1 Cyclotron Road
Berkeley, California 94720

Principal Investigator:

Oleh Weres

Time span:

June 1982 - July 1984
Final Report

Major achievements:

Under this contract LBL continued design and fabrication of auxiliary tools and a sample extraction system to accompany the downhole fluid sampler fabricated under a previous contract (5014-321-0278). LBL now has the full set of equipment needed to recover a downhole fluid sample from a well and transfer the sample under very clean conditions to containers for laboratory analysis. The sampler is constructed of MP35N alloy which is chemically inert to wellbore fluids. The sample extraction system is constructed of glass and stainless steel which are inert to the sampled fluids at surface conditions.

The fluid exchange rate in the flow-through sample chamber of the tool was experimentally determined. Single phase fluid exchanges with ambient fluid in less than 3 minutes under typical flowing well conditions. Two phase fluid (gas and water) samples were found to contain less gas than the true proportion, because the sampler's intake structure tends to exclude gas bubbles. The sampler is designed for operation up to 450°F and 20,000 psi.

The origin of aromatic condensates produced from several of D.O.E.'s design geopressured gas wells has been determined. These wells all have dispersed oil in their reservoir rock, and the aromatic condensates are derived from oil hydrocarbons dissolved in the brine. The paraffinic condensate and oil produced from one well represent the paraffinic part of the dispersed oil, mobilized by solution in dense, high pressure gas downhole.

Geopressured brine that was causing a serious water pollution problem was analyzed and found to contain abundant carboxylic acid anions that were responsible for the problem.

Recommendations:

The sampler is recommended for use in hot or high pressure wells where conventional samplers are not adequate or for wells where the fluids are unusually corrosive. It is also recommended for use where high sample purity is desirable and sophisticated laboratory analysis is to be done on the samples. It works best for single phase flow although it can be used for multiphase flow where it is not important to sample the exact proportions of the separate phases.

To expedite pollution control, the brine from geopressured wells should routinely be analyzed for carboxylic acid anions.

Description of work completed:

Apparatus was designed, fabricated, and tested to remove the fluid sample from the downhole sampler and transfer it to glass and metal collection bottles preparatory to analysis. This system includes a high pressure piercing needle valve to access the sample through a replaceable disk in the sampler and a means to wash the interior of the sampler to remove any solids that might have stuck to the walls. The system is mounted on a free standing support panel which also serves as one wall of its shipping case. Four sinker bars were also designed and fabricated. These fit around the cable above the sampler and add up to 290 pounds of weight if needed to help lower the sampler in a flowing well.

A flow test facility was assembled which incorporated a 10 foot long vertical, transparent pipe in which the sampler could be tested under realistic hydrodynamic conditions. Portions of the sampler's body were replaced with transparent plastic duplicates so the exchange rate of fluid in the sampler could be visually monitored. Water was then pumped up the test pipe past the sample at flow velocities up to 6.5 ft/sec and the exchange rate in the sample chamber measured using a tracer dye. Two phase flow was produced by injecting nitrogen into the water pump so that the flowing water contained a flood of small gas bubbles.

Various methods to analyze the samples once they are recovered from the sampler were evaluated. This included procedures for trace elements and organic compounds. In addition to more routine fluid and gas analysis methods, LBL has sophisticated instrumentation including a gas chromatograph-mass spectrometer which allows computerized identification of complex organic compounds from their mass spectra.

Wellhead samples of brine, gas and condensate from several geopressured gas wells were analyzed for their organic constituents. These analyses proved the analytical methods, and led to some significant geochemical inferences.

Project implications:

This contract was part of a GRI project aimed at determining differences that may exist in geopressured- geothermal gas aquifer fluids at down hole conditions as compared to well head or surface conditions where samples are normally taken. Knowledge of the physical and chemical properties of the brine and gas is important in relation to scale control and fluid handling. Early attempts to devise downhole diagnostic instruments such as pH probes were largely unsuccessful. The bottom hole sampler constructed of highly corrosion resistant and chemically inert materials was conceived as an alternate

way to bring relatively unperturbed samples to the surface where conventional chemical analytic procedures could be used. These measurements can be compared to similar measurements on samples taken from the surface equipment. Differences can be fairly well represented by thermodynamic reconstruction of the analytical results and the known downhole temperature and pressure.

The sampler was constructed and given preliminary testing in only one well under this contract. Cutbacks in the DOE Geopressured- Geothermal program and the GRI Co-Production program along with the general recession in the gas business preclude using the sampler as intended during the contract period. The sampler is now completed and available for use.

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INTRODUCTION

Overall program objectives

The general objectives of this program were:

(1) To produce a downhole fluid sampler for geopressured wells and demonstrate its use in the field, and

(2) To perform certain research related to the geochemistry and utilization of geopressured gas deposits.

Previous year's accomplishments

Under an earlier GRI contract (5014-321-0278) LBL accomplished the following:

(a) A downhole fluid sampler engineered for use in geopressured gas wells was designed and fabricated (Fig. 1). A power supply/ control console and valve cocking tools needed to operate the sampler were also made (Fig. 2).

(b) The sampler was used to sample a low pressure (<1000 psi) but high temperature (500°F) geothermal well at The Geysers geothermal field. This was the first time a downhole brine sample was brought up at The Geysers, despite several earlier attempts.

(c) Available information about the chemistry and geochemistry of geopressured brines and reservoirs was reviewed.

(d) Computer programs for modeling geochemical equilibria and reactions were reviewed, and evaluated regarding their suitability for modeling geopressured brines and reservoirs.

This work is described by Michel *et al.* (1982).

Objectives for the current year

The objectives for the current year were:

(1) Complete needed engineering tests on the sampler.

(2) Design and build certain auxiliary tools needed to use the sampler effectively.

(3) Select methods of chemical analysis appropriate to geopressured fluids.

(4) Analyze and interpret a variety of wellhead samples from geopressured wells.

(5) Use the sampler in one or more geopressured wells and analyze the samples obtained.

(6) Examine and evaluate a computer program for modeling geopressured brines that another contractor developed for GRI.

(7) Prepare an instruction manual to accompany the sampler and its auxiliary tools.

Rationale for the program

Downhole sampling of brine and gas is a relatively exotic well-testing procedure, but necessary in some cases.

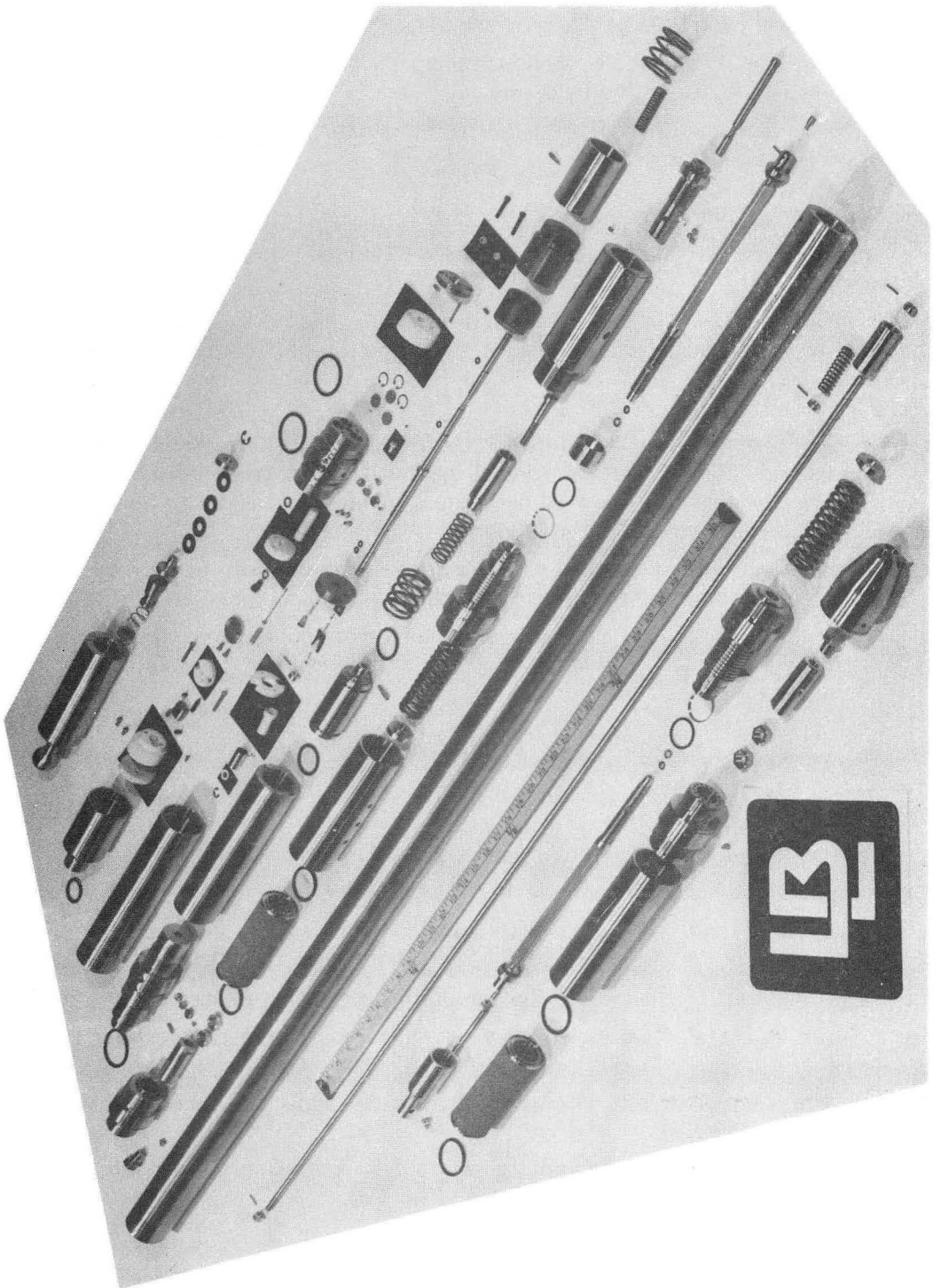

Fig. 1. The sampler disassembled.

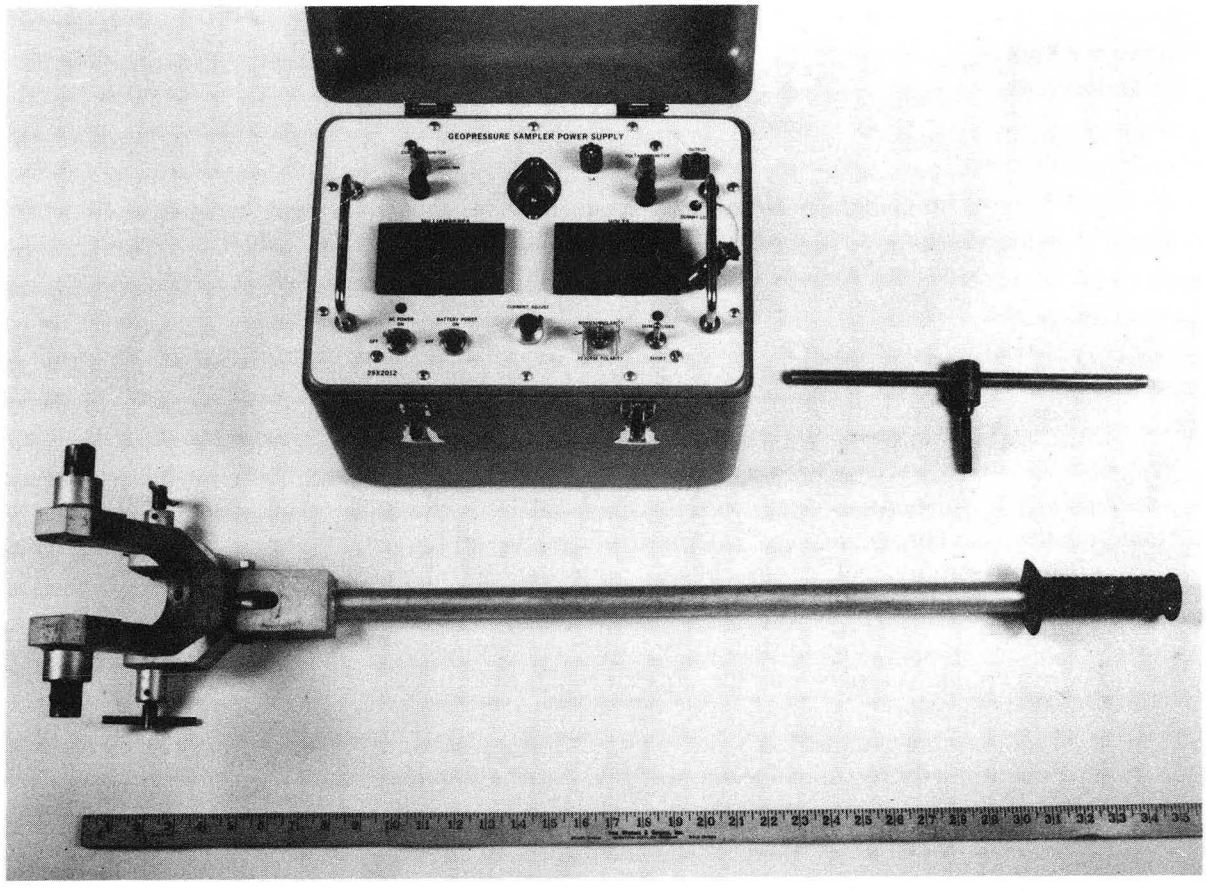

Fig. 2. Power supply and cocking tool. The T-handled screw is used to push open the lower valve before cocking the sampler.

(1) *When the gas:water ratio measured at the wellhead is unreliable.* The concentration of natural gas dissolved in the brine determines the gas content of a geopressured reservoir. Frequently, the concentration of gas in the brine cannot be determined reliably from wellhead samples. For example, brines with different gas content may be produced from two or more strata, or free gas may enter the wellbore. Actually measuring the gas-water ratio at the wellhead may itself be difficult. Properly collected bottom hole brine samples would allow these uncertainties to be eliminated in large measure.

(2) *When there is production from two or more intervals in the well.* Samples of brine and gas collected at the wellhead are mixtures of all fluids that enter the wellbore, and the gas:water ratio measured there is an average value. Knowing the gas:water ratio in the fluid from each producing interval would expedite interpretation of reservoir properties, estimation of gas reserves, and definition of targets for further drilling. A reliable downhole sample would allow one to determine the gas content

of brine produced from the lowest interval, and compare it to the average gas content. In principle, using packers with the sampler would allow one to obtain specific samples from the other producing intervals as well.

Mixing of fluids from different intervals is a frequent cause of scale deposition in the wellbore and surface equipment; for example, mixing a brine rich in calcium with one rich in bicarbonate will cause calcium carbonate to precipitate. If this happens in the well bore, downhole sampling is needed to sort out what is really happening, and to come up with an efficient solution to the problem.

(3) *When chemically reactive brine constituents need be determined.* Some brine constituents will react with the casing material or precipitate as the brine flows up the well. This is particularly true of the relatively insoluble trace metals (aluminum, iron, lead, etc.), and most sulfur compounds. Some hydrogen will be produced by reaction of casing metal with water. Scale forming ions (calcium, strontium, barium, carbonate, sulfate, sulfide, silica) may precipitate in the well bore. A downhole sample will be much less perturbed by chemical interactions of this kind.

Because the formation pressure in geopressured wells is very high, a downhole sampler must be able to retain fluid at very high pressure without leaking after it is brought to the surface. The temperature and salinity of geopressured brines also are high, causing corrosion. A downhole sampler used in geopressured wells must therefore be highly resistant to corrosion.

LBL has designed and fabricated a sampler that meets these requirements, together with several auxiliary tools needed to use it effectively. The sample extraction system allows the brine and gas to be removed from the sampler, separated, and prepared for shipment without exposure to air. With this equipment, it is possible to bring up and handle an uncontaminated sample of brine and gas from a specific interval in a geopressured well.

The sampler is engineered for safe and reliable operation up to 450°F and 20,000 psi gage pressure, and is constructed of MP35N, a very strong and highly corrosion resistant alloy. It represents the state of the art in downhole sampler design.

There are important, unresolved questions related to the nature of geopressured gas deposits and their relationship to associated hydropressured gas and oil deposits. Careful analysis of geopressured fluids helps provide a sound scientific basis for evaluating and developing geopressured gas deposits.

Projected benefit to the ratepayer

This project has made available to industry a significant new tool for evaluating geopressured gas wells. This will aid in the development of geopressured gas resources, and ultimately make more gas available to consumers. This tool is also able to bring up samples of brine, gas, and oil from non-geopressured gas wells, oil wells, and geothermal wells where other samplers will not suffice.

WORK PLAN

The following tasks were planned for the current year:

1. Engineering tests on the sampler

1.1. Flow tests

The sampler has been flow tested. The "flushing time" needed to collect a representative sample at a given well flow rate has been determined. The sampler's ability to collect a representative sample of a two phase flow has been tested. The effect of the sampler's internal brine filters on flushing time and sampling of two phase flow has been determined. Entrainment of solid particles into the sampler has been studied.

1.2. Fluid flow regime in the sample extraction system

Depressurizing the sample will produce a high velocity two phase flow, potentially capable of damaging the sample extraction system. Appropriate engineering tests showed this not to be a problem.

2. Development of auxiliary tools

2.1. The sample extraction system

When the sampler is removed from the wellhead, the fluids in it will be at very high pressure. A "sample extraction system" that depressurizes the sampler in a controlled manner and removes the fluid from it has been designed and built. This system allows the gas and brine to be separated and packaged for shipment without exposure to air.

2.2. The oil pump and heating mantle

Before it goes into the well, part of the sampler must be filled with Krytox oil, which is very viscous at ambient temperature. It is easier to pump the oil if the sampler is hot, as this reduces the viscosity of the oil. A suitable oil pump has been designed and fabricated, and a custom-designed heating mantle has been purchased.

2.3. A sinker bar

This sampler, like many well logging tools, requires extra weight to make it descend rapidly through the fluid in the wellbore. A sinker bar that surrounds the cable and is firmly attached to the sampler from above has been designed and fabricated.

2.4. Centralizer

Usually, a logging tool is equipped with a centralizing device that keeps it approximately centered in the wellbore. A centralizer of conventional design was fabricated. A commercial centralizer could not be used because of the atypically large diameter of the sampler (2.25 inches).

2.5. Brine filters

The sampler was originally equipped with brine filters made of an alumina ceramic. The alumina filters may perturb the concentration of some

brine constituents. Therefore, they were replaced with filters made of nickel mesh.

3. Methods of chemical analysis

Methods of chemical analysis suited to samples of geopressured brine, gas, and condensate have been selected and practiced on wellhead samples.

4. Analysis of wellhead samples

A variety of wellhead samples collected from several geopressured gas wells were analyzed for their organic constituents. These analyses led to useful geochemical inferences.

5. Sampling of geopressured wells

One or more geopressured wells were to have been sampled and the fluids analyzed. Unfortunately, there is very little drilling going on, and we were unable to find a suitable well.

6. Evaluation of the JAYCOR computer program

With support from GRI, the JAYCOR Company developed a computer program for modeling the chemistry of geopressured fluids. This program was studied and evaluated.

7. Preparation of an instruction manual

An instruction manual describing operating and field maintenance procedures for the sampler and sample extraction system was prepared.

WORK PERFORMED AND RESULTS OBTAINED

1. Engineering tests on the sampler

1.1. Flow tests

The resistance to fluid flow through the sampler is not known. Accordingly, the time needed to "flush" the sampler with ambient fluid at a given flow velocity in the wellbore was not known. It was necessary to determine this "flushing time", to estimate how long the sampler must remain open at the sampling depth to collect a representative sample. If it is not kept open at the sampling depth long enough, the sample collected will be heavily contaminated with fluid that entered the sampler at shallower depth, while it was being lowered.

The sampler was intended and designed to sample single (liquid) phase fluid only. In some cases, it may be desirable to sample a two phase flow that contains some free gas. This introduces the problem of proportional sampling: will the gas:water ratio in the sample captured be a good approximation to the actual gas:water ratio at the sampling point?

The sampler was designed with brine filters that are installed below the bottom valve and above the top valve. These filters keep particles in the brine from lodging in the valve seats, thereby causing the valves to leak. We speculated that the internal hydraulics of the sampler may be such that particles cannot reach the valve seats, in which case one or both filters may be

unnecessary. This possibility needed to be tested, because removing at least the lower filter would be desirable. This would eliminate the possibility that reaction with the filter is altering the brine collected, and would lessen the extent to which gas bubbles are excluded from the sample taken.

The flow test machine. A test machine to investigate these matters was designed and built (Fig. 3). In the machine, the sampler is operated in a vertical position with water flowing up past it. The water flow rate is adjustable, up to 320 gpm. This corresponds to 6.5 ft/s flow speed past the sampler. The lowest practical flow rate is about 2 ft/s or 100 gpm. Below this a stable and reproducible flow rate is hard to achieve. Gas may be injected into the flowing water, if so desired.

The test chamber is an 8 foot long, transparent plastic pipe of 5″ I.D. Water is pumped up through it by a large electrically driven pump. The pump is at the bottom of the machine, and supports the weight of the flow straightener section and test chamber. Just above the pump outlet is a crank-operated butterfly valve to control flow rate, and above that, a 40″ long section of steel pipe. Inside this pipe is the flow-straightener, which reduces turbulence before the water enters the test chamber. The flow straightener consists of a bundle of seven 1.5″ diameter steel tubes about 36″ long, tack-welded together into a hexagonal bundle. Above the plastic test chamber, there is a water reservoir made from a 55 gallon metal drum. Normally, the machine is filled with water up to the midline of the drum, which requires approximately 50 gallons of water. The water returns from the reservoir to the pump inlet through a 4″ PVC pipe (the "downcomer").

The weight of the water reservoir is supported by a wooden frame. The whole structure stands on a wooden pallet, and is about 13 feet high. Safe and convenient access to the top of the machine is provided by a 15-ft scaffold erected next to it. The scaffold has a stairway, guard rails, and platforms at six and twelve feet. Above the machine is a light-duty crane that lifts the sampler into the machine and suspends it during the tests. The machine is braced against swaying and gyration by two horizontal struts attached to adjoining permanent structures.

Water flow rate is measured with an ultrasonic flow meter. The probe is attached to the outside of the downcomer. This flow meter is essentially a Doppler sonar unit; it determines flow speed by measuring the Doppler shift of ultrasound reflected from bubbles and particles in the flow.

The water in the drum has a tendency to slosh back-and-forth, causing the whole machine to sway and gyrate. This sloshing is suppressed by suitable baffles installed inside the barrel. The main baffle is horizontal, and located about 5″ above the bottom of the barrel. It has a 6″ diameter hole in it for the sampler, plus a number of smaller holes. In dye elution experiments, these smaller holes are covered up with another, unperforated board, effectively making the horizontal baffle solid. This baffle largely eliminates the tendency to "slosh". The arrangement of baffles used in the gas capture experiments is described below.

The pressure vessel portion of the sampler, and the body section surrounding the lower ceramic filter were duplicated in clear plastic. This allows fluid flow within the sampler to be observed. In these tests, the portion of the sampler above the pressure vessel is not used, and the valve springs are removed. The top valve is closed by pulling on a metal fitting that was fabricated for this purpose, and may be locked closed by inserting a suitable

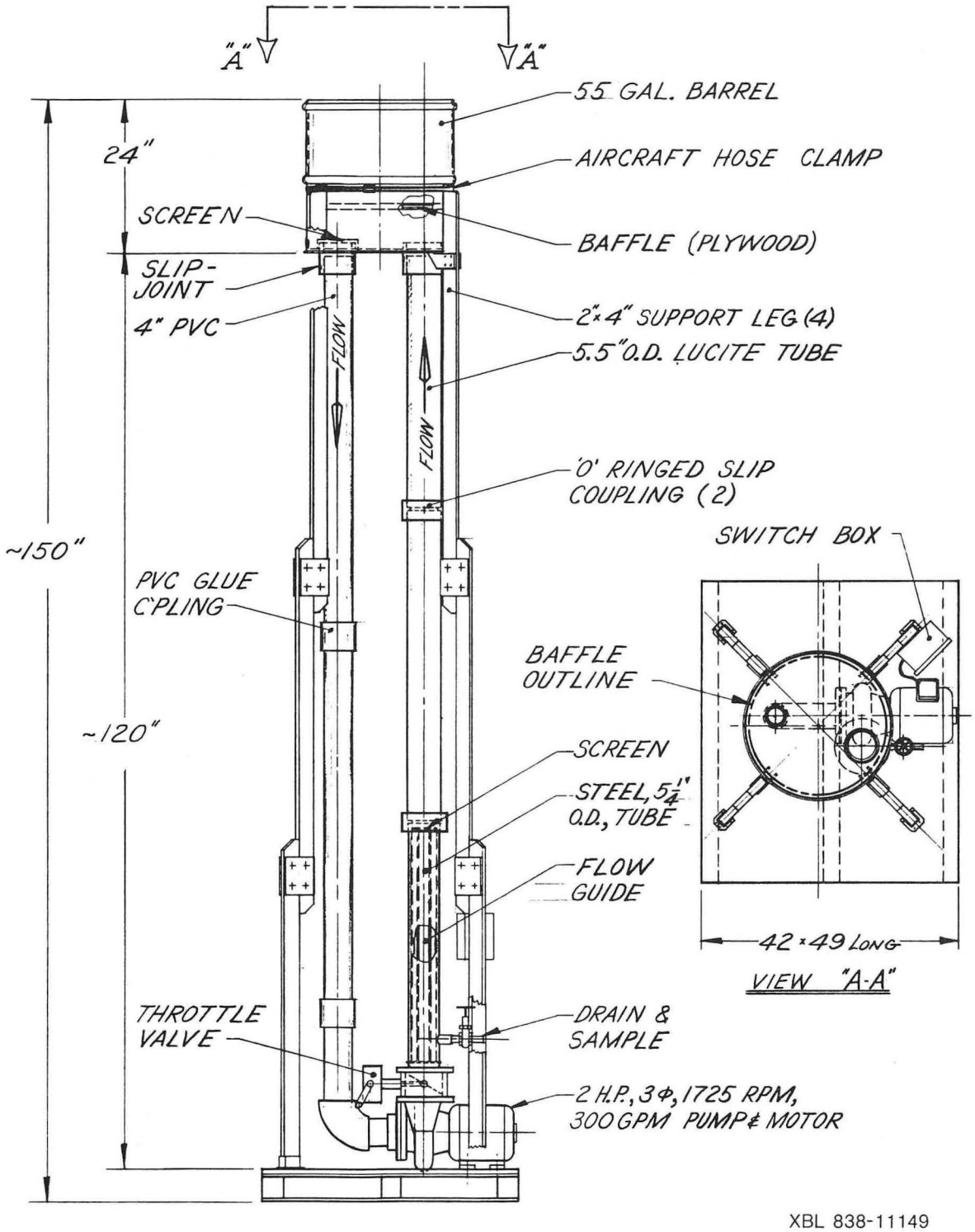

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Fig. 3. Schematic of the flow test machine.

Fig. 4(a). The flow test machine. The scaffold that provides operator access stands before it. The crane that holds the sampler is above it.

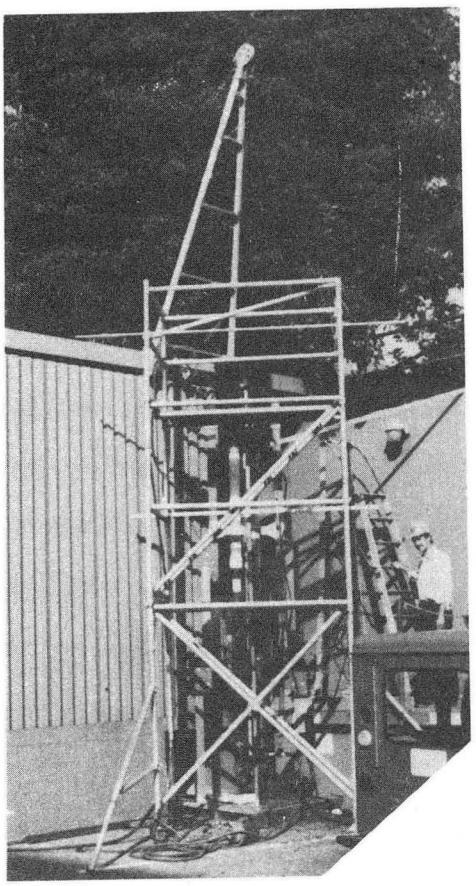
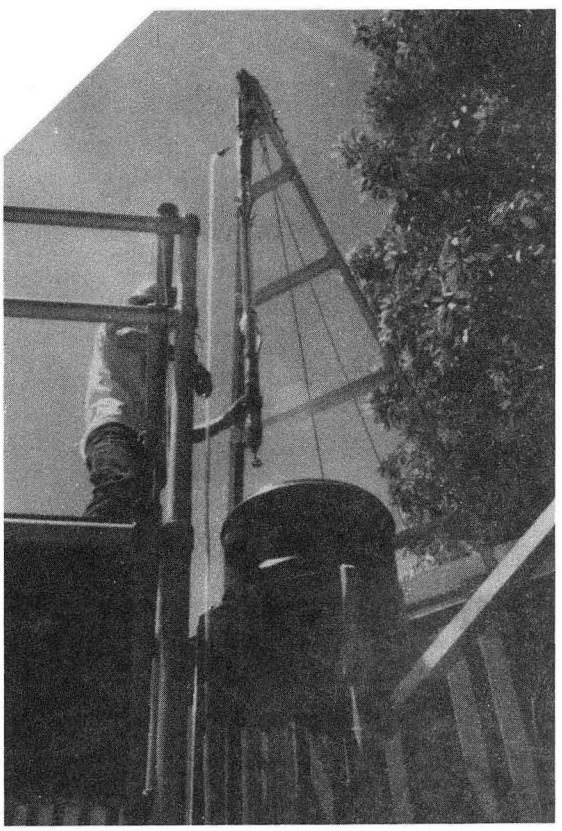


Fig. 4(b). Putting the sampler into the machine.



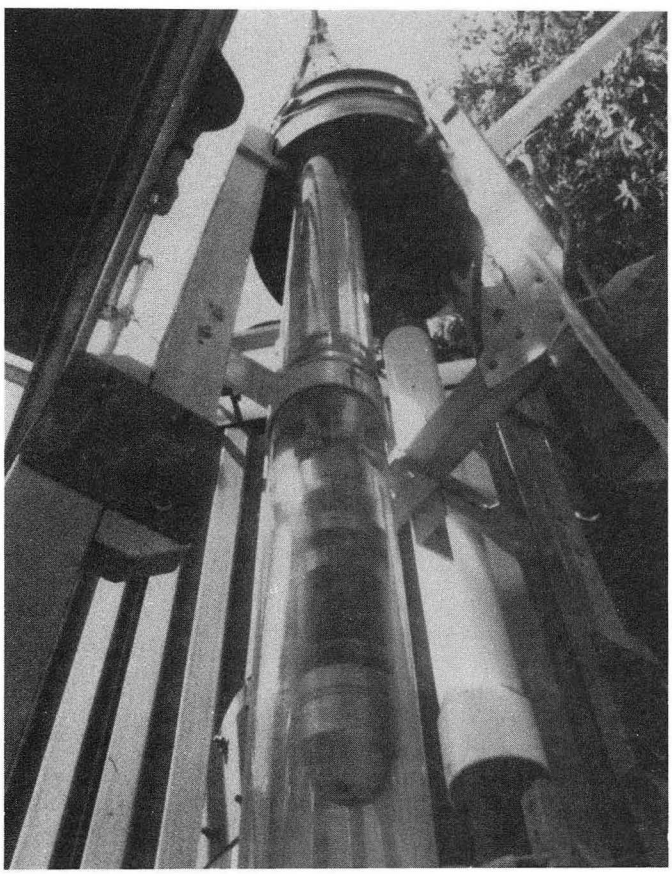


Fig. 4(c). The sampler inside the transparent test chamber.

Conversion Factors for Water Flow Rate in the Machine

1 ft/s at the sampler = 1.25 ft/s in the downcomer

= 0.80 ft/s below the sampler
= 0.11 cu ft/s
= 6.5 cu ft/min
= 49 gal/min
= 1670 bbl/day

metal clip. The bottom valve is always kept open by another small metal fitting, installed inside the bullet nose of the sampler.

Wire-wound filters were used in some experiments instead of the ceramic filters. In other experiments, no filters were used. The wire-wound filters consisted of a cylindrical brass cage wound with stainless steel wire.

Experimental techniques. The time needed to "flush" the sampler is determined by prefilling it with a suitable tracer dye solution, and monitoring the rate at which this dye is transferred to the water outside. A cryogenic vacuum pump provides suction which pulls dye solution into the sampler to fill it at the start of the experiment. The dye is kept from running out while the sampler is being hoisted up by a simple plastic "nosecone". Sodium fluorescein and methylene blue are used in these tests. The initial concentration of the dye inside the sampler is 50 or 80 ppm, respectively. As the experiment progresses, samples of water are collected from near the pump inlet for later analysis. The concentration of fluorescein in these samples is determined by measuring fluorescence at 560 nm, excited by light at 490 nm. The concentration of methylene blue is determined by measuring optical density at 660 nm.

The presence of either dye does not interfere with measurement of the other; this allows two dye flushing experiments to be performed before the water in the machine needs to be drained and replaced. The water is disposed of by pumping it to a drain in an adjacent building. Because of the dye, the water cannot be put into the storm drain or dumped on the ground.

In other tests, a known amount of nitrogen gas is injected into the flowing water near the pump exhaust. The top valve of the sampler is closed abruptly, and the volume percentage of gas inside the sampler is determined. Comparing the percentage of gas sampled to the percentage of gas in the water flow gives an indication of sampler's ability to sample a two phase flow properly.

Nitrogen is produced at up to 5 SCF/min by boiling liquid nitrogen in a device designed for that purpose. (We had this equipment on hand.) The rate of nitrogen injection is measured using a precision rotameter. The gas pressure just downstream of the rotameter is measured with a dial-type pressure gauge (0-30 psig), and this value is used to correct the rotameter reading. Simultaneously, the water flow rate is measured in the downcomer. We

believe that the ratio of gas flow: water flow calculated using these data is accurate to within 10%.

After about a minute, the top valve of the sampler is closed, and the flows of gas and water are turned off. Then the sampler is raised until the interface between gas and water inside it is a convenient distance above the top of the drum. The position of the gas-water interface is visible, because it is located within the plastic "pressure vessel" of the sampler. The sampler is rapped several times to dislodge bubbles stuck in and about the lower valve assembly, and time is allowed for the bubbles to rise to the top of the pressure vessel. The position of the interface is measured relative to a convenient reference point on the sampler, and also relative to the water level in the drum. These measurements are later used to calculate the volume percentage of gas inside the sampler. This value is corrected for the slightly sub-atmospheric pressure inside the sampler when the measurements are made.

Aside from the uncertainty in the gas:water flow ratio, there are two major sources of error in this experiment. Both spuriously increase the amount of gas sampled. First, the bottom valve of the sampler is never closed. Therefore, if some gas bubbles are stuck below the bottom valve, they too will ultimately be included in the volume of gas "sampled". In actual use, both valves would close simultaneously, and any gas trapped below the bottom valve would not be included in the sample. A related problem has largely been eliminated by turning off the gas flow immediately after closing the valve; this prevents further accumulation of gas within the sampler in excess of the volume present when the valve was closed.

Second, small gas bubbles are recirculated with the water, rather than escaping from the barrel to the atmosphere. This increases the rate of gas flow past the sampler to above the rate of gas injection. This effect was reduced by modifying the baffles in the drum. The horizontal baffle has fifteen 1.5" diameter holes drilled in it, and this reduces capture and channeling of large gas bubbles beneath the baffle. These holes reinforce the tendency of the water in the drum to slosh. A second, vertical baffle was installed above the horizontal baffle to correct this. The vertical baffle has a notch at one end, and acts as a weir. It suppresses the sloshing, and imposes a difference in water level of up to eight inches between the "upwelling" and "downwelling" sides of the drum. The water flowing past the weir is less turbulent, and forms a thin layer above the horizontal baffle on the other side. This increases the opportunity for gas bubbles to escape from the flowing water before it enters the downcomer.

Results of dye elution experiments. Test data are presented in Figures 5 and 6. The water flow speeds reported refer to water flow at the sampler, and were calculated from water flow speeds measured in the downcomer. About 2 ft/sec at the sampler (Fig. 5) is the lowest practical flow rate; below this a constant speed is difficult to maintain. This is about the speed at which the sampler would go down the well during a logging run. At 2 ft/sec and without the ceramic filters, 90% of the fluid is exchanged in about 1.5 minutes. Assume the sampler is lowered at 2 ft/s: 90% of the fluid will be exchanged over a distance of 180 feet. With the ceramic filters, 90% of the fluid is exchanged in about 2.5 minutes. This corresponds to 90% fluid

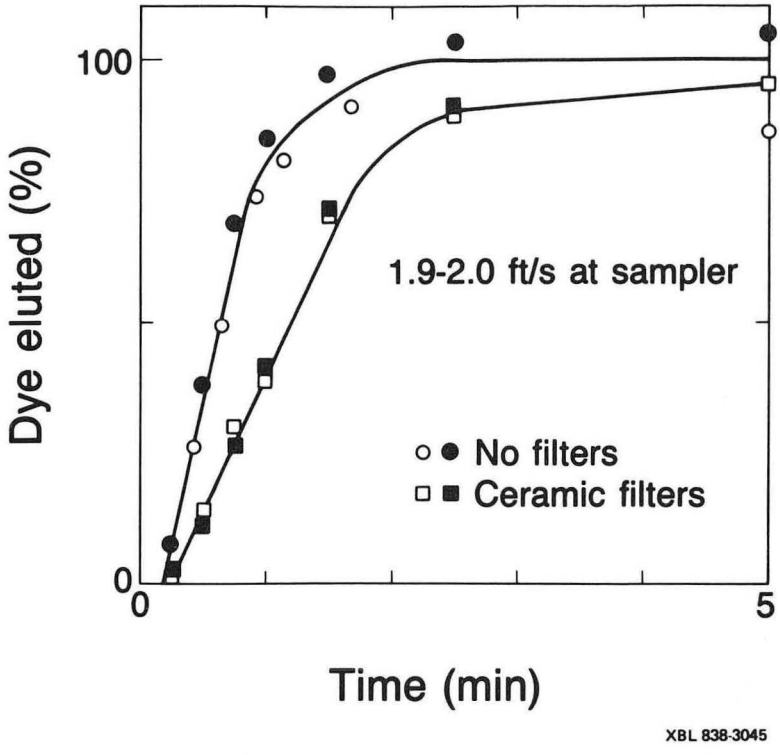


Fig. 5. Dye elution experiments. Water flow speed at the sampler is reported here and in subsequent figures.

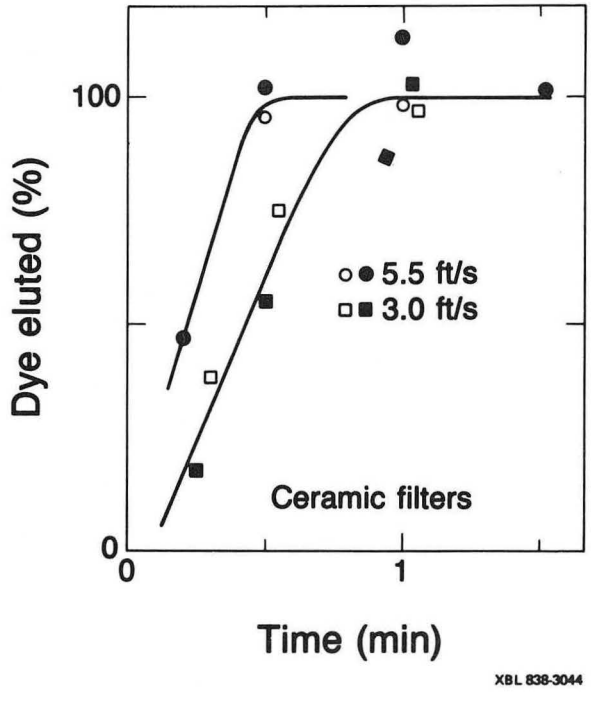


Fig. 6. Dye elution at higher water flow speed.

exchange over a distance of 300 feet.* If the sampler is lowered more slowly, the time available for fluid exchange over a given depth interval will be proportionally longer; therefore, the distance required for 90% fluid exchange will probably be about the same.

The data in Fig. 6 illustrate fluid exchange at higher water flow speed, with ceramic filters in place. In both cases, practically complete exchange occurs within one minute.

Results of gas capture experiments. The data from the gas capture experiments are presented in Figures 7 and 8. The points designated by triangles in Fig. 7 were taken with the ceramic filters in place. Obviously, the ceramic filters tend to exclude gas bubbles; at 15% gas content, the amount of gas in the sample taken is only 3%.

All other points were taken with a wire-wound filter at the bottom, and no filter on top. Solid points were obtained by closing the top valve about one minute after gas flow was initiated; open points were taken allowing at least three minutes for steady state to be attained. Crosses represent samples taken after one to three minutes flow time. The difference between the three sets of data is not significant. In every case, the amount of gas captured is between one-third and one-fifth of what it should be.

The data in Fig. 8 are completely analogous, but taken at a higher water flow speed. Apparently, the relationship between gas present and gas captured is unaffected by water flow speed. The data in Fig. 8, and also the corresponding data in Fig. 7, are fitted fairly well by a straight line with slope 0.27 and intercept +1.2%. This small positive intercept probably is associated with the sources of experimental error discussed above.

The appearance of the flow about the nose of the sampler suggested that large bubbles are deflected away from the "nostrils", behaving like solid bodies. It was reasoned that lowering the surface tension between gas and air would result in smaller bubbles, which would not be deflected to the same extent. Adding a small amount of laundry detergent (about one-half cup) to the water confirmed this (squares in Fig. 7). With detergent present, the fraction of gas in the sample was very nearly equal to that in the flow. This suggests that systematic errors in these experiments are reasonably small.

Commonly, geopressured and other petroleum associated brines contain organic anions and polar molecules that lower surface tension somewhat. The high temperature in the reservoir will also decrease surface tension, as will the high density of the compressed gas. Also, the viscosity of the brine will be lower. These factors will tend to decrease the extent to which gas bubbles are excluded. These considerations suggest that our data overstate the problem: in the field, the fraction of gas in the sample will more closely approximate the fraction of gas in the flow. However, it is not possible to predict how much better matters will be in the field.

Entrainment of sand. The possibility of using the sampler without a lower filter was considered briefly. It was reasoned that particles large enough to interfere with valve seating may not penetrate into the sampler as far as the lower valve; the water flow speed inside the sampler is small. To

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*We later realized there had been a large water leak past the upper filter when these experiments were performed. This leak decreased the sampler's hydraulic impedance, and accelerated dye elution by 10-20% with the filters in place. (Without filters, the leak had no effect.) Therefore, 350 feet may be a better estimate of the distance needed for complete fluid exchange.

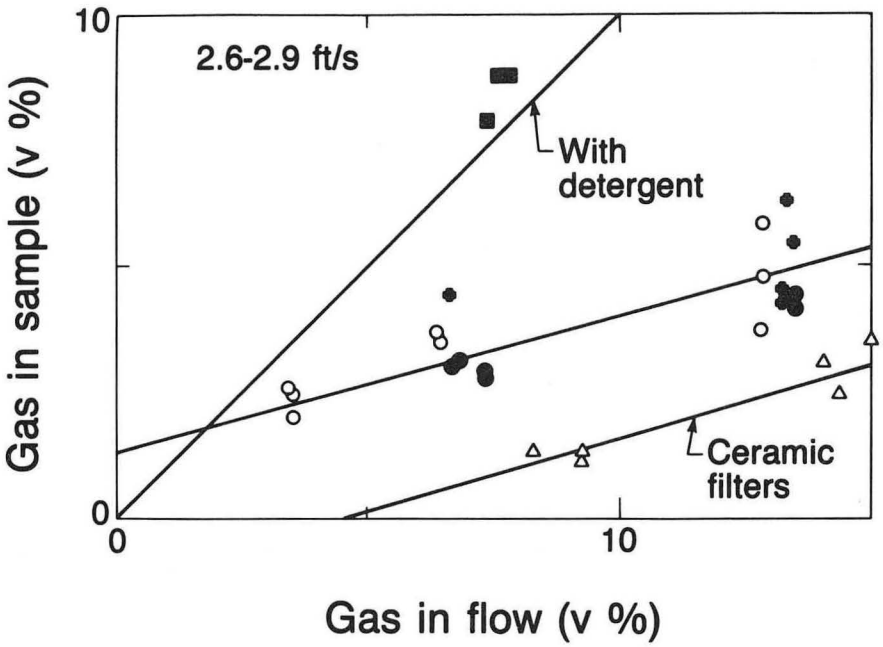

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Fig. 7. Gas capture experiments. Circles, crosses and squares are data taken with a ceramic filter at the top and a wire-wound filter at the bottom. Squares are data taken with a small amount of detergent in the water.

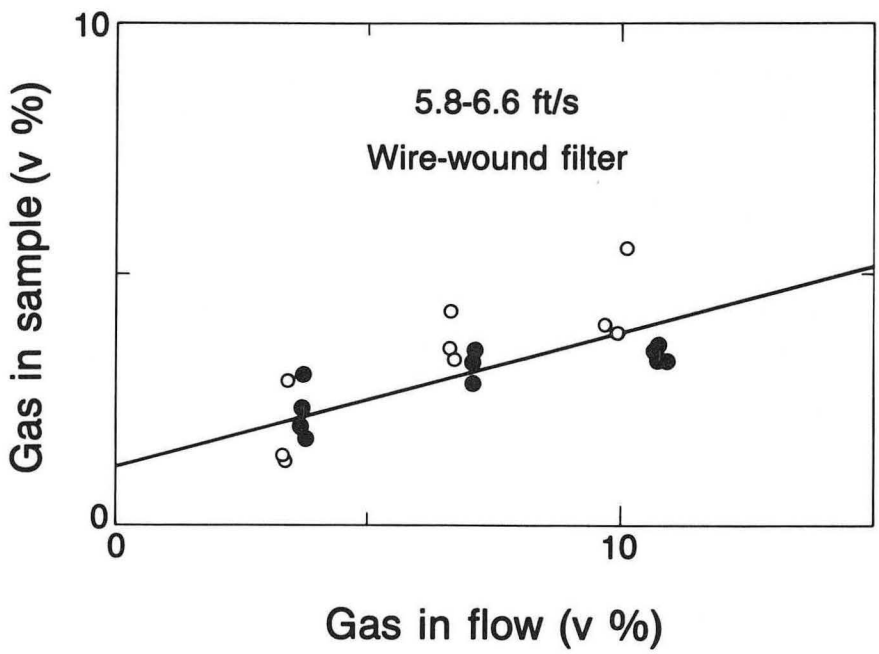

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Fig. 8. Gas capture at higher water flow speed. Wire-wound filter at the bottom and ceramic filter at the top.

test this possibility, graded rock fragments were added to the water, with water flow speed past the sampler about 6.5 ft/s. Crushed and sieved albite particles were used, in the size ranges 12-20 mesh and 30-50 mesh. The lower filter was removed, and a ceramic upper filter was used.

With the 12-20 mesh sand, particles accumulated at the bottom of the lower filter housing, and most did not go beyond that point. This was expected, because the lower filter housing has the largest cross-section within the sampler and, therefore, the lowest water flow speed. Water flow within the lower filter compartment is turbulent. The water forms small jets where it enters the filter compartment. These jets lift some particles and carry them up. A few of the smaller particles made it past the lower valve, and accumulated at the bottom of the sample chamber.

With the 30-50 mesh particles accumulations were again observed at the bottom of the lower filter compartment and at the bottom of the sample chamber. As expected, these accumulations were heavier than those observed with the coarser sand. Particles also accumulated both inside and outside of the upper filter. The particles outside the upper filter must have fallen into that compartment through the water exit holes in its wall. The particles inside the upper filter were traced to a passageway that circumvented the upper filter; evidently, some particles fell through this passageway and ended up inside the upper filter.

Clearly, both upper and lower filters are needed to keep sand away from the valve seats.

The leak past the upper filter was blocked-off, and the lower ceramic filter was put into place. An experiment was made using 70-100 mesh sand. As expected, the ceramic filters effectively blocked particles this size. The sand accumulated rapidly outside the lower filter, and after about 10 minutes had largely filled that space. When the pump was turned off, part of this sand sloughed off and fell out the bottom of the sampler. Pulling the sampler up two or three feet briefly reversed the direction of water flow through it, and most of the remaining sand was flushed off the lower filter. This suggests an easy way to clean the lower filter in the field, if accumulation of sand is suspected.

1.2. Fluid flow regime in the sample extraction system

The sample extraction system includes a cyclone separator made of glass. The fluids released from the sampler enter this glass vessel first. Proper design and safe operation of the sample extraction system required that the type of fluid flow between needle valve and separator be known in advance; i.e., will mist flow, slug flow, etc., occur there when the sample is depressurized.

A laboratory mock-up of this part of the system was devised. It includes a fitting that connects to the sampler valve, a needle valve, and a glass vessel that represents the cyclone separator. In these experiments, carbon dioxide is used in place of methane. Carbon dioxide is much more soluble in water than is methane. Thus, a saturated solution of CO_2 at 200 psia contains about 65 SCF/bbl of dissolved gas. Using CO_2 at 200 psi initial pressure therefore gives the same gas:liquid ratio as would methane at much higher pressure. This allows the fluid flow regime and entrainment of liquid to be studied safely.

The sampler was connected to the mock-up of the sample extraction system. The mock-up was evacuated with a vacuum pump. Water was saturated with CO_2 in an external vessel, and transferred to the sampler under pressure. Then the upper sampler valve was opened, and the behavior of fluid exiting the sampler was observed. As expected, the fluid extracted from the top valve was mostly gas, but carried about 10% of the water with it. Slug flow did not occur. This observation simplified the design requirements for this part of the sample extraction system.

A similar, preliminary experiment had been performed without evacuating the separator mock-up. In this case, the gas and water flowed into an air-filled vessel. The results obtained were the same as with an initially evacuated vessel.

2. Development of auxiliary tools

2.1. The sample extraction system

The sample extraction system is built mostly of glass and stainless steel (Figs. 9(a), 9(b) and 9(c)). It is mounted on a plywood board 6 feet high and 4 feet wide. This board is braced with a steel frame and mounted on a steel base. The whole assembly is free-standing, sturdy, and stable.

A subassembly consisting of the piercing valve and needle valve is screwed directly to the sampler, and is connected to the rest of the sample extraction system with a Teflon lined braided steel hose. These valves are designed for 20,000 psig working pressure, and are fabricated of MP35N (Fig. 10).

Most parts of the sample extraction system that contact liquid are made of glass. This reduces contamination of the brine, and expedites clean-up. All glass parts have been annealed and stress relieved. The tubular parts are made of heavy-walled borosilicate glass tubing. The large glass vessels were made from heavy-walled industrial glass pipe. Except for the cyclone separator, all parts of the sample extraction system that contain gas are made of stainless steel. A steel replacement is available for the cyclone, should the glass one be damaged.

The sample extraction system (SES) has a modular design. There is considerable flexibility in the configuration of the SES. Figure 9(a) shows the SES in its "minimal" configuration, which allows brine and gas to be separated and packaged for shipment without exposure to air. Figure 9(b) shows the SES in its "maximal" configuration. In this configuration, the brine can be filtered, and dissolved gases may be stripped from a portion of the brine and collected in a cold trap.

The various glass and metal parts of the SES are connected by 1/4" Cajon VCR fittings with Viton gaskets. The Cajon fittings are vacuum-tight, and may easily be unscrewed by hand, allowing individual parts to be removed without disturbing their neighbors. The parts of the SES are joined to the support plate by metal rods. One end of the rod is threaded, and attached to the support plate by large nuts. The other end has a fitting appropriate to the given part. Large glass vessels are held by large aeroseal clamps (screw-type "radiator hose clamps") that are padded with plastic to protect the glass. Cable ties are used to attach tubular parts to the support rods.

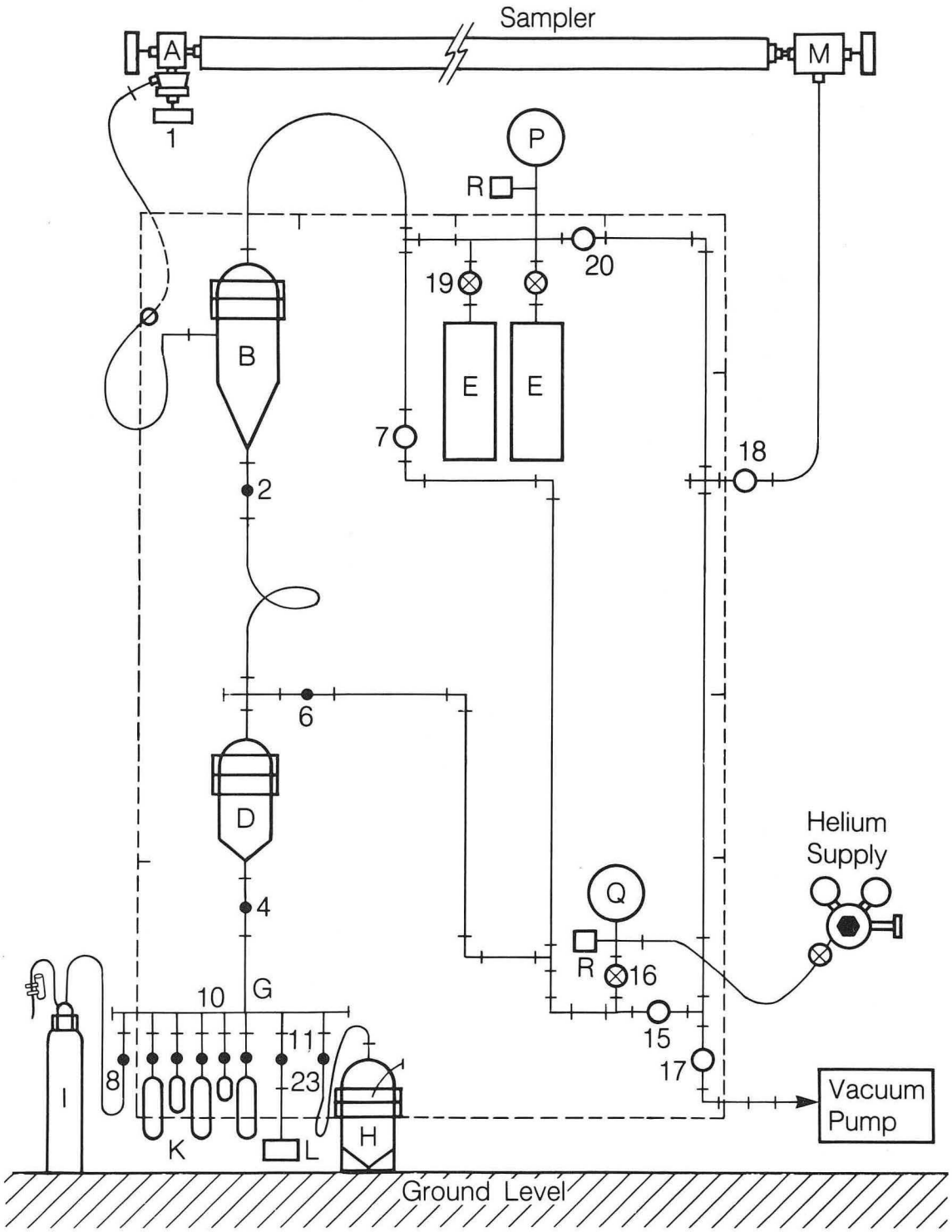

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Fig. 9(a). The sample extraction system in its minimal configuration.

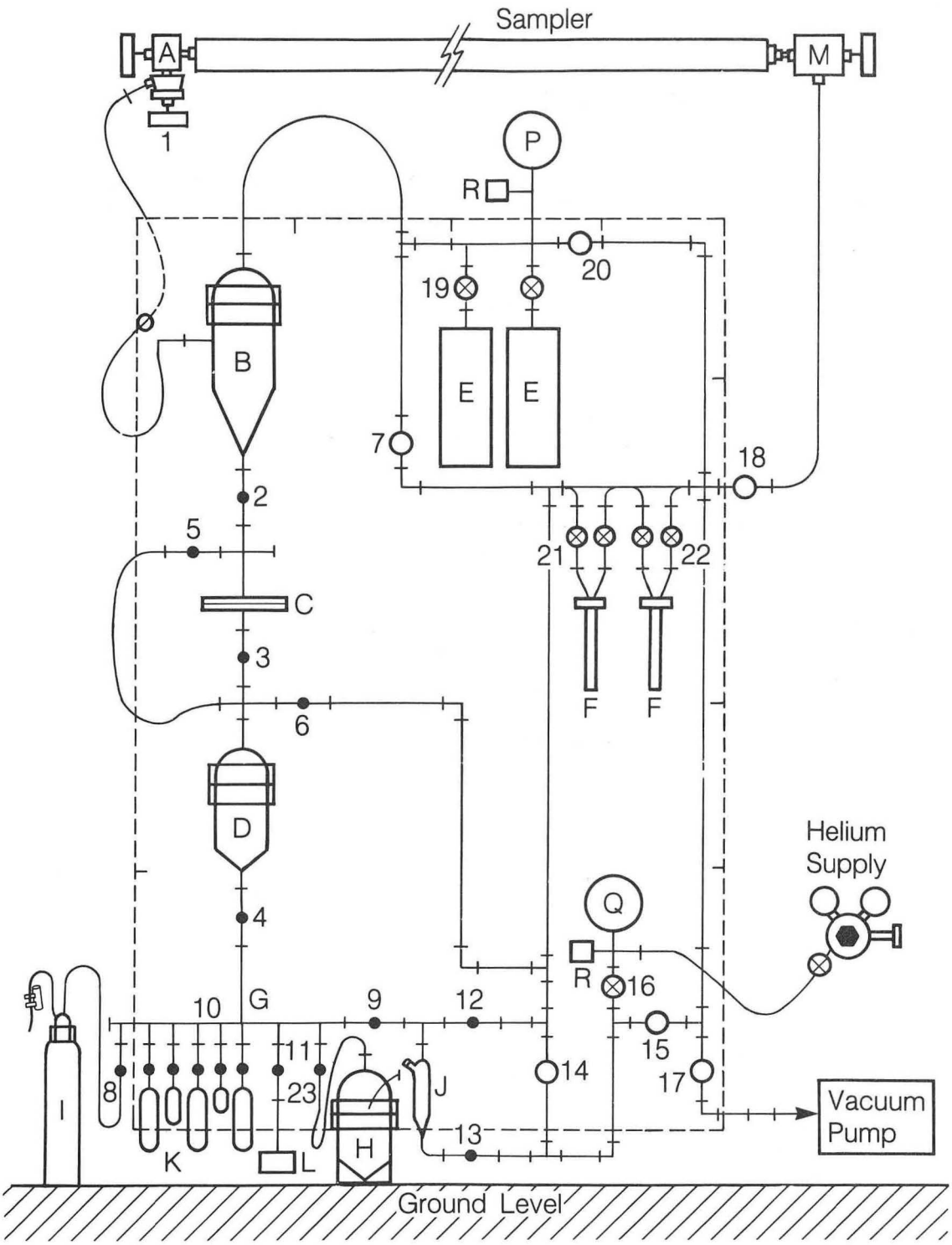

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Fig. 9(b). The sample extraction system in its maximal configuration.

NOTES TO FIGURE 9

Black dots represent glass valves. Open dots represent stainless steel bellows valves. Small crossed open dots represent needle valves. In Figure 9(a), all three connections to the cyclone separator (B) are Teflon-lined, braided steel hoses. In Figure 9(b), the filter bypass is a similar hose.

1 = needle valve that controls depressurization of the sampler (MP35N).
A = upper piercing valve (MP35N).
B = cyclone separator (glass or stainless steel).
C = filter housing (stainless steel).
D = lower brine reservoir (glass).
E = gas sample bottles (stainless steel).
F = cryotraps (stainless steel with copper gaskets).
G = brine manifold (stainless steel).
H = sub-boiling evaporator (glass).
I = modified gas washing bottle (glass).
J = gas stripping vessel (glass).
K = small glass bulbs.
L = flow-through block for pH electrode (Lucite).
M = lower piercing valve (MP35N and stainless steel).
P = precise pressure gauge (0 to 30 psia).
Q = small pressure gauge (-15 to 30 psig).
R = pressure relief valve (preset to 22 psig).

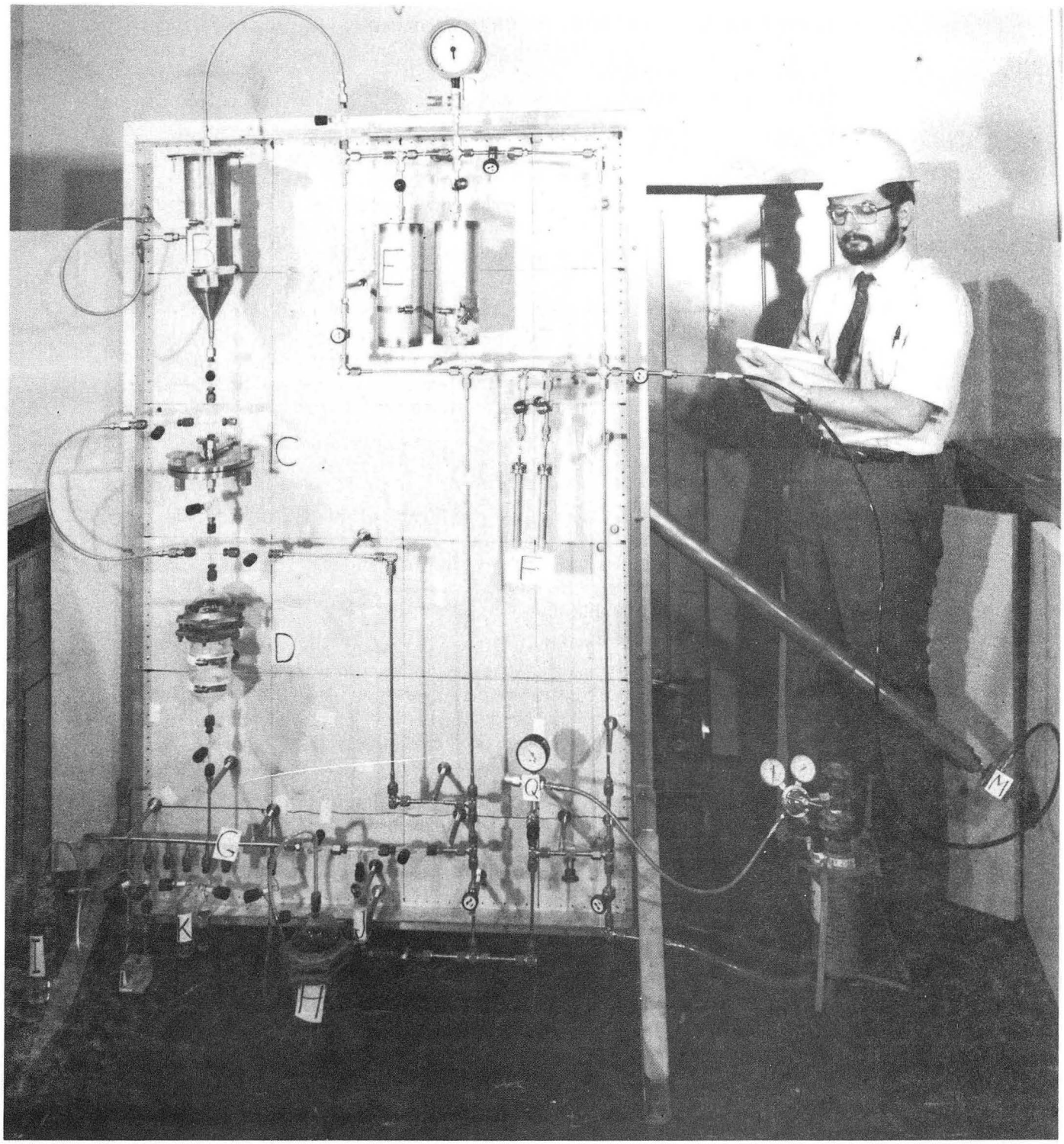


Fig. 9(c). A photograph of the sample extraction system with the stainless steel separator.

The whole system is provided with an aluminum shipping case. This is actually a reinforced shell, open on one side. It fits over the sample extraction system proper, and is bolted to the support plate. For shipment, the large, relatively fragile glass parts, and the sample containers are packed in separate, styrofoam- filled crate.

Initially, the system is evacuated with a vacuum pump. The sampler is depressurized by piercing the upper rupture disk and slowly opening the needle valve. The gas flows into the cyclone separator, carrying with it some entrained brine. From the separator, the gas will flow into the gas collector bottles. A pressure gauge on the gas manifold indicates the total amount of gas (the gas volume is known). A pressure relief valve prevents dangerous overpressure from developing. The gas bottle valves are closed.

The sampler is inverted, and helium is used to force the remaining brine out of the sampler and into the separator. Helium is then used to force the brine from the separator, through the brine filter, and into the lower brine reservoir. A 142 mm diameter, 0.2μm pore size membrane filter is used. Should the filter clog-up, a bypass valve and hose will allow brine transfer to be completed without filtration.

One of the liquid sample bottles contains a small amount of solution containing fully deuterated acetic acid, butyric acid, and phenol. These will serve as internal standards in subsequent chemical analysis. The brine flows from the liquid accumulator and through the liquid manifold to fill the sub-boiling evaporator, the gas stripper, and the liquid sample bottles save two. The valves on the liquid sample bottles and sub-boiling evaporator are closed. A small amount of brine is now forced with helium past a pH electrode that is installed in a suitable flow-through fitting.

Back at the laboratory, the brine in the sub-boiling evaporator will be evaporated with mild heating by flowing dry nitrogen through the vessel. The material in the evaporator will never be exposed to air until it has been completely dried out. The resulting solid material will be ground to homogenize it and prepare samples for analytical procedures that require solid specimens.

A small amount of hydrochloric acid is injected into the gas stripper through a rubber septum. This converts the bicarbonate in the brine to free CO_2. The CO_2 is stripped out of the acidified brine with helium. This gas stream passes through a cryogenic gas trap filled with molecular sieve material and cooled with liquid nitrogen. The molecular sieve collects the CO_2 and other gases of comparable molecular weight while allowing the helium to pass through.

About 100 ml of either dichloromethane (CH_2Cl_2) or 1,1,1-trichloroethane (CCl_3CH_3) is put into the now empty sampler. This solvent dissolves any organic compounds that may be adsorbed on the internal surfaces of the sampler. The solvent contains small, known amounts of fully deuterated toluene, octane, naphthalene, and pyridine. These will serve as internal standards in subsequent chemical analysis. The sampler is inverted and rotated so that all internal surfaces are rinsed. Then the solvent is forced out of the sampler and into the separator with helium, and follows the flow path of the brine until it reaches a single liquid sample bottle reserved for it.

If precipitation of calcium carbonate inside the SES is suspected, it may be rinsed with dilute hydrochloric acid in the same way.

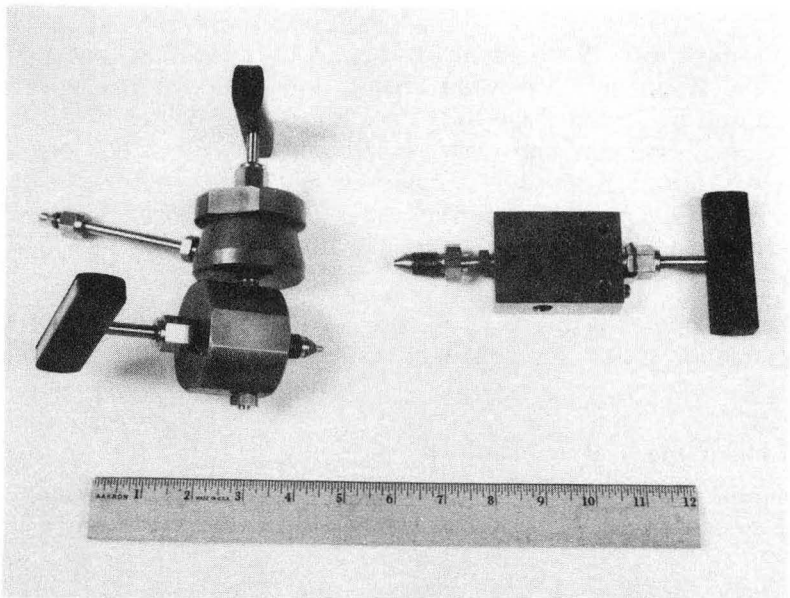


Fig. 10. High pressure piercing valve (A in Fig. 9), and needle valve (1 in Fig. 9), made of MP35N. Piercing valve (M in Fig. 9) made of stainless steel.

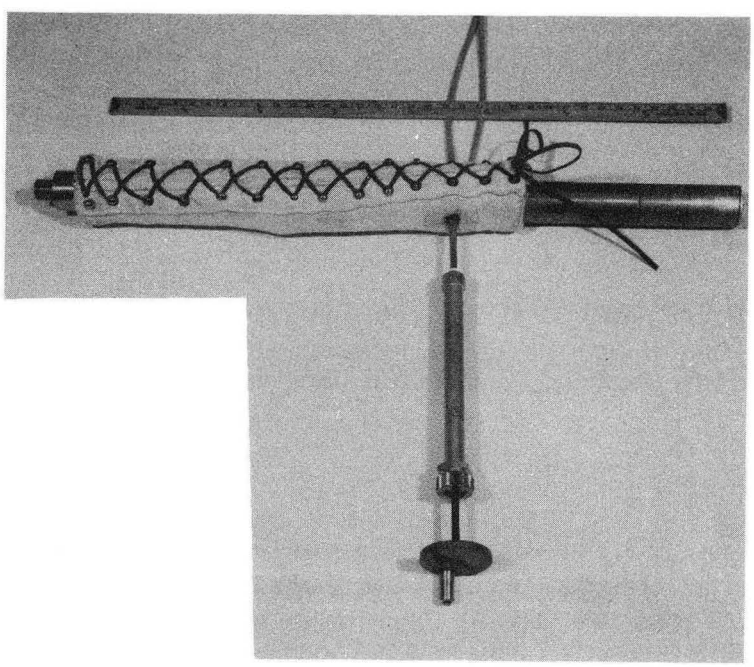


Fig. 11. Heating mantle and Krytox oil pump.

Finally, the sampler and sample extraction system are disassembled and cleaned. Any solid deposits are noted and samples are preserved for possible further study. The filter is removed and examined for accumulated solid materials.

The sample extraction system was completely assembled and thoroughly tested in the laboratory. We were able to reduce the pressure increase in the SES caused by air inleakage to 0.3 psi/hour. This degree of gas tightness requires careful assembly and well greased gaskets. The actual operation of the SES was tested, with the sampler initially filled with water that was saturated with CO_2 at 104 psia. This water contained 25-30 SCF/bbl of dissolved gas, equal to the concentration of natural gas in a good geopressured gas brine.

Detailed operating instructions and a complete description of the the sample extraction system are contained in a separate document (Weres *et al.*, 1984).

2.2. Oil pump and heating mantle

A simple pump for Krytox oil has been designed and fabricated. It is a manually operated, positive displacement pump with a screw-type mechanism.

A custom-made heating mantle was ordered from the Briskeat Co. of Columbus, Ohio (Fig. 11). It consists of an insulated heating element surrounded by glass cloth and fiberglass insulation. The mantle is 25 inches long and has an inside diameter of 2.25 inches. It fits snugly about the sampler, and has a lace closure. Only the oil-filled part of the sampler is heated. Two inches from one end of the mantle is an opening for the oil-pump nozzle. This is aligned with the oil-fill hole in the sampler, and the mantle is laced shut.

The actual heating element of the mantle is 20 inches long; the glass cloth body of the mantle and insulation extend 2 inches beyond the heating element at one end, and 3 inches beyond at the other. The heating element draws 850 watts of 115 volt power. The mantle has two built-in thermostats which cut the power when the temperature reaches 250°F. It takes approximately 15 minutes to heat the given portion of the sampler to this temperature.

2.3. Sinker bars

We have designed and fabricated a sinker bar that is mounted above the tool without requiring that the cable be interrupted (Fig. 12). This sinker bar is modular, and may be disassembled to allow easy handling and shipment.

Most of the weight is provided by four 62″ long, 2.25″ dia. rods of type 17-4 PH stainless steel. Each rod has a deep groove in it, in which the cable lies. One end of each rod has a male thread, and the other end a matching female thread, allowing them to be screwed together. The sinker bar is topped by a standard "stinger". The stinger provides something for a fishing tool to grab on to, should this ever be necessary. It screws on to the uppermost weighting rod. The stinger is not slotted, and will be strung on the cable before the cable is connected to the sampler. The weighting bars will be fitted over the cable and screwed into place between sampler and stinger after the sampler has been attached to the cable. With all four rods

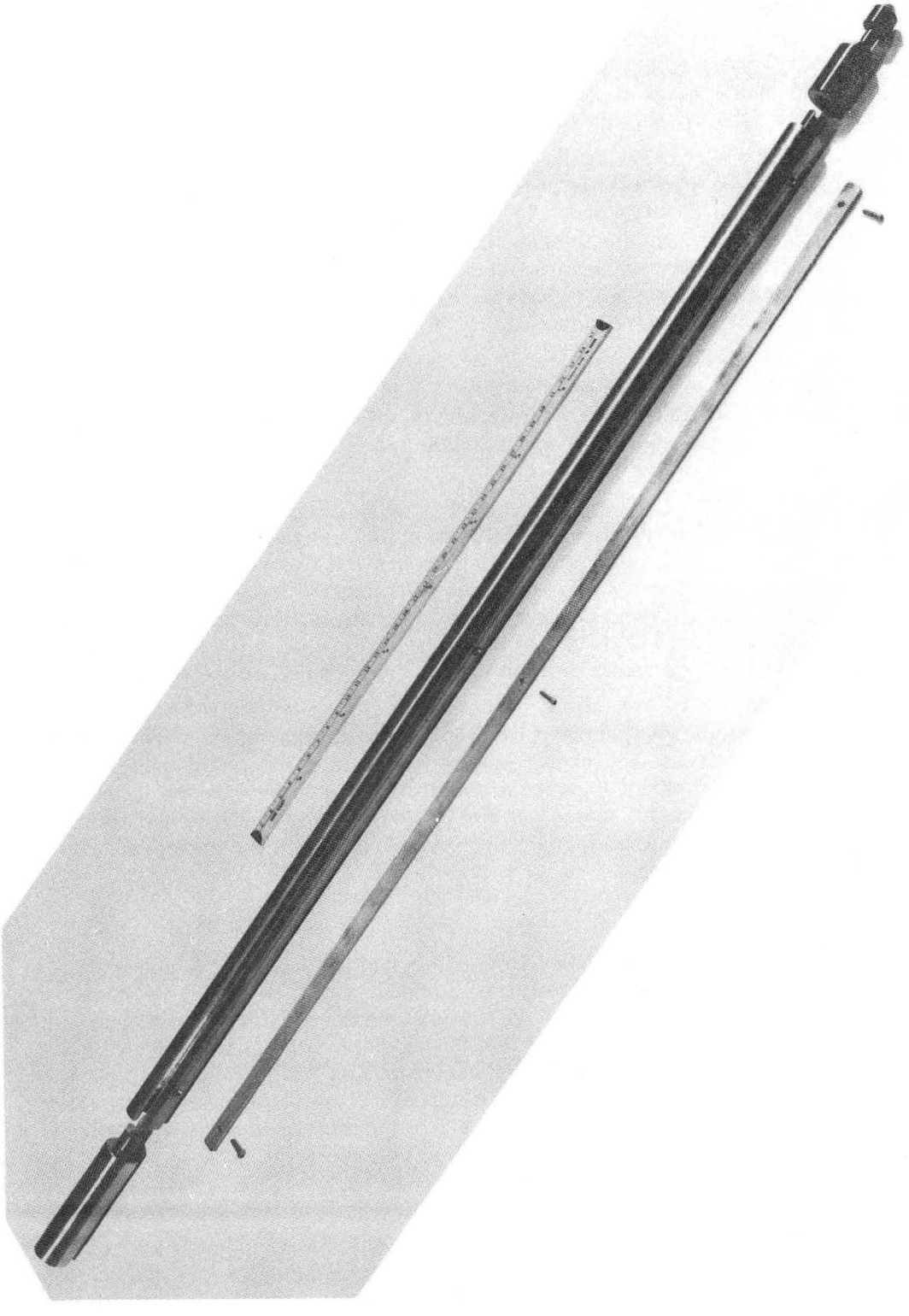


Fig. 12. Sinker bar. Only one of the four weighting bars is shown.

included, the sinker bar will provide about 290-lbs additional weight to the sampler. One or more of the weighting bars may be left off, should a shorter and lighter assembly be preferred.

After the cable is in place, a 1″ x 0.25″ strip of stainless steel is placed into the groove over it, and firmly attached with three large screws. (The heads of these screws are recessed.) Each strip is about 60″ long and runs the length of the weighting rod. This provides additional weight, and helps protect the cable by enclosing it completely.

The sinker bar is rigidly attached to the cable head of the sampler. To enable this, a modified, replacement cable head has been designed and fabricated of 17-4 PH stainless steel. Because the cable head does not withstand pressure or contact the sample, it need not be of MP35N. In place of the ball on the original cable head, the modified cable head has a male thread that matches the threads of the the weighting rods. Thus, the lowest weighting rod is screwed on to the cable head.

The weakest part of the whole assembly is the "neck" of the stinger, where the cross-section is only about 0.4 in^2. To avoid a possible failure of the neck, the stinger was heat-treated to strengthen the metal. The tensile strength of the neck is now about 70,000 lbs.

2.4. Centralizer

A centralizer of conventional design was designed and fabricated (Fig. 13). It consists of the centralizer unit proper and two positioning rings. The centralizer unit consists of two end rings connected by six spring-like bales. The bales push the sampler away from the walls of the casing. The positioning rings are installed on the sampler inside the end rings of the centralizer unit, and keep the centralizer unit fixed in one position on the sampler.

To install the centralizer on the sampler, one end ring is first slipped on to one end of the sampler. Then the two positioning rings are inserted between the bales, and likewise slipped on to the end of the sampler. All three parts are moved together to where the centralizer is to be located on the sampler. The set screws on one positioning ring are tightened to fix its position. The other positioning ring is moved to contact the opposite end ring, and likewise fixed.

2.5. Brine filters

The two ceramic brine filters in the sampler have been replaced with metal filters. Each filter consists of a metal "cage" or filter core made of MP35N. A 100-mesh nickel screen is wrapped around this core and tied to it with nickel wire. It is expected that this assembly will provide effective filtration without significantly altering the composition of the brine sample. The MP35N filter core certainly will not corrode. If necessary, the nickel screen can be replaced with other, more corrosion resistant material like Inconel 600.

3. Methods of chemical analysis

The techniques needed to analyze the inorganic components of the brine are well known, and required no development. The techniques employed by a given institution will be determined by the instrumentation that is available.

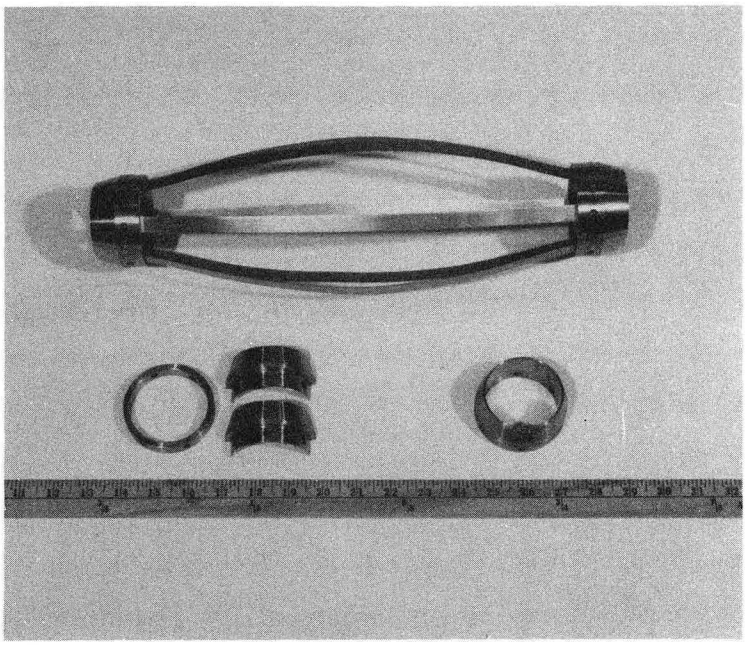


Fig. 13. Centralizer. One of the rings has been disassembled. Set screws (eight per ring) are not shown.

At LBL, we have available (1) neutron activation analysis (NAA), (2) X-ray fluorescence (XRF), (3) ion chromatography (IC), and (4) miscellaneous techniques including atomic absorption spectroscopy, Zeeman atomic absorption, specific ion electrodes, and colorimetry. NAA and XRF determine many elements at once. XRF determines all elements of atomic number 12 to 35 (Mg to Br), plus a few others. NAA determines about 50 elements scattered throughout the periodic table, some with extreme sensitivity. Both XRF and NAA require homogenized solid samples; some brine must be evaporated and the residue ground-up to prepare analytic specimens. IC is particularly well suited for analyzing certain anions. A few components like bicarbonate and ammonia require analytical procedures specific to them.

Isotope ratios of hydrogen, oxygen, and carbon have geochemical significance; these require special analytical procedures, and the work will be sent out to specialized commercial laboratories.

The major constituents of the gas are accurately determined by mass spectrometry. Non-gaseous organic compounds in the brine and gas are determined by coupled gas chromatography - mass spectrometry (GC-MS). This is preceded by suitable extraction, concentration, and derivitization procedures. Present plans call for separate analyses of liquid hydrocarbons, organic acids, and phenols. Detailed analytical procedures for organic compounds are described in Appendix C.

Components to be determined and analytical methods are summarized in Table 1. Some analyses are redundant.

Table 1

Methods of Chemical Analysis

Component	Method
Na	NAA, AA
K	XRF, AA
Mg	XRF, AA
Ca	XRF, AA
Sr	NAA
Ba	NAA
Cl	NAA, electrode
HCO_3^-	Titration, GC
SO_4^{-2}	Isotope dilution, IC
SiO_2	XRF, Colorimetric
Fe	XRF
Cu	XRF
Zn	XRF
Pb	XRF
As	XRF
Br	XRF
Al	NAA
Mn	NAA, XRF
I	NAA
Hg	Zeeman AA
Total sulfide	Electrode
Other S compounds	Colorimetric
$B(OH)_3$	Colorimetric, isotope dilution
NH_3	Colorimetric, electrode
Gases	Mass spectrometry
Liquid hydrocarbons	GC-MS
Organic acids	GC-MS, titration
Phenols	GC-MS
H isotopes	Send out
C isotopes	Send out
O isotopes	Send out
pH	Electrode

AA = atomic absorption spectrometry
GC = gas chromatography

IC = ion chromatography
NAA = neutron activation analysis
XRF = X-ray fluorescence
GC-MS = gas chromatography - mass spectrometry

4. Analysis of wellhead samples

4.1. Description of the wells

4.1.1. Geopressured gas well L.R. Sweezy #1

Located near Lafayette, Louisiana, L.R. Sweezy #1 was one of DOE's "design" geopressured gas wells*. It produced gas and brine from April 1982 to February 1983. Production was from perforations at 13,349 to 13,406 foot depth. The maximum practical production rate was 10,000 bbls/day; sand came into the wellbore at higher rates. In February 1983 a massive intrusion of sand into the wellbore damaged the well. In late 1983 the well was plugged and abandoned. The history of this well has been reviewed in the project final report (Hamilton and Stanley, 1984).

The preexploitation values of bottomhole pressure and temperature were estimated to be 11,408 psia (787 bar) and 237.4^{o}F (114°C). The gas: water ratio was typically about 17.2 SCF per barrel, and the bubble point pressure at reservoir temperature was 8550 psia. Therefore, the brine was undersaturated with gas in the reservoir, with no free gas initially present.

The producing sand had porosity about 30% and density about 2.1. The shale just below it had porosity about 25% and density about 2.2. (*Op. cit.*, p. 130.) This shale was judged to be immature and a very poor source rock for hydrocarbon generation; the average values for three samples analyzed were 2500 ppm total organic carbon, 90 ppm free hydrocarbons, and 150 ppm hydrocarbon potential. It was concluded that the gas must have migrated from elsewhere (*op. cit.*, pp. 159-167).

The most interesting geochemical observation made in the Sweezy well test program is described in the final report (*Op. Cit.*, p. 10):

> Early in the production of the well, a yellow color was noted in the gas flare along with some smokiness of the flame. A dry-ice/ acetone cold trap was placed in the gas stream to attempt to condense out the hydrocarbons that were responsible for the unusual flame. The material condensed was highly aromatic in nature; approximately 33% benzene, 36% toluene, with the remainder made up of ethylbenzene and xylenes. The amount of aromatic material in the gas stream apparently increased during production; in September, 1982, aromatic condensate was noted in the drainage from the water drip pot in the gas line. This continued to increase until most of the material from the drip pot was condensate. In November, 1982, approximately one barrel of heavy, dark, highly parafinnic oil was discovered while cleaning the separator. The well continued to produce small amounts of oil for the remainder of the production test. The source of the condensate and oil is unclear; possible explanations involve the solubility of hydrocarbons in brine, coning of thin layers of oil, and movement of dead, or "irreducible" oil.

Other D.O.E. design wells have produced similar aromatic condensates. Typical condensate/ gas ratios are: L. R. Sweezy #1 = 15ml/MCF, Gladys McCall #1 = 86ml/MCF, and Pleasant Bayou #2 = 123ml/MCF (*op. cit.*, p.

*This well is frequently called "the Parcperdue well".

345).

We collected well head samples of brine and gas from the Sweezy well on August 12, 1982. Professor D. F. Keeley of the University of Southwestern Louisiana (USL) provided us with samples of condensate and oil from Sweezy and other D.O.E. design wells.

4.1.2. Geopressured well Prets Unit 1

Prets Unit 1 is a moderately geopressured gas and oil well in Texas. GRI has supported studies of this well which exemplifies the coproduction of gas and brine. The operator is Secondary Gas Recovery, Inc., of Tyler, Texas. The waste brine from this well caused a serious water pollution problem: the biological oxygen demand of the brine is 550 ppm O_2. GRI asked LBL to perform a complete brine analysis to identify the compounds responsible for the BOD. Mr. J. R. Wible of SGR provided LBL with samples of brine and oil for analysis.

Prets Unit 1 produces from 9100 ft depth. Static reservoir pressure is about 6800 psi (470 bar). Flowing downhole pressure is 4200-5000 psi, and wellhead temperature is 196-200°F (91-93°C). The static bottomhole temperature probably is little greater than this. Typical daily production in late 1983 was 90 bbl oil, 3,300 bbl brine, and 760 MCF gas. This corresponds to 230 SCF gas/ bbl brine, and 19 liters oil/ MCF gas. Clearly, most gas production is from a free gas cap, and, on a mass basis, nearly as much oil is produced as gas. In its depth, pressure profile, and production characteristics, Prets Unit 1 falls between ordinary, hydropressured oil wells and deeper geopressured gas wells.

4.2. Brine composition

The brine sample collected from the Sweezy well was analyzed for water soluble organic compounds using methods described in Appendix C. The most abundant organic compounds in the brine were the anions of carboxylic acids. Titration indicated an aggregate concentration of about 25mN. In approximate order of decreasing abundance, these were:

acetic acid
propionic acid
butyric acid
isobutyric acid
butanedioic (succinic) acid
pentanedioic (glutaric) acid
benzoic acid
isovaleric acid
valeric acid
methylsuccinic acid
p-toluic acid

Acetic acid was the most abundant of these by far. Two other compounds, probably other acids, could not be identified.

Also present in the brine were phenol and two isomers of methylphenol (cresol). The concentration of phenol was comparable to that of benzoic acid.

No other water soluble compounds were detected.

The organic components of the Prets brine were basically similar. Titration indicated 13 mN total organic acids. Based on gas chromatography and titration data, we estimate:

700 ppm	acetate
100 ppm	propionate
50 ppm	total butyric, isobutyric, valeric, malonic, benzoic and several unidentified acids

Phenol and methylphenol totaled about 5 ppm. No other water soluble compounds were detected.

4.3. Gas composition

The gas sample collected from the Sweezy well was quantitatively analyzed by mass spectrometry. These components were determined:

Gas	Mole %
methane	95.1
ethane	2.0
CO_2	2.0
water	0.5
propane	0.24
butane	0.12
nitrogen	<0.3
benzene	0.009
toluene	0.006
xylenes	0.004

The hydrocarbon vapors were frozen out of the gas, and reanalyzed separately by GC-MS. Among the liquid hydrocarbons, aromatic compounds far outweighed the aliphatic compounds. In order of decreasing concentration, these were:

benzene
toluene
xylene
ethylbenzene
trimethylbenzene
ethylmethylbenzene
propylbenzene
naphthalene
butylbenzene

Two of the three possible xylenes were tentatively identified, two of three ethylmethylbenzenes, all three trimethylbenzenes, and both propylbenzenes. All isomers of a given molecular weight were present in roughly equal concentration, suggesting chemical equilibrium.

Small amounts of several alkanes were found. In order of decreasing concentration, these were:

methylcyclohexane
n-heptane
n-octane
dimethylcyclopentane, dimethylcyclohexane

Methylcyclohexane was present in concentration like that of ethylbenzene, and the others, in concentration like that of propylbenzene.

Very probably, various C-5 and C-6 alkanes were also present, but were not detected; they were hidden under the solvent peak.

The composition of this "aromatic condensate" isolated from the gas sample may be summarized thus:

aromatic hydrocarbons >> cycloalkanes > n-alkanes

4.4. Aromatic condensates

Aromatic condensate samples collected from L.R. Sweezy and three other D.O.E. wells are depicted in Table 2. These samples were collected by

Table 2

Composition of Aromatic Condensates[a]

	Pleasant Bayou	Gladys McCall	Sweet Lake	L.R. Sweezy[b]
Benzene[c]	49.3	56.5	46.6	26.0
Toluene	19.8	18.7	28.5	12.4
C-2 benzenes[d]	14.3	12.4	15.3	19.2
C-3 benzenes	5.3	3.6	4.0	10.4
Naphthalenes	2.7	trace	1.3	3.4
Total aromatics	91.4	91.2	95.7	71.4
Cycloalkanes	6.0	6.9	2.7	5.7
n-alkanes	0.6	0.5	0.4	10.8
Branched alkanes	1.9	1.5	1.2	11.8
Total alkanes	8.5	8.9	4.3	28.3

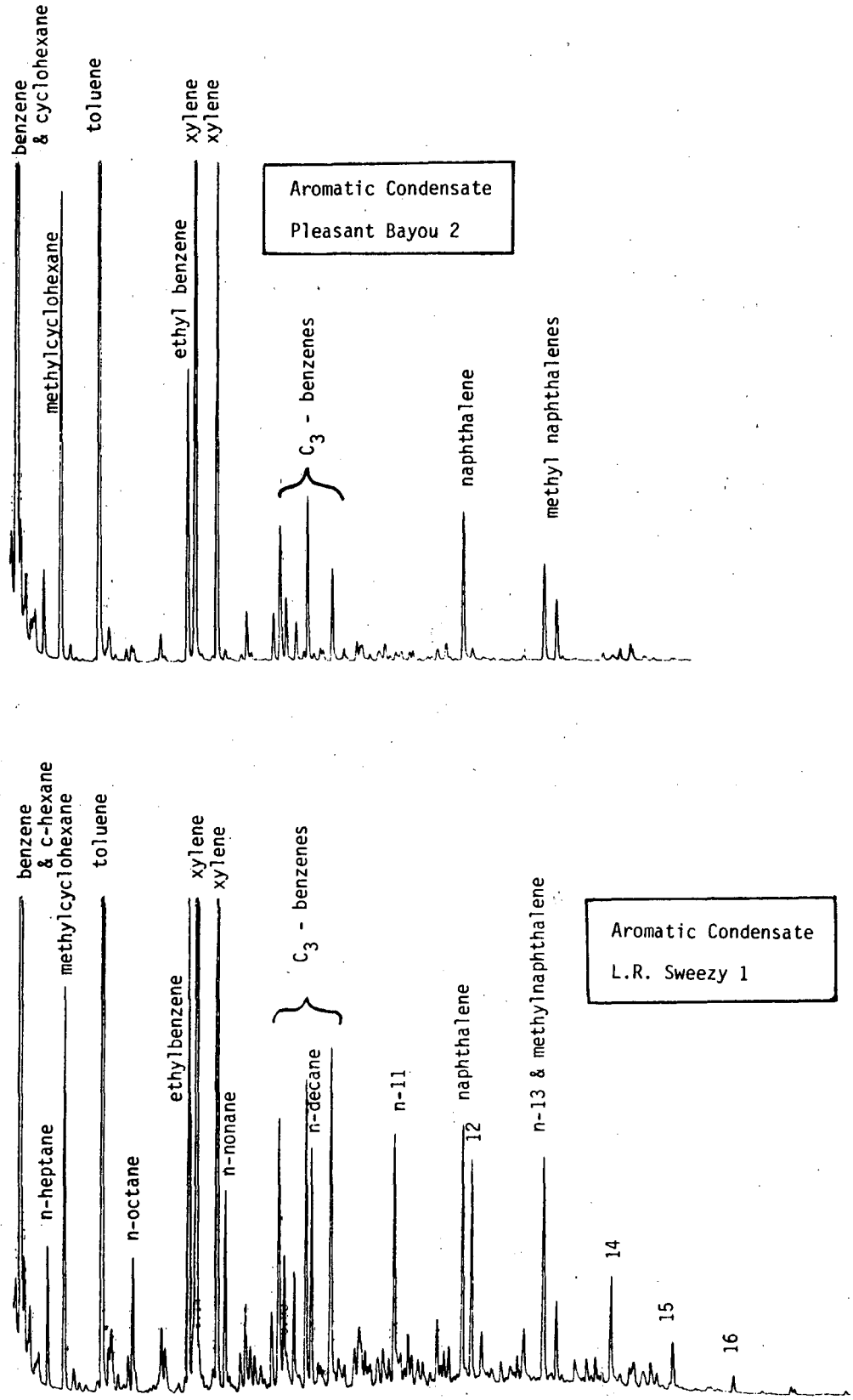
Notes:

(a) Peaks identified by GC-MS. Reported concentrations are proportional to sums of peak areas determined with a flame ionization detector. These samples were diluted in n-hexane for analysis; therefore, C-6 alkanes are hidden under the solvent peak. Parallel analyses of undiluted samples indicated that methylcyclopentane, isohexane, and n-hexane are the major light alkanes present, amounting to 5-10% of the total specimen.

(b) The composition of this sample may have been perturbed by evaporation of lighter compounds.

(c) Includes cyclohexane, which cannot be resolved from benzene.

(d) Includes ethylbenzene and xylenes.



XBL 846-2409

Fig. 14. (a) Aromatic condensate from geopressured design well Pleasant Bayou 2, collected March 12, 1983. (b) Aromatic condensate from geopressured design well L.R. Sweezy 1, collected January 4 and 5, 1983.

USL staff, using a dry ice/ acetone trap. Gas chromatograms of aromatic condensates from the Sweezy and Pleasant Bayou wells are presented in Figure 14.

The condensates from Pleasant Bayou, Gladys McCall, and Sweet Lake are very much alike. The light aromatics are by far the major components, followed by light cycloalkanes; normal and branched alkanes are relatively unimportant. The distribution of compounds closely parallels solubility in water: aromatics >> cycloalkanes > branched alkanes > n-alkanes. Within each group, the concentration decreases rapidly with increasing molecular weight.

The aromatic condensate isolated from the Sweezy gas sample resembles the aromatic condensates collected from the Pleasant Bayou, Gladys McCall and Sweet Lake wells. The Sweezy condensate collected in January 1983 (Table 2 and Figure 14(b)) is different: it contains 28% alkanes, and the n-alkanes don't fall off until about C-15. The alkane fraction of this condensate looks like the volatile fraction of paraffinic oil, while the aromatic fraction is practically identical with the other condensates in Table 2. Very likely, it is a mixture of these two components.

When the Pleasant Bayou condensate was reanalyzed more closely by GC-MS, a minor paraffinic component was found, similar to that in the Sweezy condensate. Two samples of the Pleasant Bayou condensate contained different amounts of the paraffinic component.

4.5. Paraffinic condensates and oil

Figure 15 depicts the liquids collected from the knock out trap and separator of the Sweezy well, and the oil from Prets Unit 1. The "paraffinic condensate" from the knock out trap was analyzed in detail by GC-MS. The n-alkanes peak at C-15, and the approximate composition is:

Class	% response
n-alkanes	46.6
branched alkanes	36.0
cycloalkanes	7.0
Total alkanes	89.6
alkylbenzenes	0.9
naphthalenes	3.7
biphenyls, etc.	1.2
naphthenoaromatics	1.9
Total aromatics	7.7
Polar and unid.	2.7

The specific gravity is 0.830, and H/C = 1.82.

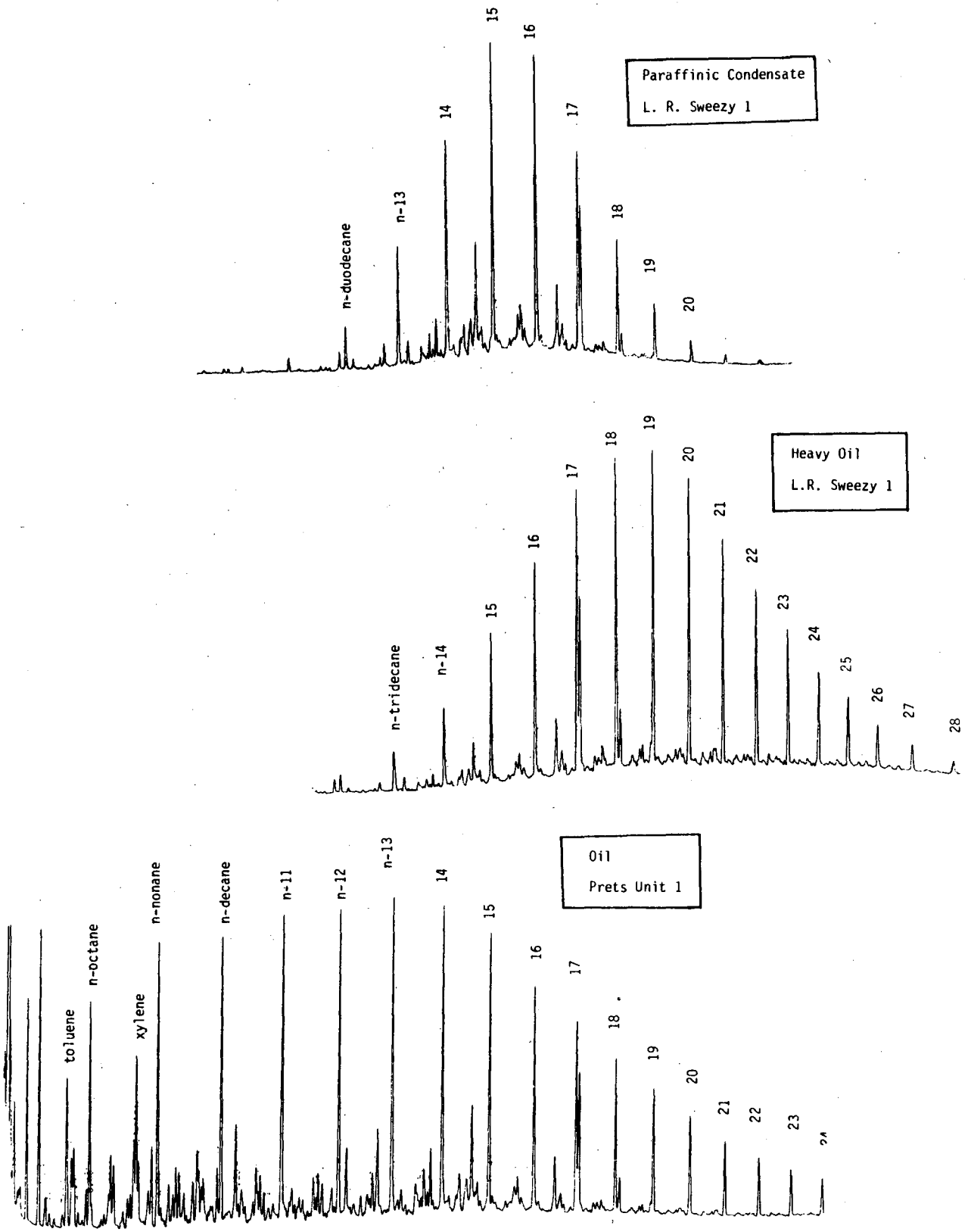


Fig. 15. (a) Paraffinic condensate from the drip pot at L.R. Sweezy 1. (b) "Heavy oil" from the separator at L.R. Sweezy 1. (c) Paraffinic oil from Prets Unit 1.

XBL 846-2410

The dark, viscous "heavy oil" collected from the separator is similar, except for the molecular weight distribution; the n-alkanes peak at C-19 in this case. Over half of this oil consists of many unresolved branched alkanes and cycloalkanes. The specific gravity is 0.876, and H/C = 1.76. These values suggests that polycyclic alkanes and naphthenoaromatics comprise a substantial fraction of the unresolved manifold. The heavy oil is completely miscible with pentane, indicating the absence of asphaltenes.

The sample from Prets Unit 1 is a light paraffinic oil, with n-alkanes peaking at C-13. Based on GC-MS data we estimate:

n-alkanes	45%
branched alkanes	45
aromatics	8
cycloalkanes	2

The specific gravity is 0.806, and H/C = 1.89. This oil contains 0.72% sulfur.

4.6. Discussion

Carothers and Kharaka (1978) have reported the presence of acetate and other organic acid anions in many oil and gas field brines from reservoirs between 80 and 180°C. They proposed the hypothesis that these anions are precursors to methane and other light hydrocarbons. Kharaka *et al.* (1983) have demonstrated that acetic acid will decarboxylate at high temperature to give methane and carbon dioxide.

D.O.E. supported work at LBL (report in preparation) has shown that, in high temperature water, oil shale, humic acid, and carboxylic acids of higher molecular weight will decompose to produce abundant acetate and similar anions. This appears to be the major decomposition mechanism for aliphatic carboxylic acid groups, and fully accounts for the presence of acetate in gas field waters. Once formed, acetate decomposes much more slowly to give methane. Therefore, the role of acetate as an intermediate in formation of natural gas has been demonstrated in the laboratory. (Other reactions also produce methane; e.g., loss of methyl groups.)

The organic anions in the Prets brine account for the high BOD and the pollution problem. Because acetate is practically ubiquitous in hot gas field brines, this problem will become more common as more geopressured gas wells go into production.

Almost certainly, the aromatic condensates are derived from hydrocarbons dissolved in the brine. The distribution of compounds makes this conclusion almost inescapable. Bean *et al.* (1980) equilibrated Prudhoe Bay petroleum with sea water, and then extracted and analyzed the hydrocarbons dissolved in the sea water. The gas chromatogram they published is very similar to our Figure 14(a).

If combined, the alkane fraction of the Sweezy condensate, the paraffinic condensate, and the heavy oil would produce a mixture that resembles the oil from Prets Unit 1. It appears they are fractions of an oil similar to Prets Unit 1, separated by fractional condensation in the wellhead equipment.

Probably, some oil similar to the Prets oil is present in the rock matrix of all the wells. In the reservoir, the more soluble (i.e. aromatic) hydrocarbons in the oil dissolved in the brine. When a separate gas phase formed in the course of brine production, the hydrocarbons partitioned into the gas phase. At the surface, the aromatic hydrocarbons in the gas were collected in the cold trap to produce the aromatic condensate.

The production of the paraffinic condensates requires a different explanation. Liquids of this composition are practically insoluble in water. Conventional theories of oil migration require that enough oil be present to form a continuous oil phase. In the Sweezy well, this is certainly not the case.

The Sweezy well probably produced from a free gas cap, along with gas dissolved in the brine. The appearance of the gas flare at the Sweezy well fluctuated: intermittently, it became bright orange and very sooty, indicating a large increase in the concentration of aromatic hydrocarbons. This suggested intermittent production of free gas enriched with aromatic hydrocarbons. Probably, the gas cap was present just above the perforations in the casing. Occasionally, the gas:water interface dropped below the top perforations, and some free gas was produced together with brine.* This gas cap probably developed in response to production and drawdown.

The pressure and density of this gas cap were very high, approaching the density of gas condensate. These are the conditions for tertiary oil recovery by gas flooding, usually done using CO_2. Zhuze *et al.* (1962) and Price *et al.* (1983) have demonstrated that in this range of temperature and pressure oil hydrocarbons are soluble in natural gas. The water insoluble alkanes dissolved in the gas, and were produced with it. Being less soluble in the dense methane, asphaltenes were left behind. The least volatile fraction of the oil dropped out of the gas when pressure was reduced at the choke; this was the "heavy oil". The more volatile compounds in the oil stayed in the gas phase as vapors. An intermediate fraction condensed from the gas and collected in the drip pots; this was the paraffinic condensate. The remaining, most volatile alkanes stayed in the gas together with the light aromatics until collected in the cold trap; they formed the paraffinic fraction of the aromatic condensate.

The peculiar liquids obtained from the DOE design wells are now merely a curiosity. However, the experience with the Sweezy well suggests that oil may be produced directly from source rock, by coupling the processes of gas production and tertiary recovery by gas solution. The method for producing this oil is remarkably simple: draw down a geopressured well until it goes two phase in the formation. At that point, tertiary recovery of oil by solution in supercritical methane will begin. The Sweezy well apparently reached that point. Unfortunately, the shale near the wellbore was very poor in hydrocarbons, and this resulted in economically insignificant oil production. It is possible that some commercial geopressured wells, like Prets Unit 1, are actually producing oil in this way.

If commercialized, coproduction of oil with geopressured gas could significantly improve the economic prospects for geopressured gas utilization, thereby increasing the economic resource base for natural gas and oil both.

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* Downhole sampling would confirm this phenomenon. A brine sample taken near the bottom of the perforations would not include any contribution from the free gas cap; therefore, the gas:brine ratio in this bottom hole sample would be substantially lower than the average ratio at the well-head. The concentration of liquid hydrocarbons and the ratio of ethane to methane

It is commonly held that reservoirs much above 100°C contain little oil, because oil is presumed to decompose to gas and graphite at high temperature. However, Price *et al.* (1979, 1981, 1982) have reported significant hydrocarbons and hydrocarbon potential in core and cuttings from deep wells with temperatures up to 300°C. Perhaps this oil has not migrated because the pressure in these very deep wells is too high for a free gas phase to exist, making migration by gas solution impossible. Price's observations suggest that there may be an enormous resource of immobile oil in the geopressured zone.

5. Sampling of geopressured wells

We were unable to find a suitable geopressured gas well to test the sampler in. Because of its relatively large diameter (2.25″) the sampler cannot be used in a well that has production tubing inside the casing. Practically, this means that only a newly-drilled well may be sampled, before the production tubing is installed. Unfortunately, there is very little drilling activity at this time.

We approached four companies about sampling their gas wells. In each case, these terms were offered:

(1) LBL will supply the sampler, an operator for the sampler, and complete chemical analysis of the fluids obtained, and cover all costs associated with these activities.

(2) The company will supply the wire-line rig and crew, and engineering services needed to operate the well, and cover all associated costs.

(3) The company will assume all risk for damage to the well. LBL and GRI will assume all risk for loss of the sampler.

(4) The detailed test plan will be worked out by the company and LBL jointly, and will be subject to approval by GRI.

(5) All data obtained by LBL will be available to the company.

(6) This data will be interpreted by LBL and the company jointly, and scientifically interesting results will be published. Such publications will be co-authored by LBL and the company's personnel.

The inducement offered was the opportunity to have their wells sampled with the best tool available for that purpose, and to have the most thorough analysis available performed on the fluids obtained, free of charge.

One company did not respond. Another company declined our offer, citing the large diameter of the tool. A third company was drilling a deep gas well, but also declined. Their main concern was that every downhole test carries with it some risk of damaging the well. Because they saw no necessity for sampling their well, they chose not to take the risk.

The most positive response was received from the Aminoil USA. They expected to drill an experimental, deep gas well in Texas in mid-1983, and agreed in principle to allow us to test our sampler in this well. Unfortunately, this well was not drilled.

We have a standing invitation from Aminoil USA's office in Santa Rosa, California to use the sampler in additional wells at The Geysers. People associated with the Department of Energy's Continental Scientific Drilling Program

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in the bottom hole sample also would be lower than in well-head samples.

have expressed an interest in using the sampler in deep, hot research holes.

6. Evaluation of the JAYCOR computer program

GRI suggested that we assist the Institute of Gas Technology (IGT) in finishing up work on the JAYCOR computer program. We received from IGT copies of all existing documentation, IGT's report about the program, a listing, and a tape of the code itself (Schreiber and Osif, 1983). We also reviewed literature relevant to the chemical models in the program, and studied the code.

The JAYCOR program was not specifically written to model brine or rock-water interactions. Rather, it is a program that can be used to model heterogeneous chemical equilibrium problems in general. The phases may be defined as brine, gas, minerals, etc., and it includes the "phase models" needed to model them. In particular, the brine model is based on Pitzer's theory of electrolyte solutions, which is potentially the best available for this kind of work. Therefore, the JAYCOR program may be used to calculate the chemical equilibrium relations between brine, gas and rocks, but it has not been optimized for this application.

The extreme generality of the JAYCOR program is a practical handicap. Making the program so general greatly increased the complexity and bulk of its code. For example, an intermediate, "working" data base is constructed when calculating a given problem, and a given chemical species is referred to by different numerical labels in different places. This complexity is compounded by a very idiosyncratic style of coding; for example, the same variable name often is used to represent different quantities in different places. The problem is compounded by a nearly total lack of comment statements throughout most of the code.

There are a few bugs in the code, some of them potentially serious. It is impossible to figure out the code enough to modify or debug it. The documentation includes a "user's manual" and a fair description of the physical and chemical models incorporated in the program, but says little about the actual code; a glossary of variables is omitted.

The program requires that pressure and temperature be specified, and it will then calculate the equilibrium distribution of species. As it happens, the most important modeling problem associated with the system brine, oil, and gas is that of calculating adiabatic phase separation. In setting up such a problem, one would like to specify mole numbers, enthalpy and pressure, and have the program calculate the temperature, what phases are present, and the chemical equilibrium within and between them. The JAYCOR program is incapable of this. Rather, one would need to calculate the temperature and phase separation using some other program, and then feed results into the JAYCOR program to calculate the detailed chemical equilibrium state.

As the program is written, *all* chemical reactions to be considered in calculating the chemical equilibrium must explicitly be input whenever a problem is run. In practice, this would mean thirty or more input records per problem.

The quality of the the brine and gas phase models, and the program's ability actually to calculate gas/brine equilibria appear adequate. However, the data base is incomplete, and partially out of date. In particular, many of the parameters required to apply Pitzer's model were of necessity estimated,

while good, empirically derived values have been published since. A related problem is that the data base contains data from different sources, many of which are not identified. It is highly probable that the data base contains incompatible data. The data base includes only a few hydrocarbons, too few meaningfully to model a liquid hydrocarbon phase.

We started a review of the data base, and a review of needed data that is available in the literature. This review has emphasised the things that most need extension or improvement. These are:

(1) The parameters needed to apply Pitzer's model of electrolyte solutions,

(2) The solubility in brines of hydrocarbons other than methane,

(3) The solubilities in brine of important scale-forming mineral phases, and

(4) The properties of high pressure gaseous mixtures of methane, water and carbon dioxide.

We have also outlined what would be necessary to calculate adiabatic phase separation, and have done some rudimentary code development in this direction. In this we have have been greatly assisted by Professor Pitzer, who gave us copies of his students' research codes, which contain the most complete and most accurate thermodynamic model that exists of the system $NaCl - H_2O$ (Pitzer *et al.*, 1983). The information gathered is useful, and will be applied to ongoing, DOE funded projects related to deep gas reservoirs.

7. Preparation of an instruction manual

An instruction manual for the sampler and sample extraction system has been prepared and printed as a separate document (Weres *et al.*, 1984). This document describes the assembly, operation, and field maintenance procedures for the sampler and the sample extraction system. It is also contains a detailed description of how the sampler operates. The operating instructions for the sample extraction system have been tested in the laboratory, and modified as needed.

TECHNICAL PROBLEM AREAS ENCOUNTERED

Sampler design. Because of its large diameter, the sampler cannot be run down production tubing. We do not consider this a practical limitation, because a down-hole sample taken inside the production tubing would be of little interest. Fluid can enter the tubing only at the very bottom; therefore, a well-head sample should be essentially identical to a bottom-hole sample. Also, a well with production tubing in it will usually be beyond the stage of testing and evaluation.

Development of the sample extraction system. Devising a way to determine the pressure inside the sampler before depressurizing it was the most difficult problem encountered in designing the sample extraction system. It is impossible actually to measure the pressure inside the unopened sampler; instead, we decided to connect the pressure transducer between the piercing valve and the needle valve in the sample extraction system. This would allow the pressure to be determined after the rupture disk has been pierced, but before the sampler has been depressurized. Knowing the pressure at this stage would enable better control of the sample extraction operation; for example, the pressure reading would indicate if the rupture disc has been ruptured, and give an idea of the gas collection volume required.

Unexpectedly low pressure would indicate sampler leakage.

A pressure transducer system has been designed, but not yet fabricated; temporarily, the pressure transducer port in the body of the piercing valve is closed with a plug made of MP35N. A commercially available pressure transducer of stainless steel would be used. This cannot be exposed to the brine at high pressure. Instead, Krytox oil would be used to transmit the pressure from the brine to the transducer. This would eliminate the need for special and very costly fabrication of the transducer from MP35N.

Sinker bars. A common arrangement is to have "screw-on" sinker bars, installed between the tool proper and the cable head. In this case, the electrical connection between the cable and the tool must go through a conductor that runs the length of the sinker bar. This introduces two additional electrical connections into the circuit, which usually are banana plugs. This arrangement was rejected from the start, because the presence of additional electrical connectors increases the risk of premature closure of the sampler; it will close prematurely if there is even a brief interruption in the electric current through the cable.

Another common arrangement is to have the sinker bars suspended underneath the tool; this arrangement was considered at one time, but ultimately rejected. Suspending the sinker bars underneath the tool might interfere with fluid flow into the sampler, or may contaminate the brine sample. Also, the connection between the sinker bars and the sampler would have constituted a weak point in the tool string.

The third alternative was the one ultimately selected: a slotted sinker bar above the sampler and attached to it.

With a 2.25 inch diameter, this sampler is unusually "fat" for a well logging tool. Originally, a ball-and-socket joint was envisaged between sampler and sinker bar. The intention was to allow the assembly to flex somewhat, thereby allowing it to "squeeze" past bends in the casing. A flexible joint would have been the weakest point in the assembly, and would have complicated design and fabrication of the sinker bar.

In fact, a flexible joint proved unnecessary. Within limits, the length of the assembly is more important than its diameter. Because the diameter of this assembly is 2.25 inches, it is substantially shorter than would be an assembly of equal weight and smaller diameter. We believe the sampler and sinker bar may safely be used in casing of internal diameter 5.5 inches or greater.

CONCLUSIONS

At a water flow speed of only 2 ft/sec, 90% of the fluid in the sampler is replaced by ambient fluid within three minutes. Clearly, fluid exchange rate poses no significant limitation on the use of the sampler. A few hundred gallons of brine production with the sampler in place will assure a sample that is representative of the fluid in the formation. The rate and duration of fluid flow during the test may be determined by reservoir engineering criteria. They are not practically restricted by the fluid exchange characteristics of the sampler.

The ceramic filters noticeably retard fluid exchange, but not enough to matter in practice. Therefore, the choice between wire filters and ceramic

filters may be based on other criteria. If the sampler is operated without the lower filter, solid material in the water is readily entrained. Therefore, a filter is necessary at the bottom. A filter is also needed at the top to keep material from falling down into the sampler.

In a two phase flow, the amount of gas in the sample collected is always much less that proportional to the amount of gas in the flow. Therefore, the sampler cannot not be relied on to sample a two phase flow properly.

Ideally, the well to be sampled should be cased, but without tubing. If the casing is perforated at one depth only, a down-hole sample probably will not differ from a well-head sample. If the casing is perforated at more than one depth, fluids of different composition probably will mix in the wellbore. This is the situation most likely to produce a need for downhole sampling.

In our discussions with the oil companies we found they were most interested in sampling wells that were still being drilled, and therefore uncased. A downhole sample obtained under these conditions would give the most valuable information of all: the amount of gas to be had from the lowest horizon penetrated. Putting the sampler into an uncased hole carries with it a greater risk of losing the sampler, but is in principle not much different from sampling a completed well. However, drilling mud in the wellbore would probably clog-up the sampler and make it inoperable. Ideally, the wellbore should be cleaned out before sampling; this may be an impractical requirement in many cases.

RECOMMENDATIONS

If possible, samples should be taken under conditions where most or all of the gas remains in solution. This means a low flow rate, after the downhole pressure has built up to near its static value. Otherwise, free gas bubbles will be excluded from the sample, and an incorrect (too low) gas:water ratio will be determined.

If sand accumulates about the lower filter, it should be possible to clean it out before taking the sample. After lowering the sampler to the depth desired, pull it up about 300 feet as rapidly as possible, and then lower it again. This should clean deposits off the lower filter, and refill the sampler with ambient fluid. This procedure may work even if the sampler has been lowered through drilling mud; let the well flow long enough to get at least a few hundred feet of clean brine below the mud. This should be done after the sampler has reached the bottom of the well; the heavier mud will quickly contaminate the brine beneath it.

When sampling a newly drilled well, be aware of materials that may have gone into it during drilling; e.g. barium sulfate, diesel oil, etc. If contamination of the sample is suspected, also collect and analyze a sample of the drilling mud for comparison.

A suitable well to test the sampler in should be found, and an appropriate field test conducted. The main problem that prevented us from finding a well during this contract year was that very little drilling activity was going on. We are confident of finding a well once drilling resumes; if we make the availability of this unique tool known to the industry, someone is bound to see a need for it in his well.

This sampler has unique capabilities that make it applicable to many practical and scientific problems outside the province of geopressured gas. GRI should seriously consider making the sampler available for use in research holes, like those planned under the auspices of DOE's continental scientific drilling program.

Several modifications to the sampler should be considered to extend its range of application.

(a) The sampler could be used to measure the temperature by using the electromagnetic coil as a resistance thermometer. The sampler's power supply delivers a specified current by varying the voltage. There are digital readouts of both voltage and current on the power supply; therefore, the resistance of the coil plus cable may easily be calculated. The coil of the magnet has higher electrical resistance than the cable. The resistance of the cable may be estimated and subtracted from the total resistance to obtain the resistance of the coil. The resistance of the coil may then be used to estimate the temperature. This calculation requires that the resistance of the coil and cable be known as a function of temperature. Because temperature varies with depth, the resistance of the cable will also vary with depth; this needs to be taken into account. Ideally, one would record resistance as a function of depth, and then use a small computer program to convert this to temperature as a function of depth.

(b) The maximum operating temperature of the sampler could be increased substantially. The metal is strong enough and sufficiently resistant to corrosion to allow this.

The practical temperature limit of the sampler is set by its nonmetallic components. These are: the Viton O-rings that serve as static seals, the insulation of the electromagnet's coil, the fluorocarbon oil (Krytox) that protects the electrical subassembly, and the fluorocarbon grease that lubricates the sampler. Replacing the present electromagnetic coil by one with ceramic insulation and carefully selecting the O-ring material would increase the maximum operating temperature. We believe that simple improvements like this would enable a maximum operating temperature in the range 600-700°F to be achieved. Systematic laboratory testing of different O-ring materials would be required to accomplish this.

Going beyond 700°F probably would require a completely different sampler, one with provisions for limiting the temperature of critical components.

(c) In sampling an uncased well, it would be desirable to place a packer below the sampler. This would allow to be taken a sample produced at a precisely known depth. Such packers are widely used and available; a well logging engineer might know how to combine this sampler with an appropriate, existing packer.

In the interest of pollution control, geopressured gas well brines should routinely be analyzed for organic acid anions. The total concentration of organic anions may routinely be determined using the differential titration procedure described in Appendix C. If necessary, the individual acids may be determined by gas chromatography of propyl esters prepared from the brine. An ion chromatographic method should be developed for this

purpose, because it would probably be simpler and cheaper for routine use.

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Appendix A - List of companies supplying services

The following companies supplied specialty items or provided special services to LBL in performance of this work.

Briskeat Co.
P.O. Box 628
Columbus, OH 43216
(614)294-3376

Custom designed electric heating mantle for sampler.

Chalet Tool Co.
2406 Eagle Avenue
Alameda, CA 94501
(415)522-8646

Machining of high pressure valve bodies for sample extraction system.

ESCO
1280 65th St.
Emeryville, CA 94608
(415)654-2732

17-4 PH stainless steel bar, 2.25″ O.D., for cable head and sinker bars.

G.M. Cooke & Associates
935 Pardee Street
Berkeley, CA 94710
(415)845-5110

Gas flow meter for flow test machine. Fischer-Porter, Model FP10A3555A, FP 1/2-21-G-10 tube, 1/2-GNSVT-45 float (brass).

KOR Isotopes
56 Rogers Street
Cambridge, MA 02142
(800)343-7743

Fully deuterated organic compounds used as internal standards in organic chemical analysis of fluids: acetic acid, benzoic acid, butyric acid, naphthalene, n-octane, phenol, pyridine, and toluene.

McMaster-Carr
9601 John Street
Sante Fe Springs, CA

Hand winches for crane used with flow test machine.

Northwest Dichronite
1954 Middlefield Way
Mountain View, CA 94043
(415)967-6940

Dichroniting of high pressure valve bodies.

Plastic Center
1170 Terrabella Avenue

Mountain View, CA
(415)969-9280

Lucite tubing, 5″ I.D.; transparent test chamber for flow test machine.

Sierra Controls
P.O. Box 762
Orinda, CA 94563
(415)254-2740

Rental of ultrasonic water flow meter for flow test machine. Dynasonics, Model UFT-603 Survey Flowmeter.

Terrell's Plastics
3618 Broadway
Sacramento, CA

Lucite rod, 2.25″ O.D., for transparent duplicates of sampler parts.

Tony's Machine & Gundrilling
2020 Walsh Avenue
Santa Clara, CA 95050
(408)727-1220

Gun-drilling of lucite mock-up of sampler's pressure vessel.

Appendix B - List of LBL drawings

Date	Drawing Number	Drwg. type	Category Code	Drawing title
1/17/83	20D6103	D	47-30-01	17-4 PH Stainless cablehead
2/1/83	20D6113	D	47-30-01	17-4 PH Stainless sinker bars
2/6/83	20D6123A	D	47-30-01	Sinker bar end-cap (stinger)
3/23/83	20D6312	D	47-30-01	Sinker bar line retainer
6/24/83	20D7094	A	47-30-01	Centralizer - ass'y & detail
12/7/82	20D6074	L	22-32-04	Flow test rig - layout
2/7/83	20D6084	L	22-32-04	Suction & discharge lines
1/17/83	20D6096	L	22-32-04	General layout & probe crane
1/13/83	20D8003		22-32-04	Crane, support end, layout
1/13/83	20D8013	L	22-32-04	Crane, sheave end, layout
6/24/83	20D6134	A	47-30-01	Extraction system valve bodies
6/14/83	20D7034	A,L	22-32-05	Chemistry stand, pictorial
	20D7043	D	22-32-05	Lattice board
6/15/83	20D7053	SA	22-32-05	Lattice frame
6/15/83	20D7063	SA	22-32-05	Chemistry stand - base
6/15/83	20D7073	D	22-32-05	Cover box
6/21/83	20D7083	L	22-32-05	Fluids receiver

Appendix C - Procedures for organic analysis

Here we describe analytical procedures for determining the organic compounds in geopressured brine and gas. They were developed in connection with D.O.E. supported work on the chemical origin of oil and gas, and used in the analyses reported in Section 4 of this report.

These analytical instruments are used:

(1) *Mass spectrometer* (MS); Consolidated Engineering Corporation (CEC), Type 21-103A; upgraded in various ways at LBL. The MS is used for quantitative analysis of major components in the gas.

(2) *Capillary gas chromatograph* (GC); Hewlett-Packard Model 5880A, equipped with flame ionization and electron capture detectors. The FID and a bonded polysilicone column (J&W Scientific, Type DB, 0.32 mm I.D.) are used routinely. The GC is used for quantitative determination of known organic compounds.

(3) *Gas chromatograph - mass spectrometer* (GC-MS); Finnigan Model 4023. This instrument consists of a Finnigan Model 9610 Capillary Gas Chromatograph coupled to a Finnigan Model 4000 Quadropole Mass Spectrometer. The GC is equipped with a Carle-Erba injection port, and is capable of accepting either gas or liquid samples. Mass spectra are identified and recorded by a Nova-3 computer running under the Incos 3.1 data system, and equipped with hard disk mass storage. A DB-5 bonded quartz capillary column is used. The GC-MS is used to identify specific organic compounds, and to determine the ratios of natural compounds to the corresponding deuterated standards.

Descriptions of specific analytic procedures follow.

Major components of the gas. Cool gas bottle to room temperature or lower to reduce the concentration of water vapor. Inject directly into mass spectrometer.

Heavier hydrocarbons in the gas. Collect the gas in a metal bottle. In the laboratory, connect the gas bottle to a vacuum line. Also connect a vacuum bulb that contains about 3 ml of dichloromethane (Burdick and Jackson, "Distilled in glass") to which a small, known amount of fully deuterated benzene has been added. Cool the gas bottle and vacuum bulb with liquid nitrogen. Connect the vacuum pump, and draw off air (from the bulb), methane, and ethane; heavier gases and vapors will remain frozen or adsorbed in the bottle. Disconnect the vacuum pump. Allow the dichloromethane to warm to room temperature, while the gas bottle remains in liquid nitrogen. Allow several hours for the dichloromethane and d-6 benzene to diffuse, as vapor, into the cold gas bottle, where they condense. Valve off the gas bottle, warm it to above room temperature, and allow its contents to equilibrate. Connect it through the vacuum line to a liquid nitrogen cooled trap. Allow gases and solvent to diffuse from sample bottle to trap, where they condense. Open the trap to the atmosphere, and allow it to warm to room temperature. Carbon dioxide, ethane, propane, and butane will escape. The dichloromethane will remain. Dissolved in it will be the d-6 benzene and all liquid hydrocarbons originally in the gas. Analyze this liquid by GC-MS and GC. Benzene and d-6 benzene will not be resolved. Compare total response at mass 78 to mass 84 to determine the ratio of natural benzene to d-6 benzene in the benzene peak. Estimate other hydrocarbons relative to benzene by comparing integrated peak areas in GC data.

Carboxylic acids in brine. The total concentration of organic acids is determined by titration. In a separate procedure, the acids are converted to propyl esters by reaction with n-propanol catalyzed by boron trifluoride. The 15% solution of BF_3 in n-propanol is available commercially (Aldrich 15,682-5 or Kodak A10980). Fully deuterated organic acids are used as internal standards. The resulting propyl esters are analyzed by GC and GC-MS.

Refrigerate brine overnight or longer. Filter to remove precipitate formed. Pipette 20 ml of brine into a beaker, and dilute to about 40 ml with deionized water. Allow to warm to room temperature. Note initial pH. Titrate with 0.1N *HCl* to pH 3.0. Note the amount required. Strip-off CO_2 from acidified brine with nitrogen. Measure and record pH. Titrate back to initial pH with 0.1 N *NaOH*. Note amount required; it will be less than the amount of *HCl* needed in the first titration. The difference corresponds to the amount of bicarbonate in the brine. Continue titrating to pH 7. Note total amount of *NaOH* needed to go from pH 3 to 7. This corresponds to the total concentration of organic acids in the brine. If amount of acid is small, correct for amount of H^+ at pH 3.

PREPARE THE PROPYL ESTERS INSIDE A FUME HOOD. Prepare the propyl esters inside a fume hood. Set up 100-ml round bottom flask with single neck in an heating mantle. Pipette 10 ml brine into flask. Make brine alkaline with a few drops of 1N *NaOH*. Add small, known amounts of fully deuterated acetic acid, butyric acid, and benzoic acid. Evaporate brine to dryness by heating the flask gently while flushing it with nitrogen. Attach water cooled condenser to flask. Wearing gloves, pipette 10 ml of BF_3/ n-propanol solution into flask through the condenser. **CAUTION: TREAT THIS SOLUTION AS YOU WOULD CONCENTRATED HYDROFLUORIC ACID.** Allow to reflux gently for 20 minutes.

After 20 minutes, add 25 ml of water (or saturated sodium carbonate solution) through the condenser. Wait until fumes inside the apparatus have disappeared. Wearing gloves, remove flask from mantle and transfer contents to a separatory funnel. (In this and all other procedures, use separatory funnels with greaseless Teflon or equivalent stopcocks.) Add 25 ml nanograde hexane (Mallinckrodt 4159) to the flask, swirl around, transfer to separatory funnel. Close and shake funnel, allow phases to separate, discard aqueous phase. Wash hexane phase with 25 ml of water, separate and discard aqueous phase. Dewater hexane phase by filtering it through anhydrous sodium sulfate. Filtrate should be crystal clear.

Analyze dewatered hexane extract by GC-MS to identify propyl esters. By comparing integrated base peaks, determine ratio of natural form to fully deuterated form for acetic acid, butyric acid, and benzoic acid. Reanalyze extract by GC. Use integrated peak areas together with GC-MS data to estimate proportion of other organic acids. Use titration results to estimate absolute concentrations.

This reaction may also be catalyzed by hydrogen chloride. In this case, use a saturated solution of *HCl* in n-pronanol as the reagent, and allow two hours reaction time. All else as above.

Organic acids may also be analyzed as the methyl or butyl esters. Solutions of BF_3 in methanol are commercially available, and the procedure is exactly as described above. A solution of *HCl* in methanol may also be used. The methyl esters of acetic, propionic, and butyric acids cannot be determined by GC or GC-MS because they pass the column too quickly, and

are hidden by the solvent peak. Therefore, only acids C-5 and above may be determined as the methyl esters.

Butyl esters may be prepared by using a solution of *HCl* in n-butanol as the reagent, and are even easier to determine than the propyl esters. Unfortunately, n-butanol is more soluble in hexane than in water, and must be removed before chromatographic analysis. After the water is added to the flask, and its contents transferred to the separatory funnel, about ten (10) washings with water are required to remove most of the butanol. This makes the procedure extremely tedious and time-consuming. Otherwise, the procedure is exactly as with *HCl* in propanol.

Phenols. The phenols are converted to methylphenylethers and determined as such. To 100 ml brine add a small, known amount of fully deuterated phenol. Then add 20 ml 10N *NaOH*. A precipitate of calcium hydroxide will form. Remove this precipitate by filtration and/or centrifugation. Transfer 50 ml of the filtrate to a 125-ml glass stopped Erlenmeyer flask, add magnetic stir-bar. Inside a fume hood, set up an ice-bucket on top of a magnetic stirrer. Set up the flask inside the ice-bucket and initiate medium stirring. Allow the flask to cool. Wearing gloves, carefully pipette 3.5 ml of dimethyl sulfate into the flask. **CAUTION: DIMETHYL SULFATE IS A CARCINOGEN, AND DAMAGES SKIN, EYES, AND LUNGS.** Stop the flask, and leave it to react overnight, still stirring. Make sure the bucket and flask both are stable, so the neither will be overturned when the ice melts.

The solution should still be alkaline the next morning. If not, start over, using more *NaOH*. Transfer contents of flask to separatory funnel. Add 25 ml nanograde hexane to the flask, swirl, transfer to separatory funnel. Shake, separate, discard aqueous phase. Dewater hexane extract by filtering it through anhydrous sodium sulfate. Determine methylphenylethers by GC and GC-MS, as with propyl esters above.

Gas condensates. Accurately dilute to 1000 ppm in nanograde hexane or pentane. Identify compounds present by GC-MS. Determine their relative concentration by GC. This procedure is adequate for any "clean" hydrocarbon liquid of fairly simple composition.

Oil. Oil and other complex, "dirty" hydrocarbon liquids may require pretreatment. Fill a chromatographic column of approximately 25-ml volume with nanograde hexane. Pack column with Grade 1 neutral alumina. Carefully weigh about 0.2g of the sample, and dissolve in 100 ml nanograde hexane. Add small, known amounts of fully deuterated toluene, n-octane, and naphthalene. Pour this solution on to the column. After passing through the column, this fraction will contain the aliphatic hydrocarbons. Elute column with 100 ml dichloromethane. This fraction will contain the aromatic hydrocarbons. Finally, elute column with 100 ml methanol. This fraction will contain the polar compounds, if any. The asphaltenes will remain on the column. Dewater each of the three fractions by filtering over anhydrous sodium sulfate, and analyze by GC and GC-MS.

Liquid hydrocarbons washed out of the sampler and sample extraction system. After use, the sampler and sample extraction system are washed with an organic solvent to remove any organic liquids that may be adsorbed on solid surfaces. The solvent used should be either dichloromethane or 1,1,1-trichloroethane. It should contain small, known amounts of fully deuterated n-octane, toluene, and naphthalene.

After washing the sampler and sample extraction system with it, filter the solvent through anhydrous sodium sulfate to dewater it. If the solvent appears to be clean and nearly colorless, analyze it directly by GC and GC-MS. Otherwise, remove asphaltenes by passing the solution through a column of neutral alumina, and then analyze it.

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