

IMPROVED METHOD FOR EXTRACTION AND QUANTIFICATION
OF HYDROCARBON CONTENT OF SPONGE CORE LINERS

by

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ABSTRACT

We report a technique to extract and accurately quantify the amount of oil in a sponge core liner. We have successfully tested this technique for crudes having a wide range (15 to 40) of API gravities.

The main advantages of sponge coring are that it is a comparatively inexpensive alternative to pressure core and operationally simpler. As the core is cut, it enters a half-inch thick polyurethane sponge liner inside the inner core barrel.

As the core is brought to the surface, expanding gases displace otherwise immobile oil which is then captured by the sponge liner. By adding the amount of oil captured in the sponge to the amount left in the core, one obtains more accurate values of oil saturation.

However, a major disadvantage of sponge coring had been the absence of a reliable technique to quantify the amount of oil retained by the sponge. Various techniques had been tried by various service companies, including solvent extraction, hydraulic press, and retorting. We observed problems with each of these techniques. These included incomplete extraction of oil, mistaking extracted sponge components for oil, and the inability to either completely separate or account for the amount of solvent remaining in the crude extracts.

We have found that Freon-11 (trichlorofluoromethane) is a good solvent for the extraction of crude oil from the sponge liner. Freon-11 is gentle on the polyurethane sponge, has good solvating power for all crude components, and its low boiling point allows easy removal of most of the solvent from the extracted crude oil. In this paper we describe the apparatus and procedures for extracting crude oil from sponge core.

INTRODUCTION

Sponge coring is a comparatively inexpensive alternative to pressure coring. It can save as much as 70 percent of the cost of cutting pressure core and of the subsequent analysis. In this technique, as the core is cut, it enters a half-inch thick polyurethane sponge liner inside the inner core barrel. As the core is brought to the surface, expanding gases displace otherwise immobile oil which is then captured by the sponge liner. By adding the amount of oil captured in the sponge to the amount left in the core, one obtains more accurate values of oil saturation.

This report details a new extraction and analytical technique for the quantification of the oil captured by the sponge liner.

PROBLEMS WITH SOME OTHER TECHNIQUES

A major disadvantage of sponge coring had been the absence of a reliable technique to quantify the amount of oil retained by the sponge. Various techniques were developed employing everything from solvent extraction, to mechanical extraction (hydraulic press), and retorting.

Some of the problems associated with these techniques have included incomplete extraction of oil, loss of light ends, mistaking extracted sponge components for oil, and the inability to completely separate or account for the amount of solvent remaining in crude extracts.

In 1985, several service companies were in the process of developing sponge core analysis techniques. Shell decided to conduct a blind test (Figure 1) of several of these techniques using synthetically prepared samples. Ideally, all points in Figure 1 should lie on the equal value lines. Instead, these data show considerable random and systematic error.

Except for some data reported by Company B (points denoted by squares), all these techniques used solvent extraction as one of the steps in their procedure. Shell felt that the problem was not in solvent extraction itself, but in the choice of a suitable solvent and a suitable analytical technique so Shell began a research program to identify such solvents and techniques.

SHELL TECHNIQUE

Selection of Extraction Solvent

The ideal solvent¹ for the extraction of crude oil from the sponge liner should have the following characteristics:

- a. gentle on the polyurethane sponge,
- b. good solvating power for all crude components including asphaltenes,
- c. a low boiling point to allow easy removal from the extracted crude oil.

The cycloalkanes, ethers, and Freons are three classes of solvents which have these characteristics. Since large volumes of the extraction solvent are required, safety is an important concern. The flammability of cycloalkanes and the potentially explosive peroxide formation of ethers precluded these two solvent classes from production-scale use. Since Freons are nonflammable and relatively safe, they are the solvent class of choice.

Of all the Freons considered, Freon-11 (trichlorofluoromethane, boiling point 23.8°C) was chosen as the extraction solvent because it most closely met the above criteria.

Initial Tests of Freon-11

As an initial test of the chemical compatibility of Freon-11 with polyurethane sponge, a clean sponge of known weight and dimensions was soaked in Freon-11 for several hours. Its dimensions did not change, even while submerged. No visual evidence of attack such as discoloration was observed either. This contrasts with the severalfold swelling of the sponge material when submerged in methylene chloride or toluene.

Gas chromatographic analysis of the Freon found few sponge components; those that were found were in the C_{15} - C_{17} and C_{25} - C_{28} range. This was probably due to a well-cured sponge and the brief exposure time of the sponge to crude and solvent in these initial experiments. Subsequent experiments showed

that the sponge components are highly variable but can be accurately quantified. This is discussed later in this report.

To test the solvating power of Freon-11, a viscous, high-asphaltene Ecuador crude was mixed with Freon-11. The crude dissolved immediately and showed no evidence of asphaltene flocculation or precipitation even after several hours. Table 1 shows a quantitative comparison of pentane versus Freon-11 precipitation of asphaltenes for three crudes.

These data illustrate that although some asphaltenes are precipitated by Freon-11, the amount is significantly less than what is precipitated by normal pentane. Since these asphaltenes can be about fifty percent more dense than the light fractions of crude, the volumetric percents of precipitate are only about two thirds the weight percents of precipitate listed in Table 1. Thus, for the purpose of quantifying the volume of oil in the sponge, this level of asphaltene precipitation is not considered significant.

A major consideration in the choice of Freon-11 was its low boiling point. It was hoped that a simple distillation would separate the Freon solvent from the extracted oil. In order to test the ease of Freon removal, known volumes of Wasson crude were injected into pieces of sponge. The sponge was then soaked in Freon-11 and squeezed several times. This was repeated several times with fresh Freon-11.

The resulting extract was then heated to just above room temperature and brought to a boil. As the extract became more concentrated, the pot temperature was adjusted in order to maintain a constant boiling rate. Eventually, neither a temperature increment nor vigorous stirring could generate more bubbles, and it was assumed that virtually all the solvent had been distilled off. This occurred at about 65°C. The volume of crude oil was recorded once it returned to room temperature.

The recovered volumes were close to the injected volumes. Chromatographic analysis of the extract revealed that some Freon-11 remained and that some loss of light hydrocarbons had occurred. In order to prevent loss of light ends, a more sophisticated method of extract processing and analysis was developed. This method leaves about 15 percent Freon-11 in the extract which is then quantified by gas chromatography. A complete description of this method is given later in this report.

DETAILS OF EXTRACTION APPARATUS AND PROCEDURE

When sponge core is manufactured, the sponge is foamed in place inside its aluminum liner. Because removal of the sponge from its liner is difficult and time consuming, the extraction Soxhlets (Figure 2) were designed to accommodate one foot sections of sponge still bonded to its aluminum liner. These Soxhlets have 1.5 liter solvent reservoirs, but we usually use 1 liter or less of solvent for extraction.

Because of Freon-11's low (23°C) boiling point, it was important to choose an efficient condenser. Leibeg, Friedrich, Graham, and Allihn condensers were tested. An oversized 5-bulb Allihn condenser proved to have the highest efficiency. The condenser was maintained at 3°C by passing a chilled ethylene glycol/water mixture through it.

In the usual operation of a Soxhlet extractor, solvent vapor is condensed by the chilled condenser and drips down over the center of the sample. Since the sponge core has a hollow-tube shape, the refluxed solvent would drip down the center of the cylinder without contacting the sponge.

To solve this problem, solvent dispersers² were designed to rest on the top of the sponge, catch the falling drops of solvent, and disperse them uniformly over the top of the sponge

tube. The first dispersers were filter-paper cones with vents cut out to allow rising solvent vapor to pass through to the condenser. However, these tended to get soggy and collapse with use.

The current dispersers are illustrated in Figures 3 and 4. The dimensions of the sponge core barrels they are designed to fit are given in Tables 2 and 3. The dispersers are made from sintered stainless steel (40 micron pore size) cut into a circle the same size as the sponge core. Vents are cut in the circle, and the center hub is raised $\frac{3}{8}$ inch above the rim to allow both gravity and wicking action to spread the solvent uniformly over the disperser.

The underside of the hub and spokes of the disperser is burnished to reduce its permeability in this region. The burnishing directs the solvent out to the rim of the disperser, which is not burnished and is in direct contact with the top rim of the sponge. In this way, the disperser distributed drops of condensed solvent out to its rim and onto the top of the sponge itself.

Water displaced from the sponge floats on top of the Freon-11 in the boiling pot. This aqueous phase is not miscible with the Freon-11. As the Freon-11 boils underneath the water, its vapors bubble up through the water and on to the condenser.

PARAMETERS FOR HEATING, COOLING, AND REFLUX RATE

Because of Freon-11's low boiling point, it is necessary to refrigerate the extraction system condenser coolant. Based on the total wattage of all the Soxhlet heating mantles, one can estimate the total cooling capacity required.

Two different sponge core liners are used; the large liner has a bulk volume of 1,580 cc per foot and a typical pore volume of

1350 cc per foot, while the small sponge core has a bulk volume of about 730 cc per foot and a typical pore volume of 620 cc per foot. Each heater received about 100 watts of power, corresponding to 341.3 Btu/hr, and a reflux rate of 1.33 liter/hr. Thus, during extraction, we typically reflux about one pore volume per hour through the large liner and about two pore volumes per hour through the small sponge liner.

FREON REMOVAL AND OIL QUANTIFICATION METHOD DEVELOPMENT

Having developed an extraction method, we needed a method³ for quantifying the extracted volume of oil. In this paper we describe a method consisting of removal of most of the Freon-11 by distillation and subsequent analysis of the concentrated solution for percent Freon-11 by gas chromatography (GC).

Nuclear Magnetic Resonance (NMR) is another analytical technique that can be used to analyze sponge core extracts⁴. We will not discuss NMR here except to say that it is much faster than GC, but it also requires more expensive equipment.

To remove most of the Freon-11, we used a distillation apparatus consisting of a 100 ml round bottom flask, a Vigreux fractional distillation column, and a condenser. These are configured as shown in Figure 5.

Initial tests of this apparatus were performed by distilling a mixture of Wasson crude oil and Freon-11. Samples of the crude-Freon mixture, receiver fluid, and gases escaping from the top of the condenser were analyzed by gas chromatography. Our objective was to determine if the Freon could be removed from the oil-Freon mixture without significant codistillation of light hydrocarbons or loss of hydrocarbons through the top of the condenser.

We discovered that much higher pot temperatures than anticipated (over 150°C) were necessary to distill 98 percent of the Freon. Under these conditions, codistillation of C₅-C₈ hydrocarbons and loss of hydrocarbons from the top of the condenser occurred. Thus, if a complete distillation was to be carried out, both a higher efficiency fractional distillation column and condenser would have to be found.

Because of these difficulties, a different approach was then taken. We chose to only partially distill the Freon-oil mixture. We found that if the distillation was carried out until the vapor temperature reached 65°C, roughly 85 percent of the Freon-11 could be removed without significant loss or codistillation of light hydrocarbons. The remaining Freon-11 could then be measured by gas chromatography, and its volume contribution could be subtracted from the mixture volume leaving the true oil volume.

In order to test the accuracy of both the extraction and analysis procedure, a number of simulated samples were prepared and analyzed. These samples consisted of one foot sections of sponge in their aluminum liner. As would be done on real field samples, the sponge was saturated with water, and a known volume of oil was injected into the sponge at random points and depths.

Samples of four oils of different API gravities and a range of saturations were prepared. Extraction of the sponge samples was performed using one liter of Freon-11 at a reflux rate of approximately 1.33 liters/hr, corresponding to roughly one pore volume per hour. The samples were extracted for 48 hours.

At the conclusion of the extraction, the water was separated from the Freon-oil mixture using a separatory funnel, and the remaining Freon-oil mixture was distilled. The best results were achieved using a 100 ml boiling flask and 15 centimeter

Vigreux column. A larger distillation apparatus resulted in an unacceptable level of solvent hold-up when distilling samples containing oil volumes less than 5 milliliters.

The oil-Freon mixture was distilled until the vapor temperature within the distillation apparatus reached 65°C at which time it was halted and the mixture was allowed to cool. The concentrated oil-Freon mixture was transferred to a calibrated glass tube and centrifuged. Centrifugation was necessary to separate both particulates as well as a gelatinous sponge material from the Freon-oil mixture.

A sample of the oil-Freon phase was then taken, and the residual Freon concentration was determined by gas chromatography. The total volume minus the residual Freon and extracted sponge material volumes yields the volume of oil extracted.

The results of these tests are illustrated in Figures 6-9. These figures illustrate good agreement between the injected and measured oil volumes. The inner set of dashed lines on the plots represents the error (95 percent confidence level) in the slope of the equation defining the best fit line. The outer set of dashed lines represents the error (95 percent confidence level) limits for the predicted oil volume.

True boiling point gas chromatography was performed on the original oil and the distilled oil mixture. The resulting volatility distribution is presented in Figure 10. These data demonstrate that some sponge components in the C_{14} - C_{17} and C_{24} - C_{30} range are extracted along with the oil and are not removed by centrifugation. However, the contribution of these components to the oil volume is negligible since good agreement between the injected and measured oil volume for the four oils was achieved.

This method has been applied to sponge samples from the Wasson field in West Texas. The only difference observed between the simulated and real samples was that significantly more sponge material was extracted in the field samples. This may be a result of incomplete polymerization of the field-prepared sponge core liners or chemical degradation of the sponge due to exposure to hydrogen sulfide and elevated temperatures during the coring procedure.

The amount of extracted sponge material was highly variable, often differing significantly between contiguous samples. The gelatinous material was easily separated from the distilled oil-Freon mixture by the addition of aqueous base and centrifugation. The addition of base also serves to "lift" the oil away from the precipitated polymer allowing simple volume measurements.

CONCLUSIONS

Sponge core has been taken in West Texas (Wasson) and in California (Ventura). In Wasson the formation water salinities are high and water flooding is done with fresh water. Therefore, the post flood salinities are not well known, and sponge core is taken to determine oil saturations and calibrate logs. Similarly, in Ventura sponge core is taken after carbon dioxide flooding because logs alone cannot be used to distinguish between carbon dioxide and oil. Where formation water composition and resistivity are well known and where reliable log data are available, we have found excellent agreement between sponge core analysis and well log calculations of oil saturations. To date, over 3000 feet of sponge core samples have been successfully analyzed with this method.

1. DiFoggio, R., Ellington, W. E., and Dangayach, K. C. B., Method for Determining the Amount of Oil in Sponge Core, U.S. Patent 4,787,983.
2. DiFoggio, R., Solvent Dispenser for Removing Oil from Sponge Core, U.S. Patent 4,771,634.
3. Ellington, W. E. and Calkin, C. L., Method for Analyzing Solvent Extracted Sponge Core, U.S. Patent 4,785,661.
4. Vinegar, H. J., DiFoggio, R., and Tutunjian, P. N., Analytical Methods and Apparatus for Measuring the Oil Content of Sponge Core, U.S. Patent 4,866,983.

Appendix A

QUANTIFICATION OF OIL IN FREON-11 EXTRACTS OF SPONGE CORE LINERS

Scope

This method employs distillation and gas chromatography to quantify the oil in Freon-11 extracts of sponge core liners.

Method Summary

The extract from sponge core liners forms an immiscible, two-phase system consisting of water and Freon/oil. The Freon/oil phase is isolated from the water using a separatory funnel. Freon is then partially removed by distillation, leaving a concentrated oil/Freon solution that is measured volumetrically. The residual Freon volume is then determined by gas chromatography and subtracted from the Freon/oil volume to determine the volume of oil extracted.

Interferences

- a. Chromatographic: periodic replacement of the GC guard column is necessary since oil components will eventually elute and interfere with Freon peak quantification.
- b. Sponge Residue: the extraction of sponge material often necessitates the addition of a potassium hydroxide solution. Addition of the solution causes the sponge material to precipitate and leaves a clear meniscus at the Freon/oil-sponge interface.

Apparatus

- a. Gas Chromatograph: Shimadzu Model GC8A or equivalent, equipped with a thermal conductivity detector.
- b. Guard Column: 6 in. x 1/8 in. ID packed with 80/100 mesh Porapak Q.
- c. GC Analytical Column: 8 ft x 1/8 in. stainless steel column packed with 80/100 mesh Porapak Q.
- d. Integrator: Hewlett Packard 3390A or equivalent.
- e. Syringe: 5 μ l
- f. Separatory Funnel: 2 liter
- g. Flasks: round-bottom 100cc boiling flask with three necks on flask
 1. ground 14/20 joint for Vigreux column
 2. ground 10/30 joint for thermometer
 3. 1/4 in. glass tubing attachment with a stopcock for attaching 1/4 in. Viton tubing.
- h. Recirculating Bath: able to maintain a temperature of -5°C .
- i. Boiling chips: small size
- j. Cotton: nonhydrophobic, extracted with chloroform/methanol

- k. Culture tubes with caps: 20 ml volume
- l. Vigreux reflux column (20 cm) with 14/20 joint
- m. Condenser head with side arm
- n. Column condenser
- o. Viton tubing: 1/4 in. ID
- p. Heating mantles for 100cc round-bottom flasks
- q. Rheostat
- r. Power strip
- s. One milliliter Eppendorf pipette
- t. Disposable pipettes
- u. Test tube rack

Reagents

- a. Acetone
- b. Chloroform
- c. Methanol
- d. 5N aqueous potassium hydroxide
- e. Ethylene glycol
- f. Freon-11 (trichlorofluoromethane)

Procedure

Concentration of Oil in Sponge Core Extracts

A recirculating bath is used to maintain a temperature of -5°C for the distillation condensers. Turn on the bath and allow it to reach -5°C . Set up the separatory funnel at a height that will allow flow from it to a 100 ml three-neck round-bottom flask via a length of Viton tubing. To prevent particulate matter from reaching the distillation flask, insert a plug of glass wool in the Viton tubing being careful not to pack the wool so tightly as to hinder flow. Pour sponge core extract into separatory funnel. Let stand for 10 minutes. Add 4 small boiling chips to the 100 ml three-neck round-bottom boiling flask and record weight. Insert the thermometer into the

thermometer well of the boiling flask. Connect the 100 ml receiver flask to side arm of condenser, place the boiling flask in the heating mantle, and attach the Vigreux column. Open the stopcocks and fill the flask 2/3 full, turn on the power to the rheostat, power strip, and heating mantles. Add Freon/oil phase to boiling flask and remove the distilled Freon captured in the receiver flask as necessary. After the last of the Freon/oil solution is added to the boiling flask, the temperature of the flask will begin to rise. Remove the flask from the heating mantle when the vapor temperature reaches 65°C. Allow the boiling flask to cool down while still attached to the Vigreux column, then remove from the system.

Phase Separation of Sponge Material and Freon/Oil

After the boiling flask has cooled down, pour the contents into a 20 ml culture tube. Weigh the boiling flask and subtract the tare weight to determine the residue. Add 2 ml of distilled water to the culture tube containing the extract; spin the tube in a centrifuge at 1000 rpm for 10 minutes. If no phase separation is achieved, add 2 drops of 5N potassium hydroxide which should precipitate any sponge material.

Determination of Freon/Oil Volume

Using a one milliliter Eppendorf pipette, prepare a volume per millimeter calibration for the 20 ml culture tubes. Serially add 1 ml volumes to the tube marking each point of the tube. This calibration will be used to determine the volume of the Freon/oil phase in the sample tubes.

Determination of Residual Freon

a. Preparation of Calibration Standards

Oil-Freon standards prepared on a volume-to-volume

basis are required. However, because of the volatility of Freon, it is more accurate to prepare them on a weight-to-weight basis and then convert them to volume-to-volume basis. This is done by injecting a known weight of Freon into a vial sealed with a mininert valve containing the known weight of oil. Conversion to a volume-to-volume ratio is done by dividing by the densities of the Freon and oil. The respective component volumes can then be calculated for a volume-to-volume standard. See calculation section for an example calculation. Standards have been found to be stable for approximately two weeks if care is taken to keep the mininert valve closed when the standard is not being used.

b. Gas Chromatograph Operating Conditions

Oven Temperature	220°C
Detector/Injector Temperature	250°C
Thermal Conductivity Detector Current	120 MA
Injection Volume	3 µl
Carrier Gas	Helium
Flow Rate	35 cc/min

c. GC Calibration

Inject 3 µl of the Freon/oil standard into the gas chromatograph and determine the retention time and response factor for Freon. Freon standards covering a concentration range of 2 percent to 25 percent volume to volume should be analyzed and the data used to construct a calibration curve. Clean the syringe after each injection by flushing first with chloroform, next with acetone, and then blowing the syringe barrel and plunger dry with air.

Residual Freon Determination

With a 5 μ l syringe, withdraw 3 μ l of the concentrated Freon/oil phase. Inject the sample into the gas chromatograph; measure peak area for Freon. Determine concentration in the sample from previously constructed calibration curve.

Calculations

a. Amount of oil extracted

Volume of oil = Volume of conc Freon/oil - Volume of residual Freon

b. Weight/weight conversion to volume/volume

Determine the density of the oil, e.g., .85 density.

Determine the density of the Freon, e.g., 1.50 density.

Example: 26% wt/wt std. conversion to 16.7% vol/vol std.
wt/wt

Freon-11	26 g/1.5 g/ml = 17.40 ml
oil	74 g/0.85g/ml = 87.06 ml
total volume	104.46 ml
vol/vol Freon 11 (17.4 ml/104.5 ml) * 100 = 16.7 %	

Table 1

COMPARISON OF PENTANE AND FREON-11 ASPHALTENE PRECIPITATION
FOR SOME CRUDES

Crude	API Gravity	Weight Percent of Asphaltenes Precipitated Normal Pentane	Freon-11
North Belridge	28.6	.35	.17
Wasson	34.5	1.08	.09
Beta	15.2	12.58	3.55

Table 2

DOWDCO SPONGE CORE DIMENSIONS

Outer/Inner Diameters	Small Barrels	Large Barrels
OD of Aluminum Liner	3.56 in.	4.81 in.
ID of Aluminum Liner (= OD of Sponge Tube)	3.31	4.56
ID of Sponge Tube	2.50	3.25
Sponge Wall Thickness	.41	.66

Table 3

DIMENSIONS OF DISPERSER PLATES

	Small	Large
Rim Outer Diameter	3.25 in.	4.50 in.
Rim Inner Diameter	2.50	3.38
Rim Thickness	.38	.56
Hub Diameter	1.19	1.50

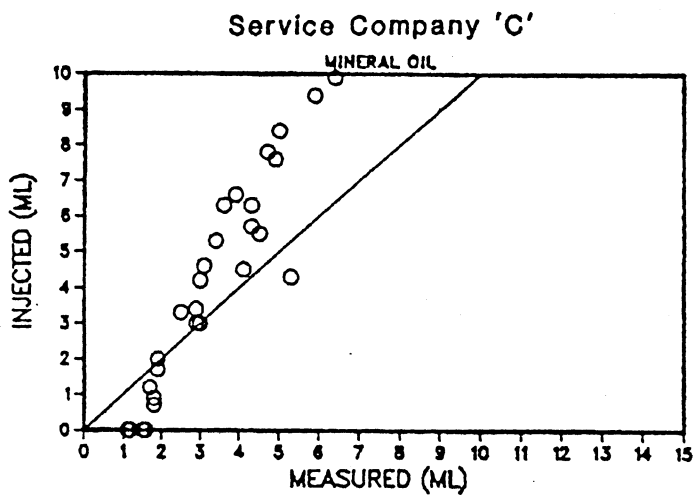
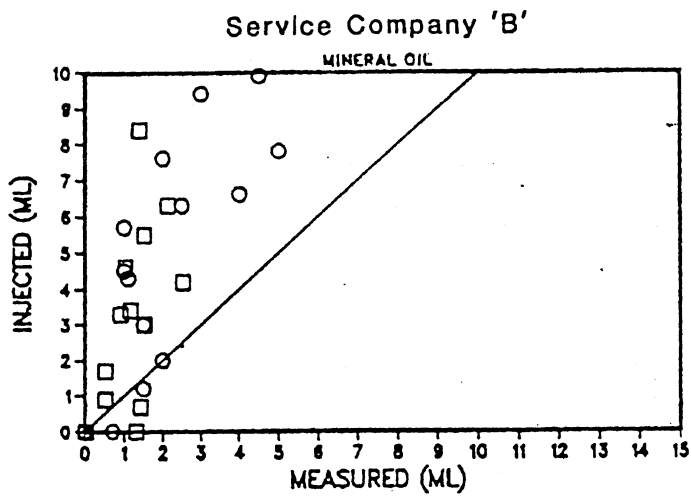
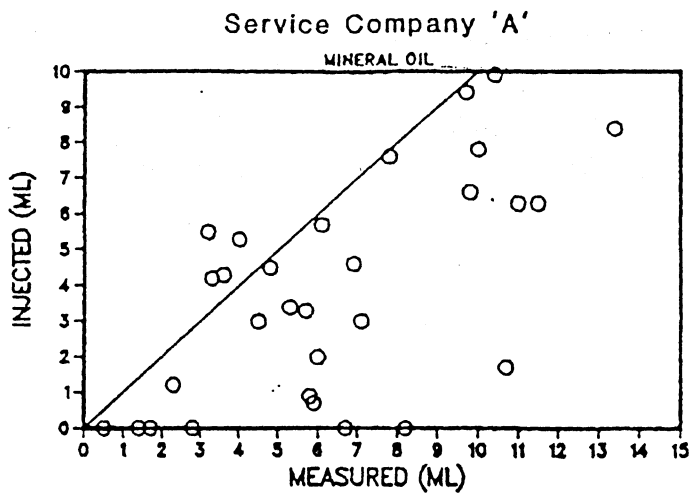


Fig. 1 - A comparison of sponge core oil volumes measured by different service companies in 1985. Notice that very few of the points fall on or near the ideal equal-value line.

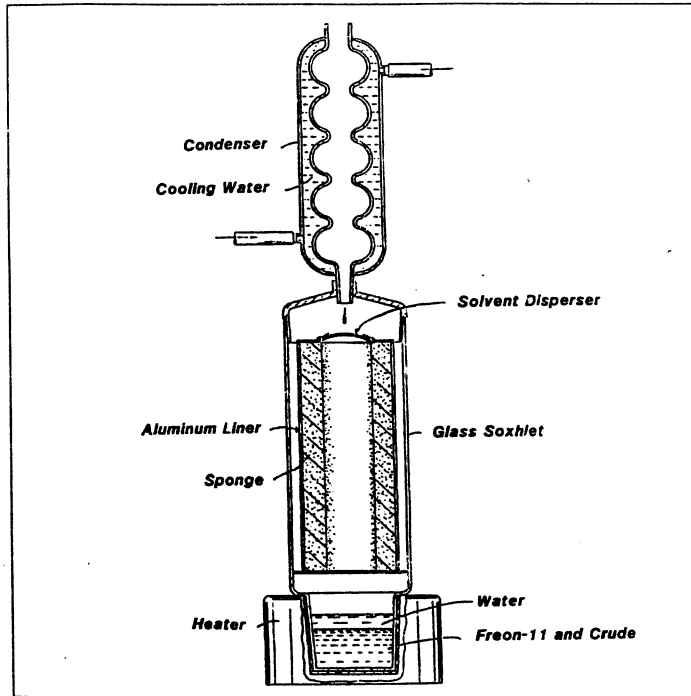


Fig. 2 - A cross-sectional view of the large glass Soxhlet into which one can place one foot of sponge core including its aluminum barrel.

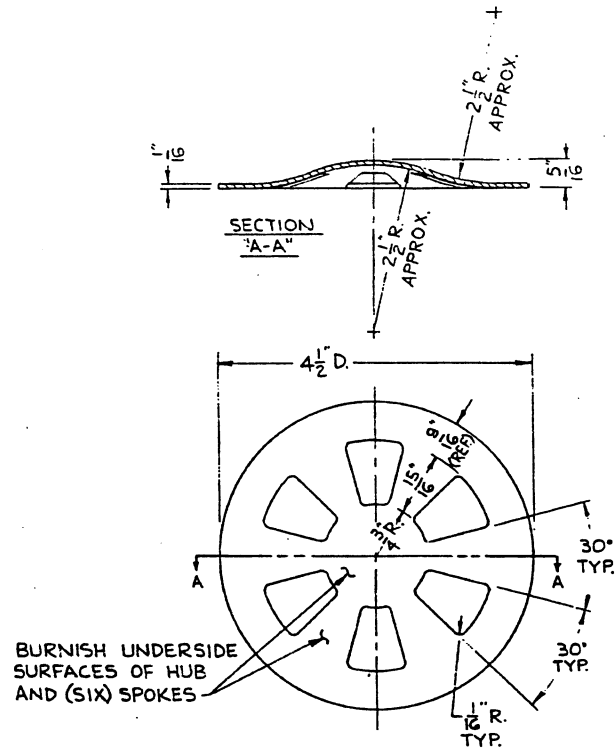


Fig. 3 - Cross-sectional and top view of the large solvent disperser that is used for 4.8-inch diameter sponge core barrels.

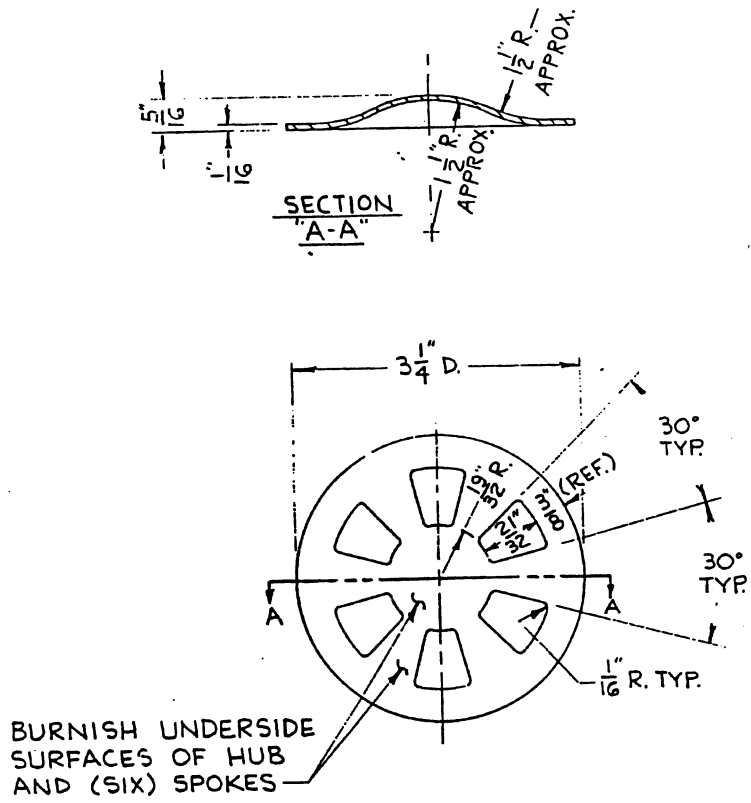


Fig. 4 - Cross-sectional and top view of the small solvent disperser that is used for 3.6-inch diameter sponge core barrels.

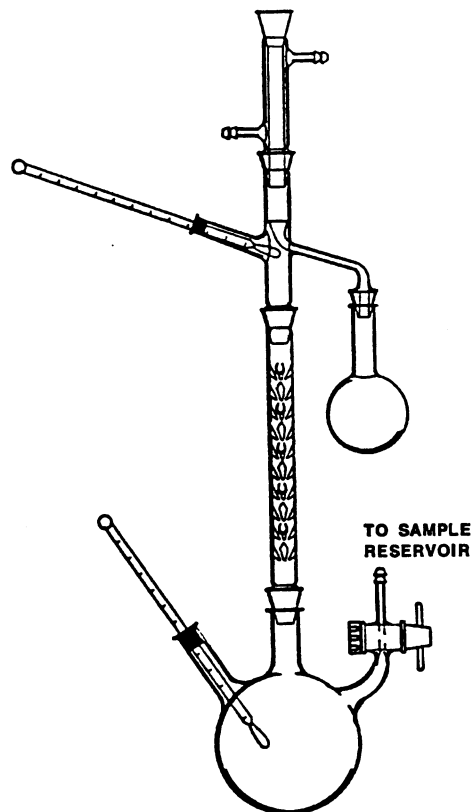


Fig. 5 - Freon distillation apparatus.

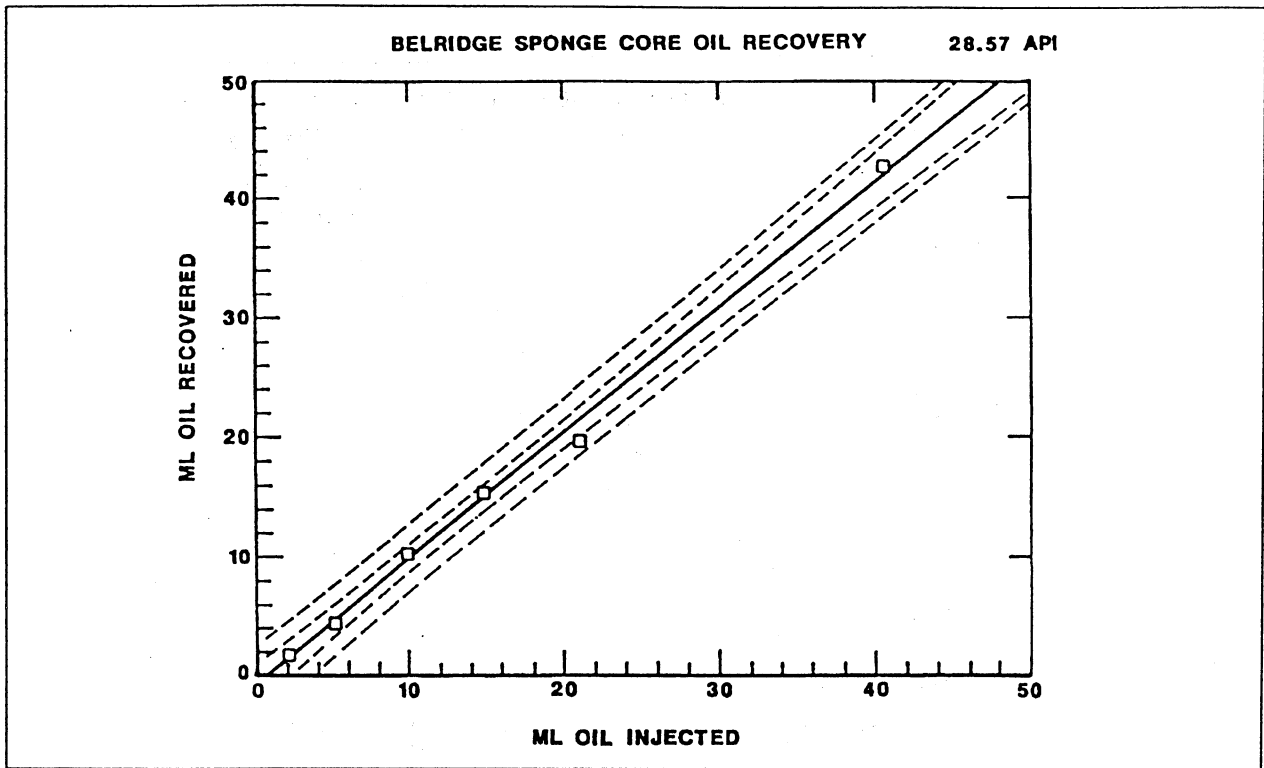


Fig. 6 - Belridge sponge core oil recovery.

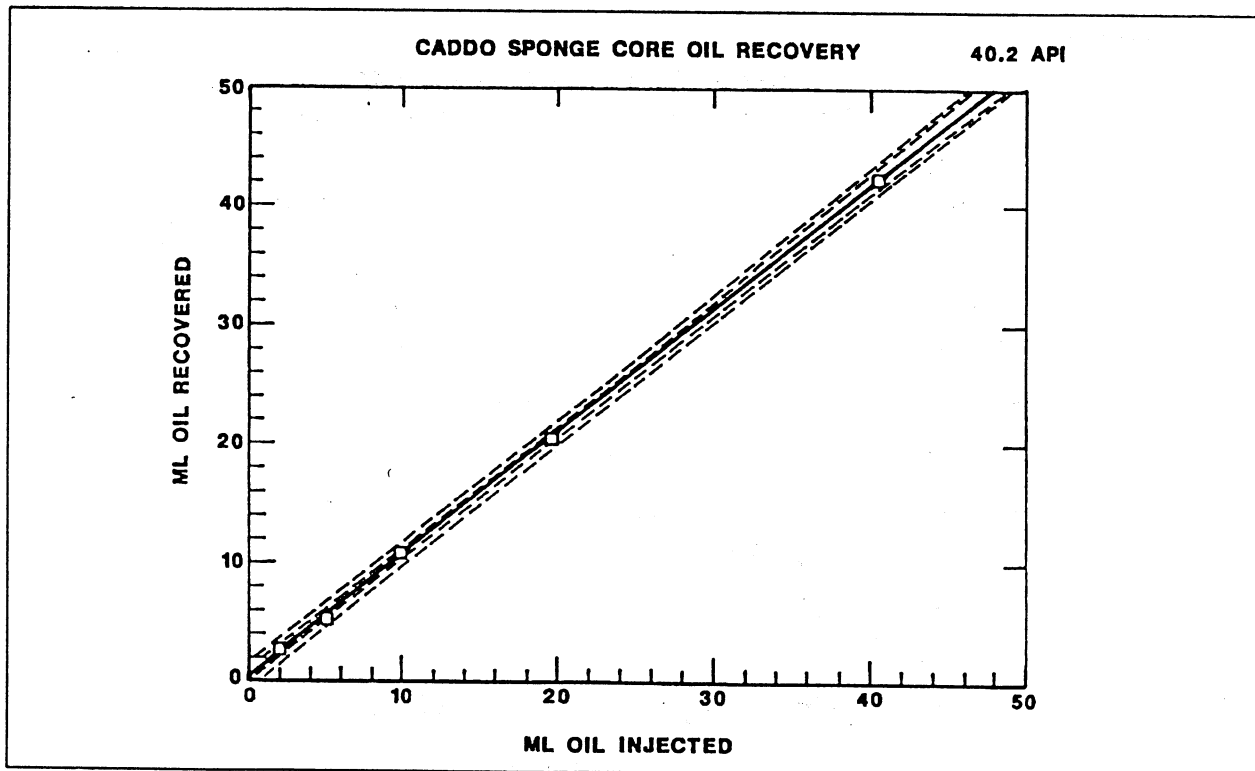


Fig. 7 - Caddo sponge core oil recovery.

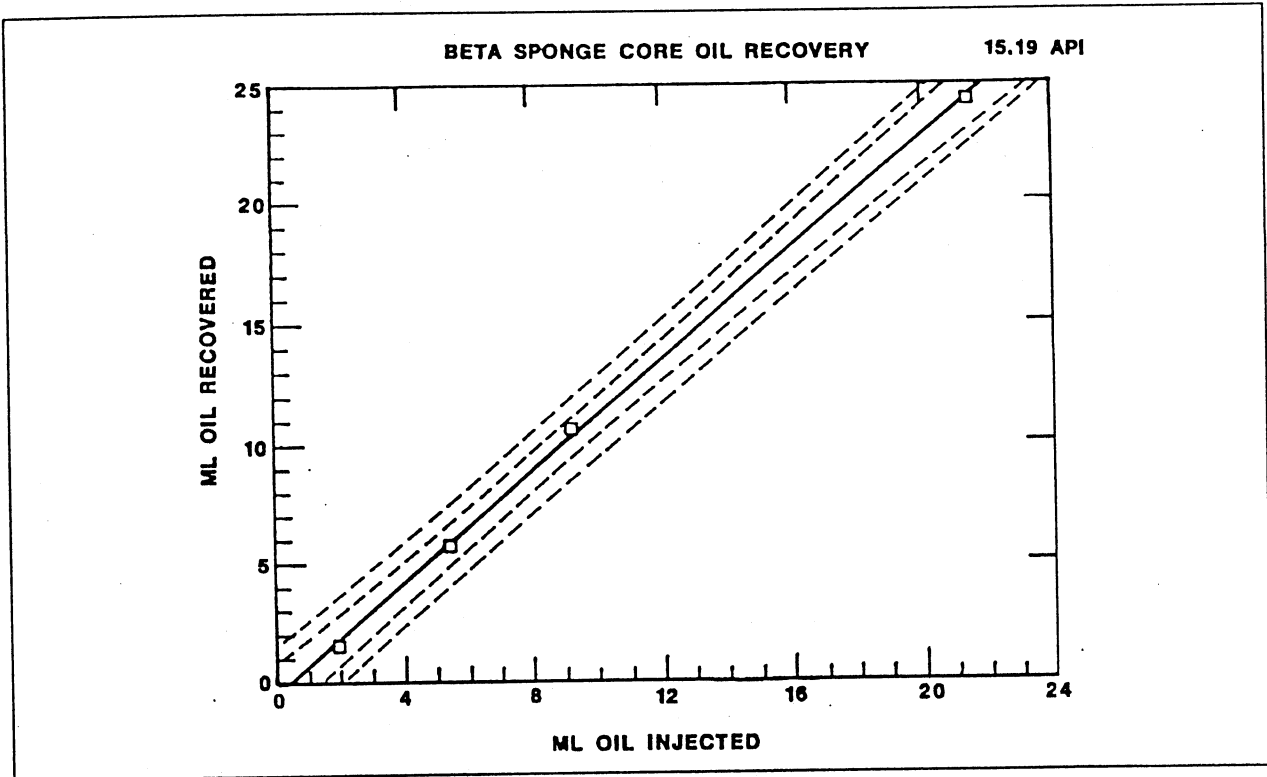


Fig. 8 - Beta sponge core oil recovery.

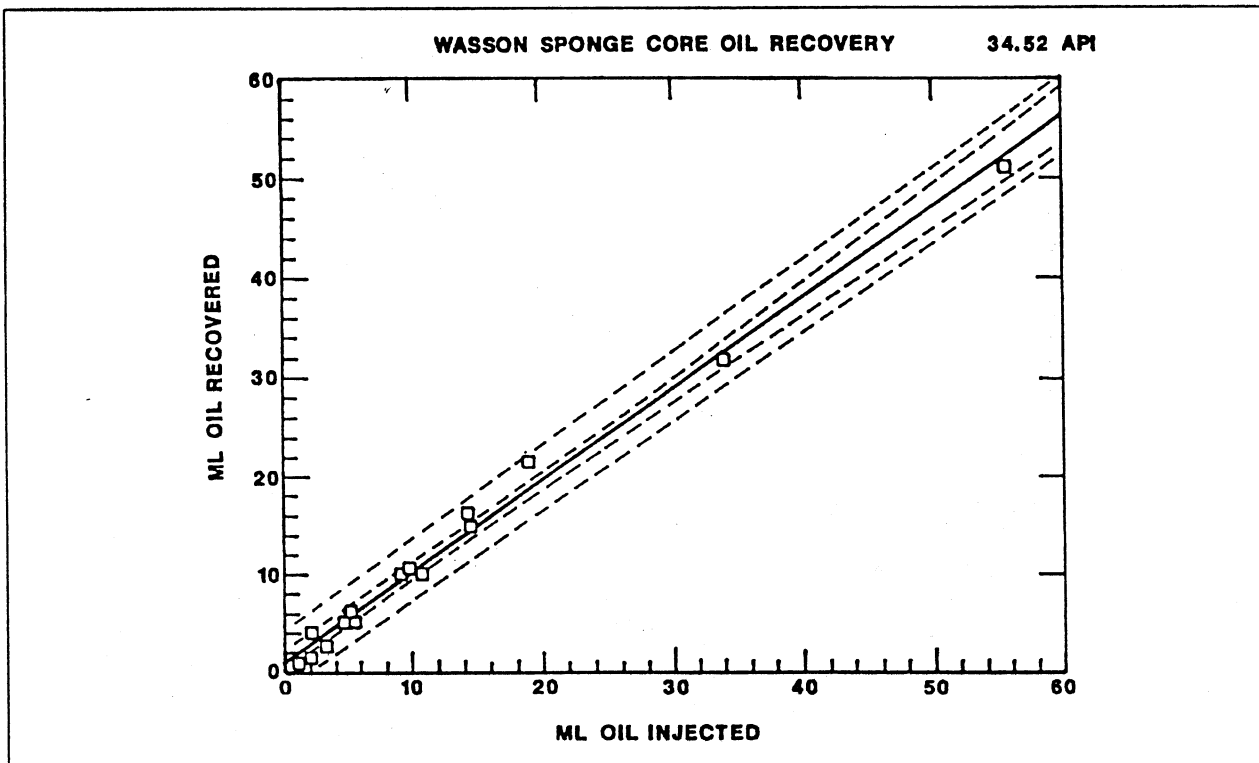


Fig. 9 - Wasson sponge core oil recovery.

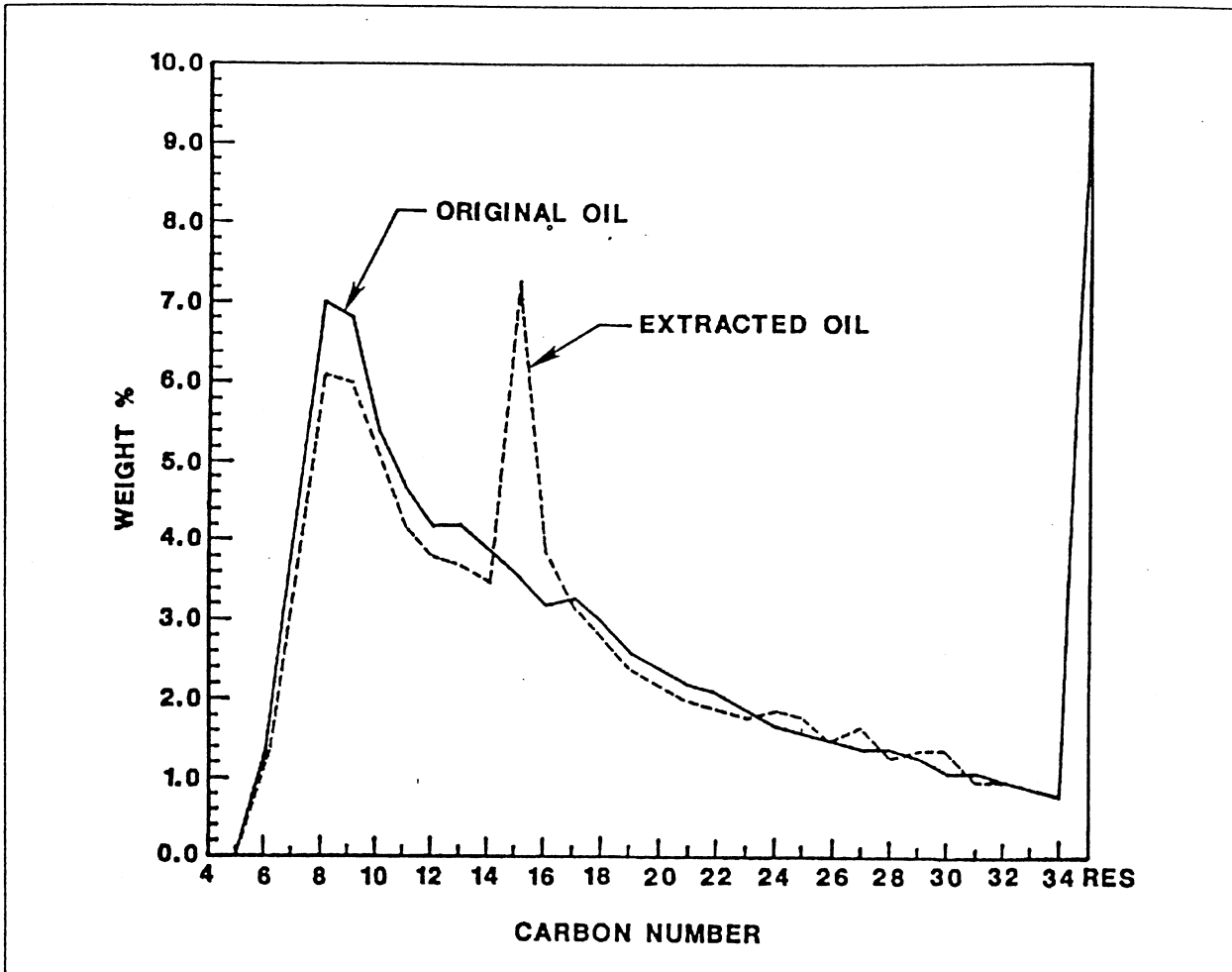


Fig. 10 - Volatility distribution of original and extracted crude oil.

