DETERMINATION OF OIL SATURATIONS IN SPONGE CORING BY GAS CHROMATOGRAPHY

by

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ABSTRACT

It is well known that the standard Dean-Stark extraction technique used for the determination of oil saturations in core samples is not suitable for analysis of the sponge used in sponge coring. There are two reasons for this. Firstly, small amounts of the sponge itself dissolve in most of the commonly used extraction fluids. Secondly, the presence of (clay) particles caught in the sponge can lead to overestimation of the amount of oil in the sponge, since these particles are partly washed out of the sponge during analysis.

Both problems can be avoided by using gas chromatography to measure the amount of oil in the extraction solvent. The system is calibrated on a selected number of peaks, e.g. the series of normal alkanes C10 - C19, using known solutions of the field crude in the extraction fluid (toluene). Components of the sponge that are dissolved in the extraction fluid also yield chromatographic peaks, but these do not coincide with any of the peaks for the normal alkanes selected. This approach allows oil saturations in sponge or core samples to be determined to within 0.1 per cent pore volume. It can be used with any type of solvent, and is insensitive to the amount of sponge dissolved in the solvent and to the presence of solid particles in the sponge. Gas chromatography was found not to offer significant advantages over Dean-Stark extraction for analysis of the core material itself.

INTRODUCTION

Sponge coring was introduced a few years ago as an improved coring method for determining residual oil saturations [1]. Sponge coring differs from conventional coring in that the inner core barrel is lined with polyurethane sponge. This relatively soft material protects the core against mechanical damage and, more importantly, catches any oil bleeding from the core during transport to the surface. Sponge coring finds its main application in in-situ S_{or} determination in flooded reservoirs. Although the amount of oil in the sponge is usually small in such cases, it may still contribute a couple of saturation percentages and should be determined with sufficient precision. If, however, (parts of) the cored interval are not fully swept, the amount of oil in the sponge can be quite substantial. Hence, the analysis of the fluids in the core should be designed to cover a wide range whilst having the greatest absolute precision at the lower end of the range.

COMPLICATIONS IN SPONGE EXTRACTION

After an initial series of tests, we concluded that the Dean-Stark extraction technique [2] yields sufficient accuracy to determine the volume of oil in one-foot whole-core sections if used in an extended form in which the extracted volume of water is measured directly, and the volume of oil is inferred from the difference in core-sample weight before and after extraction. However, even the extended technique was found to give problems when used for analysis of the sponge. Firstly, small amounts of the sponge dissolve in most of the commonly used extraction fluids. The amount of sponge dissolved is not constant, and may be related to the amount of additives in the polyurethane. Attempts to correct for the dissolution effect by monitoring the weight loss of control samples during extraction were unsuccessful, as these samples came from different batches of sponge. The presence of (clay) particles in the sponge was also found to give problems. When the core is cut, small amounts of mud and cuttings accompany the core into the inner barrel and are wiped off by the part of the sponge nearest to the drill bit. During analysis these particles are partly washed out of the sponge, resulting in overestimation of the amount of oil in the sponge. Fig. 1A shows an SEM (scanning electron microscope) image of an unused sponge, while Fig. 1B shows the corresponding image for a used sponge after extraction.

Several investigators [3,4] have suggested that the first problem might be solved by using solvents that did not dissolve the sponge. Unfortunately, the few solvents that are suitable in this respect have the disadvantage of being highly inflammable, toxic and/or environmentally hazardous. Moreover, they do nothing to solve the second problem associated with the presence of solids in the sponge.

Other authors suggested that methods such as colorimetry and fluorimetry might permit direct quantification of the amount of oil in a solvent [2]. While these techniques may be accurate in principle, they are also sensitive to sponge dissolution and the presence of foreign solids in the sponge.

After some experimentation we concluded that the solution to the above-mentioned problems should be sought in a technique that clearly discriminates oil from all other components of the extract. This would make it possible to use standard extraction fluids, such as toluene, that can be safely used on a large scale. Gas chromatography proved to be a suitable technique for this purpose.

GAS CHROMATOGRAPHY

Gas chromatography is commonly used to determine the composition of crudes. A chromatogram typically consists of a series of sharp peaks, as illustrated in Fig. 2. Each peak represents a certain chemical compound, and the area under the peak is proportional to the amount of this compound in the mixture analysed. In the present application, these areas are calibrated for a selected number of compounds, e.g. the series of normal alkanes C10 - C19, using known solutions of the field crude in the extraction fluid (toluene) and covering the entire range of concentrations expected.

Components of the sponge dissolved in the extraction fluid also yield chromatographic peaks. Fortunately, these did not coincide with any of the peaks of the normal alkanes selected in our experiment, as shown in Fig. 3. When the conditions change, all peaks used for analysis must be rechecked for the absence of such coincidence.

There is no need to determine the area of all crude oil peaks: the sum of peak areas for a selected range of compounds C10 - C19 is found to correlate excellently with the concentration of (dead) crude in the solution. This thus obviates the need for full recovery of the light ends and heavy components of the crude. The extraction equipment should be designed so as to keep evaporation losses of solvent to a minimum. The volume of dead oil can then be calculated from the concentration of crude in the solution.

The volume of dead oil obtained in this way is converted to a volume of in-situ live oil by multiplying by the volume expansion factor, B_o. Since sponge coring is mainly used for S_{or} determination, the PVT properties of the oil are likely to be well known.
It should be noted that this gas-chromatography method does away with the need for distilling the solvent off from the extract - a time-consuming and delicate operation.

FIELD EXAMPLE

The method described above has been applied to a number of sponge cores taken as part of a Shell campaign to improve the determination of S_{or}. The example presented here is from a large oil field in the North Sea. A calibration curve was determined for dead crude in toluene in concentrations up to 3% by weight. As expected, a linear relationship between the summed peak area and the crude concentration was found over this range (Fig. 4).

The method was tested on a sample of sponge 5 feet (150 centimetres) long. Evaluation of the open-hole logs indicated that the oil saturation was residual, so that oil concentrations in the sponge could be expected to be low and fairly uniform. The total length of sponge was cut into four pieces, each of which was trimmed to a length of 29 cm. The four resulting samples were extracted by the Dean-Stark technique with toluene as solvent. The toluene extract obtained in this way was subjected to gas chromatography, and the amount of oil in each sample determined from the calibration curve. The results are shown in Table 1. It will be seen that the oil content found in this way is indeed low, with little variation from sample to sample, as expected.

By way of comparison, the amount of oil in the four sponge samples were also determined by the extended Dean-Stark method, i.e. by inference from the weight loss of the sponge and the amount of water collected during extraction. (This method can be combined with gas chromatography on the same samples, since the extended Dean-Stark method does not actually make use of the toluene extract at all.) The results of the Dean-Stark estimation are also given in Table 1. It will be seen that the oil contents determined in this way show much more variation, indicating that the Dean-Stark technique is indeed much more sensitive to disturbing factors that occur during analysis of the sponge.

Sample No.	Length	$V_{toluene}$	Gas chromatography				Dean-Stark
			Summed C_{10}- C_{24} peak area	C_{oil}	W_{oil}	W_{oil} /ft	W_{oil} /ft
	cm	litre	arbitrary units	%w	g	g/ft	g/ft
1	29	1.20	44.6	0.525	6.30	6.6	8.0
2	29	1.18	52.5	0.618	7.32	7.7	5.6
3	29	1.18	40.0	0.470	5.55	5.9	4.1
4	29	1.24	37.6	0.443	5.48	5.8	0.6

Table 1. Determination of oil content in four sponge samples by gas chromatography and by extended Dean-Stark extraction.

W_{oil} = total estimated weight of oil in sponge sample.

C_{oil} = oil concentration in sponge.

Notes: (1) 8.50 arbitrary units correspond to 1 ml oil / 1 l toluene.

(2) 1 g/ft of oil corresponds to 0.3% PV in a 3.5-inch core of 25% porosity.

The oil content of the corresponding four core samples were determined by both methods; the results are given in Table 2. It will be seen that the results obtained by the two methods now show much better agreement - no doubt because the amounts of oil involved are much larger.

Core sample	Remark	S_o (%PV)	
		Gas chromatography	Dean -Stark
A	swept zone	37.1	37.6
B	swept zone	12.1	12.6
C	water leg	7.3	7.1
D	water leg	5.2	4.5

Table 2. Comparison of oil saturation in four core samples determined by gas chromatography and by extended Dean-Stark extraction.

Taking the combined effects of all sources of error into account, we estimate the precision of the new method to be better than 0.4 ml of oil per 1 ft length of sponge. For a core 3.5 inch in diameter with a porosity of 0.25, this corresponds to an error in the oil saturation of less than 0.1 per cent pore volume under surface conditions.

CONCLUSIONS

A practical, cost effective procedure, based on gas chromatography, has been developed to quantify crude-oil saturations in sponge coring.

The technique has a high precision, typically better than 0.4 ml/ft of sponge, equivalent to 0.1% PV for a core with 25% BV porosity.

It can be used for all oil gravities, with any extraction fluid, and is insensitive to the presence of solids in the sponge.

The extended Dean-Stark extraction technique is sufficiently accurate for determining the oil content of the core itself.

REFERENCES

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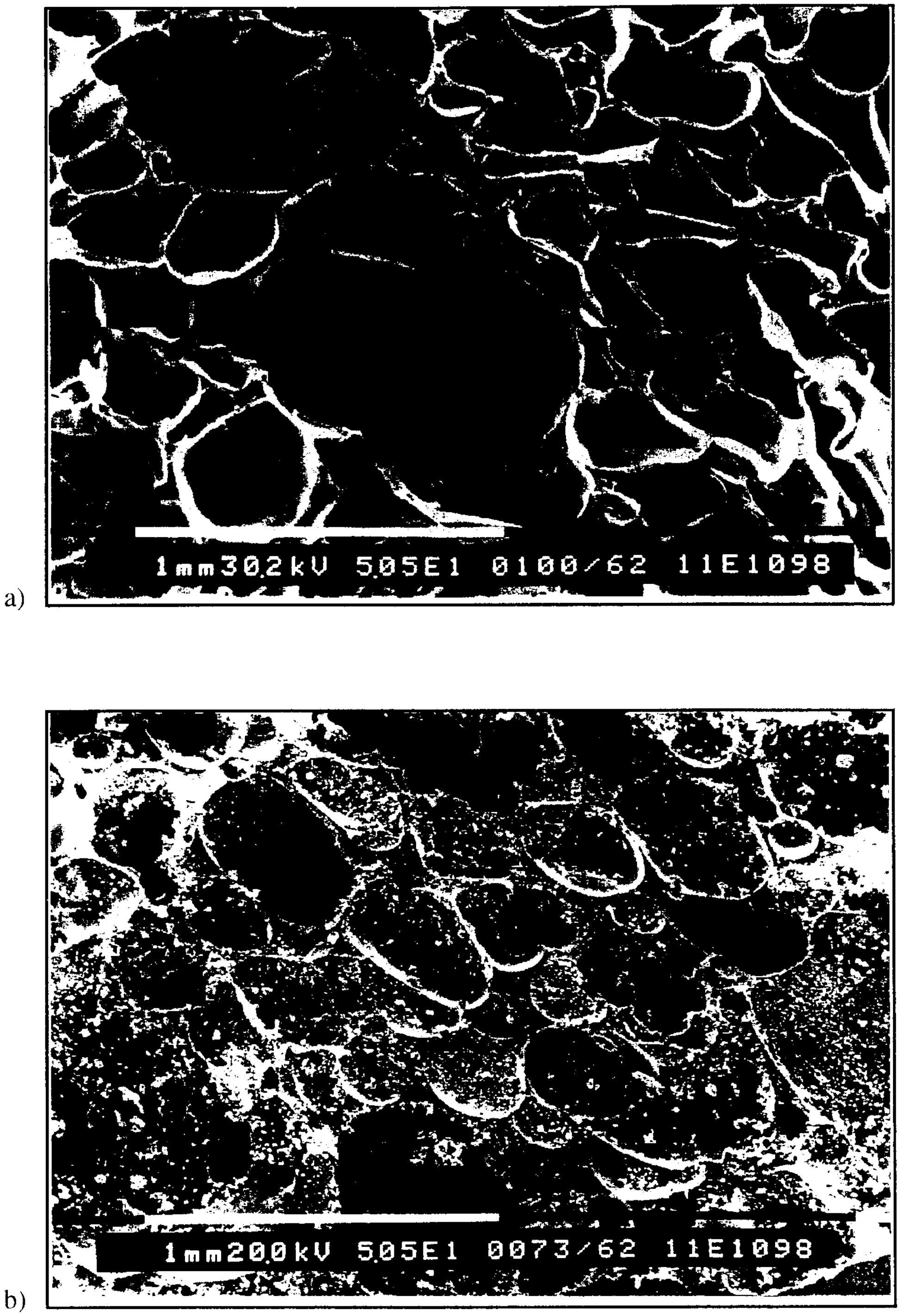

Fig. 1 Scanning electron microscope (SEM) images of surface of clean, unextracted sponge (a) and of extracted sponge (b). Note the debris on the sponge surface (b).

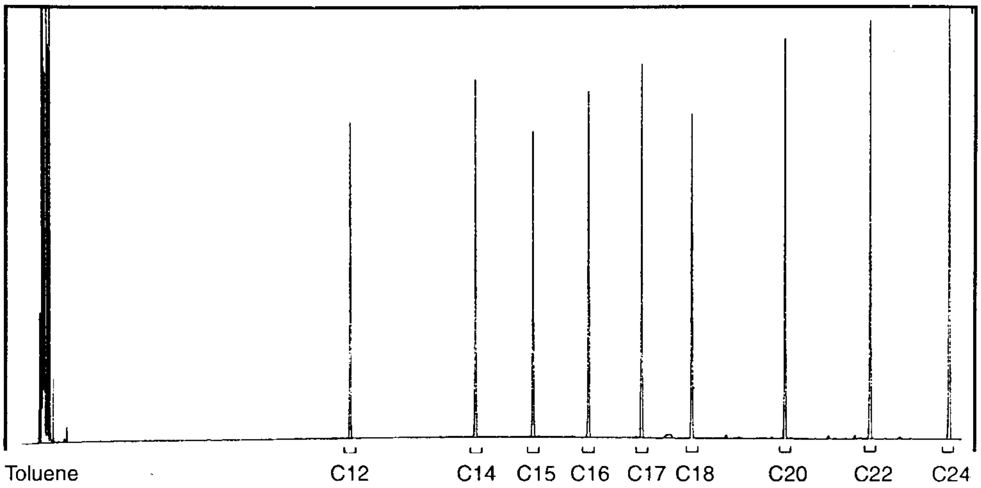

Fig. 2 Gas chromatogram of a toluene extract of a series of n-alkanes from a North Sea crude

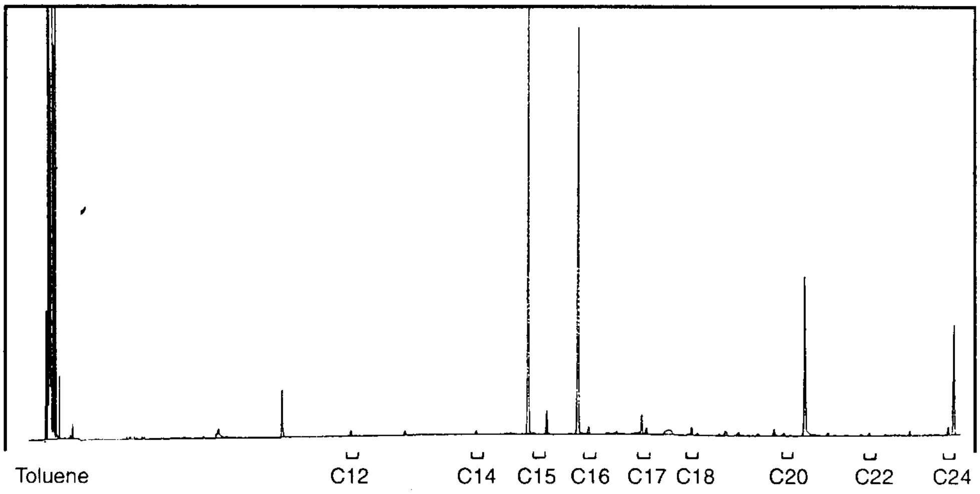

Fig. 3 Gas chromatogram of a toluene extract obtained by 60 hours extraction of a clean sponge.

The positions of the n-alkane peaks are indicated. It will be seen that none of the "sponge" peaks coincides with an n-alkane peak.

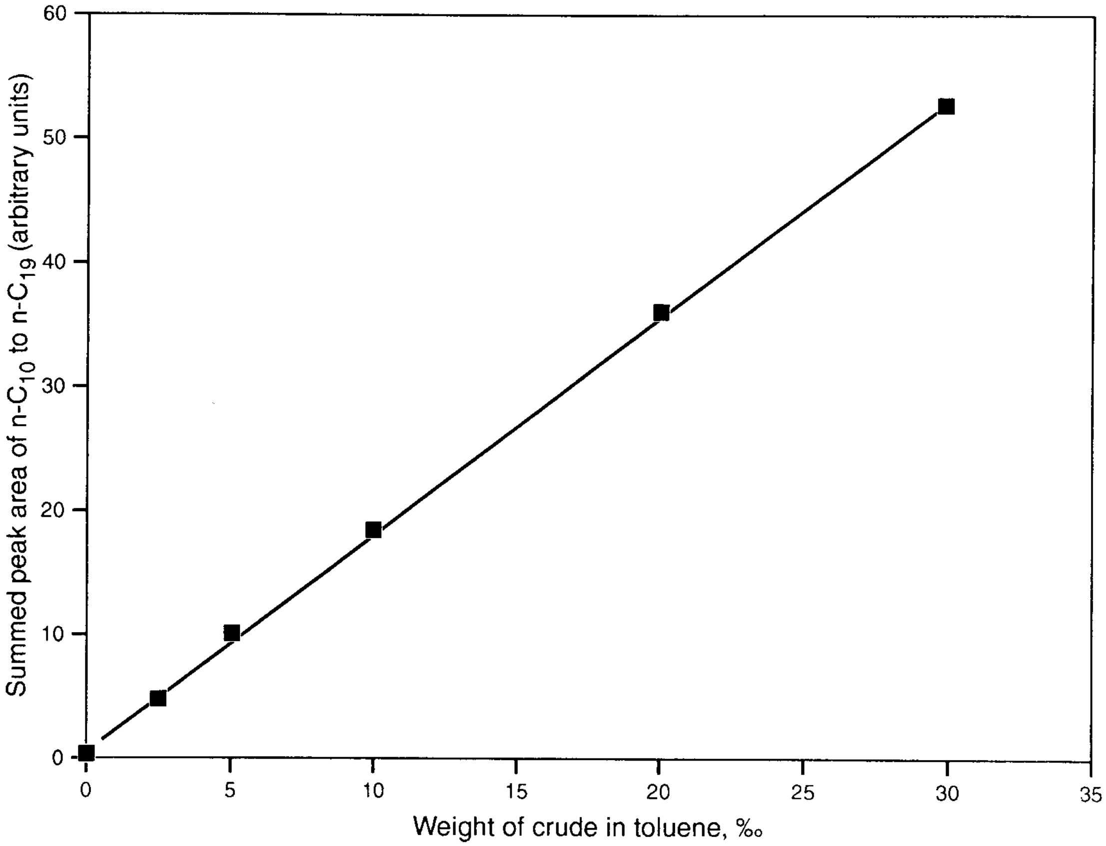

Fig. 4 Calibration curve for gas chromatography of a North Sea crude in toluene.

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