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A RAPID LABORATORY AND FIELD METHOD FOR THE DETERMINATION OF BITUMEN CONTENT OF BITUMINOUS SANDS

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INTRODUCTION

The need for a simple and rapid method for the assaying of drill-core samples of Alberta bituminous sands for bitumen content, and especially one that can be applied in the field, has led to the development of a new and rapid method that is described in this paper. This need has become more urgent recently due to drilling operations in the Fort McMurray area, Alberta.

The method is essentially the determination of the density, or true specific gravity of the sample. The principle involved is that in a system of two nonmiscible components having different but constant densities, the volume of the material varies directly with the relative concentration of each component, the variables being related by a linear equation. Bituminous sand is such a system and by measuring accurately the volume of a weighed sample, the bitumen content as a percentage of the sample taken can be readily calculated.

APPARATUS

The apparatus required is simple and inexpensive, the essential parts being:

1. Calibrated volumetric flasks as shown in Figure 1. Flask (a) has a capacity of 250 ml. and is suitable for 100 to 200 gm. samples. Flask (b) has a capacity of 1000 ml. and is suitable for 500 to 1000 gm. samples.
2. Balance, the capacity and sensitivity of which depends on the size of sample and volumetric flask used.
3. Calibrated pipettes and burette.
4. Assortment of beakers, flasks, and bottles.
5. Solvent for determining the volume of the sample and suitable solvents for cleaning the volumetric flask.

EXPERIMENTAL INVESTIGATION ON ACCURACY OF METHOD

The experimental work described below was confined to drill-core samples obtained from the Steepbank River locality.

The feasibility and accuracy of this method depend upon the ability to measure the volume of the sample and upon the uniformity of the mineral aggregate-bitumen material tested. The volume is obtained by weighing the sample into the volumetric flask, and then filling the flask to the calibration mark with the solvent, the volume of the flask minus the volume of the solvent added giving the volume of the sample.

To obtain the volume it is necessary that the solvent fill all the void space in the bituminous sand. Also, the solvent should not be so volatile as to cause losses through evaporation that will affect the accuracy of the method. Toluene was found to be satisfactory. It is a non-oily solvent and gives the same delivery as water from pipettes or burettes. In all the determinations made on different samples of bituminous sand of varying bitumen content, it was found easy to effect a complete penetration of the solvent into the void spaces of the sample.

Bituminous sand deposits are often interbedded with clay bands of varying thickness, from a fraction of an inch to a few feet. This clay may contain as much as 5 per cent bitumen. Even when ground to 100 mesh the removal of the bitumen from the mineral matter is usually incomplete by solvent extraction methods due to the difficulty of penetration by the solvent into the microcapillaries of the sample particles. This gives low results as to per cent bitumen content. In the density method the same difficulty is experienced, giving high results, as incomplete penetration of void space in the sample gives a high volume. The method is therefore particularly applicable to all other types of samples where each mineral grain is surrounded by a film of bitumen, aiding in the penetration of the solvent into the void spaces of the sample.

The mineral aggregate is practically all sand of various particle sizes. The density of a series of samples of dry, bitumen-free mineral aggregate, obtained by soxhlet extraction of a series of bituminous sand samples with CCl_4, was determined. The method used was the same as in the routine measurement of the volume of the bituminous sand samples, using toluene as the solvent. Table 1 shows that the density is reasonably uniform and can be treated as a constant. Clay is a weathering product of various silicate minerals, with a range of density from 2.5 to 2.7. Pure sand, which is quartz, has a density 2.65. It is reasonable to expect that the mineral aggregate containing some clay will have a density close to that of pure sand. It is interesting to note that the density of pure, coarse, white sand is practically the same as the average of the extracted sand examined. The results in the last column of the table show that the maximum deviation from the mean value is not more than 0.02. In the calculation of the bitumen content, an error of 0.02 in the density of the mineral aggregate causes a corresponding error of 0.4 per cent bitumen content for a sample containing 5.0 per cent bitumen. This error slightly decreases with an increase in bitumen content, being 0.3 per cent when the bitumen content is 15.0 per cent. The average density of 2.62 for the mineral aggregate as given in table 1 was used to calculate the bitumen content of all the samples tested, giving the best results.

TABLE 1

Lab. No. of sample	Bitumen content of sample by wt. %	Screen Analysis of Mineral Aggregate: on 40 mesh %	Passing 40 mesh %	Passing 100 mesh %	Passing 200 mesh %	Density of (extracted) mineral aggregate gm/cm3
325-C	2.9	12	85	77	34	2.63
317-C	3.8	7	93	80	36	2.62
290	6.9	5	94	87	46	2.61
341	6.9	10	89	61	26	2.60
326	7.1	9	90	70	28	2.62
324	7.2	7	93	78	29	2.62
363	5.4	50	49	11	5	2.63
313	11.3	54	43	17	5	2.61
323	12.9	1	98	86	10	2.63
343-C	13.2	1	99	36	5	2.64
329	13.3	1	98	51	7	2.64
355	14.7	13	87	22	3	2.60
360	14.7	53	47	9	4	2.63
356	15.3	12	87	17	4	2.63
311	15.4	34	66	9	2	2.61
354	16.5	1	99	19	2	2.63
352	16.8	-	100	30	3	2.62
	Pure coarse white sea sand					2.63
					Average	2.62

The specific gravity of bitumen from the McMurray Area, Alberta, varies from 1.00 to 1.06 as obtained by 1/Clark. Fresh unexposed bitumen from drill-core samples likely has a specific gravity range of only 1.00 to 1.02 for that entire area. This variation in bitumen gravity due to location is less than that caused by the weathering of exposed bituminous sand. The high specific gravities 1.02 to 1.06 are those of bitumen obtained from such exposed and weathered material. In all the samples from different holes tested by the density method a value of 1.00 was used for the specific gravity of the bitumen. This value gave results which closely agreed with check determinations by soxhlet extraction with CCl_4 on the same samples. The results from all the samples tested by the two methods agreed within 0.5 per cent bitumen content. This indicates that the specific gravity of the bitumen from a relatively small area is reasonably constant and may be treated as such.

The specific gravity and its constancy of both bitumen and mineral aggregate from the bituminous sand from a local area should be determined before using the density method to evaluate the bitumen content of material from that area. This may be done quite readily by testing just enough samples to cover the range of the various grades of material likely to be encountered in a local area by another method such as centrifuge or soxhlet extraction as well as the density method. If the density of both bitumen and mineral matter is reasonably constant the results, of the two methods should agree closely, providing correct density values are assigned to both components. As the approximate densities are known, it is easy to calculate by trial and error those values which will give best agreement between the two methods. The percent error in the calculated bitumen content per unit error in the specific gravity of the bitumen is proportional to the bitumen content - decreasing as the bitumen content decreases. For an error of 0.02 in bitumen gravity this error is 0.45 per cent for a sample containing 15.0 per cent bitumen.

It is necessary that there be no change in total volume when the bitumen in the sample is dissolved in the solvent. This was carefully tested with toluene and bitumen of known specific gravity. No change in volume of solution was found.

The reliability of the method depends upon the degree of accuracy obtained in measuring the volume of the sample. This depends upon the penetration of the solvent into all the void space in the bituminous sand, and upon the accuracy of all volume measurements involved. A high ratio of weight of sample to volume of flask should be used, yet not exceeding a value where penetration of the sample by the solvent is incomplete. When using a 100-gm. sample a change in volume of 0.1 cc. causes a corresponding change of 0.15 per cent in the bitumen content. When using a 1000-gm. sample a 1.0 cc. volume change causes the same per cent error in bitumen content. This error is easily calculated. The change in per cent bitumen per unit volume change decreases

1/Clark, K.A. & Blair, S.M., The Bituminous Sands of Alberta, Scientific & Industrial Research Council of Alberta, Report No. 18, 1927 with an increase in the weight of the sample. The increase in accuracy due to an increase in sample size is partly offset by the inability to measure larger volumes as exactly as smaller ones.

The sample and solvent should be close to room temperature before doing a determination to avoid volume changes during the process due to temperature changes. Using toluene, the cubical expansion coefficient is 0.001 C. to the nearest third place decimal.

TEST PROCEDURE

Method 1. This method is mainly a volumetric procedure. Weigh the sample into the volumetric flask to the required accuracy. If many determinations are made it may be preferable to use the same weight throughout so that the weight of the sample can be treated as a constant. Then measure carefully with a pipette sufficient solvent into the volumetric flask to cause complete penetration of sample with solvent. Make a correction if necessary for loss of solvent during stirring. Finally, fill the flask to the calibration mark from a burette, noting the volume added. Any air bubbles on the walls of the flask must be eliminated. Fortunately, the use of an organic solvent like toluene almost completely prevents the formation of air bubbles. Subtracting the volume of the solvent added from the volume of the flask, the volume of the sample is obtained. The volumetric flask must be well cleaned between successive determinations so as to avoid appreciable volume changes.

Method 2. The procedure in this alternative method is the same as above, except that the volume of the solvent used is derived by means of its weight. Knowing the weight, temperature, and corresponding specific gravity of the solvent, its volume is easily calculated. This method has the advantage over the purely volumetric one in that it is easy to calculate volumes to the tenth of a ml. by weighing. Also, when using large samples up to 1000 gms. it is simpler to weigh than to measure corresponding quantities of solvent. The disadvantage is that the specific gravity of the solvent must be known accurately to the third decimal place.

CALCULATIONS

Let W = wt. of sample, gms.
w = " " bitumen & water, gms.
b = % bitumen & water in sample by wt.
d_1 = density of mineral aggregate, $gm./cm.^3$
d_2 = " " bitumen & water, $gm./cm.^3$
v_1 = volume of mineral aggregate, $cm.^3$
v_2 = " " bitumen & water, $cm.^3$
V = " " sample, $cm.^3$

$$v_1 + v_2 = V \qquad (1)$$

$$d_1 v_1 + d_2 v_2 = W \qquad (2)$$

Multiplying (1) by d_1 and subtracting (2)

$$d_1 v_1 + d_1 v_2 = d_1 V \qquad (3)$$

$$d_1 v_1 + d_2 v_2 = W \qquad (2)$$

$$d_1 v_2 - d_2 v_2 = d_1 V - W$$

$$\text{or } v_2(d_1 - d_2) = d_1 V - W \qquad (4)$$

rearranging (4)

$$v_2 = \frac{(d_1 V - W)}{(d_1 - d_2)}$$

$$= \frac{d_1 V}{(d_1 - d_2)} - \frac{W}{(d_1 - d_2)} \qquad (5)$$

$w = v_2 d_2$, then from (5)

$$b = \frac{v_2 d_2}{W} \times 100 = \left[\frac{d_1 V}{(d_1 - d_2)} - \frac{W}{(d_1 - d_2)} \right] \times \frac{100\ d_2}{W}$$

$$= \frac{100\ d_1 d_2 V}{(d_1 - d_2)\ W} - \frac{100\ d_2}{(d_1 - d_2)} \qquad (6)$$

As d_1 and d_2 can be treated as constants, (6) reduces to

$$b = k_1 \frac{V}{W} - k_2 \qquad (7)$$

if W is constant

$$b = KV - k_2 \tag{8}$$

(8) is the equation of a straight line, b and V are the two axes, K is the slope of the line and k_2 is the intercept on the b axis.

The per cent bitumen in the sample by weight (moisture free basis) is given by the expression below.

$$= \left[\frac{k_1 \frac{V}{W} k_2 - \% H_2O}{100 - \% H_2O} \right] x\ 100 \tag{9}$$

To plot (8) it is necessary to evaluate the constants k_2 and K. The mean value of d_1 and d_2 was found to be 2.62 and 1.00 respectively.

k_2 is independent of the sample weight and

$$= \frac{100 \times 1.00}{(2.62 - 1.00)} = 61.73$$

K varies with the size of the sample. Assuming a 100 gm. sample.

$$K = \frac{100 \times 2.62 \times 1.00}{(2.62 - 1.00)\ 100} = 1.617$$

substituting in equation (8)

$$b = 1.617\ V - 61.73 \tag{10}$$

Plotting b against V as shown in Fig. 2, the per cent bitumen and water, corresponding to the volume of the sample, can be read off from the graph.

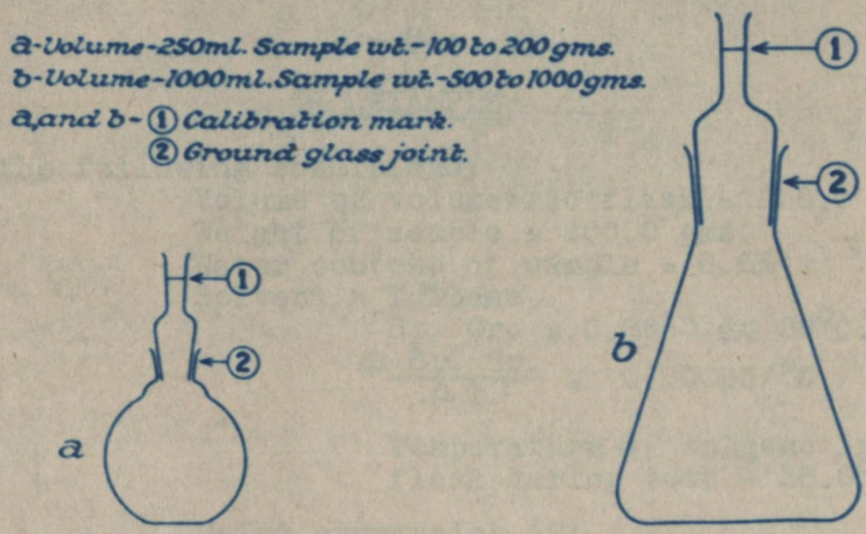

Figure 1-Volumetric (Pycnometer-type) Flasks.

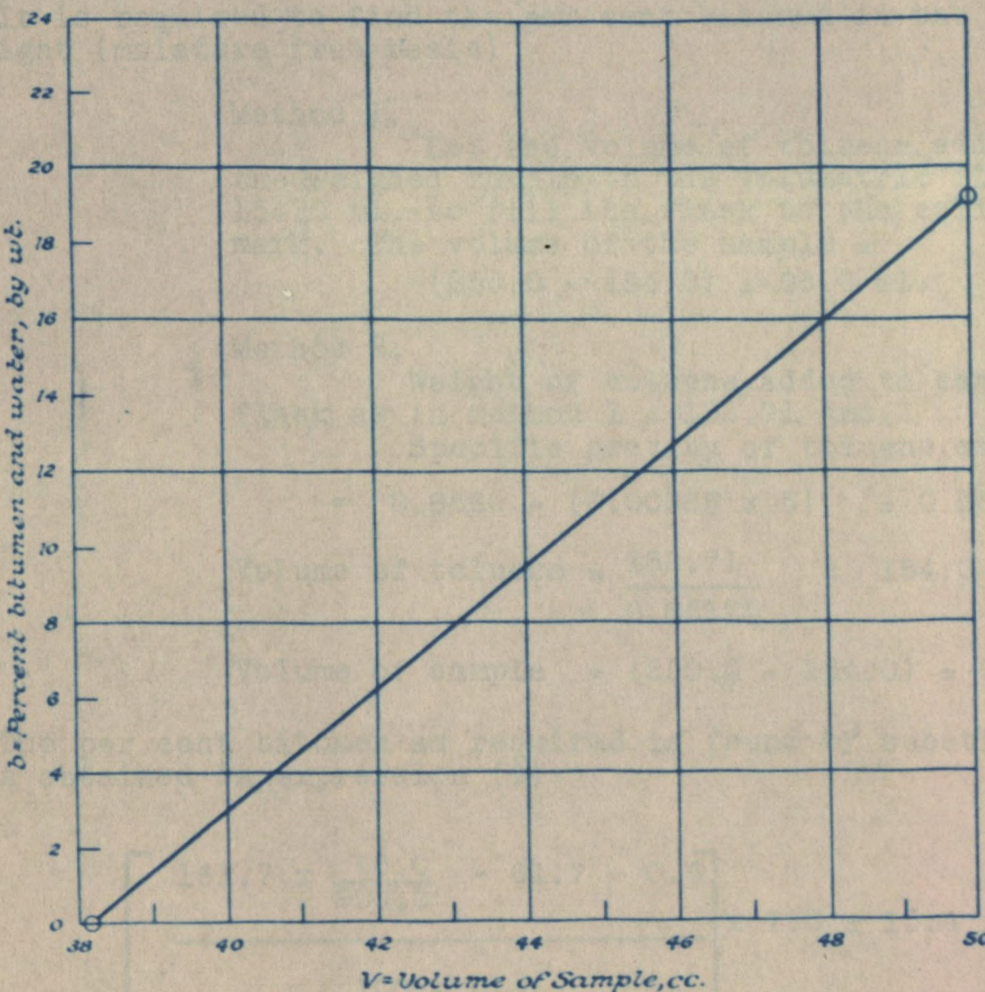

Figure 2-Percent bitumen and water vs. volume of sample. Weight of sample-100 gms.

EXAMPLE

Assume the following conditions:

Volume of volumetric flask = 250.0 ml.
Weight of sample = 200.0 gms.
Water content of sample = 0.6%
Solvent - Toluene
Sp. Gr. = 0.8660 at 20°C.

$$\frac{\Delta \text{ Sp. Gr.}}{\Delta T} = 0.00085/^{\circ}C.$$

Temperature of toluene in volumetric flask during test - 25.0°C.

Using expression (9)

$$k_1 = 161.7; \; k_2 = 61.73$$

It is required to find the per cent bitumen in the sample by weight (moisture free basis)

Method 1.

Let the volume of toluene added to the weighed sample in the volumetric flask be 154.0 ml. to fill the flask to the calibration mark. The volume of the sample =

(250.0 - 154.0) = 96.0 ml.

Method 2.

Weight of toluene added to sample in flask as in method 1 = 132.71 gms.

Specific gravity of toluene at 25°C.

$$= 0.8660 - (0.00085 \times 5) = 0.86175$$

$$\text{Volume of toluene} = \frac{132.71}{0.86175} = 154.0 \text{ ml.}$$

Volume of sample = (250.0 - 154.0) = 96.0 ml.

The per cent bitumen as required is found by substituting the values obtained in expression (9)

$$\left[\frac{161.7 \times \frac{96.0}{200.0} - 61.7 - 0.6}{100 - 0.6}\right] \times 100 = 15.4 \text{ per cent}$$

CONCLUDING REMARKS

The principle of this method is exact when applied to a material where the density of the two components is accurately known and the penetration of the solvent into the void space of the sample is complete.

When carried out with reasonable care, the method has an accuracy of ± 0.5 per cent. in terms of bitumen content, which is the same as that obtained by solvent extraction with a soxhlet apparatus. This is well within the accuracy with which the bituminous sands drill cores can be sampled, which is probably ± 1.0 per cent.

The density method is also very flexible as to size of sample required for test. For testing samples ranging from 50 to 1000 gms. not more than four sizes of volumetric flasks would be required. This simplifies the preparation of a representative test sample, as it is easier to obtain such a sample for analysis when using 1000 gms. instead of 50 gms.

The method described above compares favorably with solvent extraction methods such as those using filtering crucibles, soxhlet apparatus or a centrifuge. It requires usually about two days for a complete determination by these methods while by the density method this may be done easily in half an hour. One analyst using two volumetric flaskscan test from ten to twenty samples a day. This is comparable to two analysts using ten to twenty soxhlet extraction units.