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Fuels Division

A COMPARISON OF THREE LABORATORY METHODS
FOR DETERMINING THE BITUMEN CONTENT OF BITUMINOUS SANDS

By

R. G. Draper, A. Yates and H. McD. Chantler

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By

R. G. Draper 1/, A. Yates 1/, and H. McD. Chantler 2/

CONTENTS

	<u>Page</u>
Summary	1
Introduction	2
Brief Outline of the Methods of Assaying for Bitumen Content	3
Preparation of the Standard Samples	5
Discussion of Results and Conclusions	6
Appendix I - Laboratory Sampling and Assaying of Bituminous Sands by the Carbontetrachloride Extraction Method	12
(a) Preparation of Sample for Analysis	12
(b) Determination of Water Content	14
(c) Determination of Bitumen Content	16
(d) Screen Analysis of Sand Residue	20
Appendix II - Laboratory Sampling and Assaying of Bituminous Sands by Toluene Extraction Method	21
Appendix III - Laboratory Sampling and Assaying of Bituminous Sands by the "Density" Method	26
(a) Preparation of Sample for Analysis	
(b) Determination of Water Content	
(c) Determination of Bitumen Content	

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ILLUSTRATIONS

<u>Fig.</u>		<u>Follows Page</u>
1	Power Grinder Assembly for Sample Preparation and Manual Opener for Core Containers	13
2	Multiple Water Determination Apparatus	14
3	Multiple Soxhlet Extraction Apparatus	16
4	Metal Holder for Extraction Thimble	16
5	Modified Toluene Extraction Apparatus	22
6	Calibrated Volumetric Flask	27

A COMPARISON OF THREE LABORATORY METHODS
FOR DETERMINING THE BITUMEN CONTENT OF
BITUMINOUS SANDS

SUMMARY

The objective of this investigation was to compare three analytical methods with regard to their accuracy and precision in determining the bitumen content of bituminous sands composed of different proportions of bitumen, sand and clay. This work was undertaken to provide a basis for comparing the total quantities of bitumen estimated from the drilling operations reported in, "Drilling and Sampling of Bituminous Sands of Northern Alberta 1942-'47 Vol. I" of the Department of Mines and Resources Report No. 826, and in "The Exploration of Alberta Bituminous Sand 1952-'54 Vol. I" by Calvin and Associated Oil Companies.

Of the three analytical procedures, the toluene extraction method gave the most uniform and accurate results. The precision of this procedure was slightly superior to the carbontetrachloride extraction technique, and its accuracy was considerably better due to the more reliable moisture values obtainable by this procedure. The toluene extraction method gave results which were on the average 0.7 per cent lower in

bitumen content than the carbontetrachloride method. This difference was almost entirely attributable to the higher water content determined by the toluene method. This fact was corroborated by the observation that the water content measured by this method was 0.6 per cent higher than that determined by the A. S. T. M. method D 95 employing dilution naphtha, which was used in conjunction with the carbontetrachloride extraction procedure.

Both the toluene and carbontetrachloride extraction methods are considered satisfactory for assaying the bitumen content of bituminous sands. On the other hand, the density method of estimating the bitumen content was of a much lower order of precision than the two extraction procedures and should only be considered under circumstances which do not permit the use of the other methods.

INTRODUCTION

To secure information concerning the extent and quality of the bituminous sand reserves of Northern Alberta, an extensive drilling programme was undertaken by the Dominion Government in 1942-'47. This was later followed by drilling operations by several companies during 1952-'54. The work of the group of companies headed by the Calvin Consolidated Oil and Gas Company deserves special mention. It was evident that the economic appraisal of the bituminous sands, in addition to drilling,

required an accurate estimation of the bitumen content of the sand. The procedure devised for this purpose by the staff of the Fuels Division involved the extraction of the bitumen with carbontetrachloride. On the other hand, the laboratories of the Calvan Consolidated Oil and Gas Company developed a more rapid technique using toluene as the extracting solvent.

During the extensive drilling programme undertaken by the Calvan Company, portions of the drill cores were sent in metal containers to the Mines Branch, Department of Mines and Technical Surveys for confirmatory analysis, and some 1500 core samples were analysed by the Fuels Division. While this work was in progress it was felt that a more systematic comparison of the two analytical schemes was justified, and the analytical work described in this report was undertaken to determine the relative merits of these methods.

A rapid field method of assaying the bitumen content of bituminous sands, devised by W. J. Dyck of the Fuels Division, was also compared with the other laboratory procedures mentioned above.

BRIEF OUTLINE OF THE METHODS OF ASSAYING FOR BITUMEN CONTENT

The carbontetrachloride extraction method consisted of the extraction of the bitumen from the bituminous sand with carbontetrachloride as the solvent. The determination was made in a standard Soxhlet apparatus

using a paper extraction thimble. The amount of silt that passed through the extraction thimble was determined and applied as a correction to the bitumen content. The water content was determined on another weighed sample of the bituminous sand by distillation with A. S. T. M. dilution naphtha, according to A. S. T. M. method D 95. The bitumen content was then calculated on a dry basis. For a more complete account of the laboratory sampling and assaying of bituminous sands by the carbontetrachloride extraction method the reader is referred to Appendix I.

The toluene extraction method consisted of the simultaneous extraction of the water and bitumen from the bituminous sand with toluene as the solvent. The determination was made in a modified extraction apparatus using a paper extraction thimble. The amount of silt that passed through the extraction thimble was again determined and applied as a correction to the bitumen content. The water in the sample was distilled out of the boiling flask with the toluene vapour, and condensed and collected in a graduated trap for estimation. The bitumen content was then calculated on a dry basis. A more complete account of the laboratory sampling and assay of bituminous sands by the toluene extraction method will be found in Appendix II.

The density method consisted of the determination of the density and water content of the sample. The principle involved was that in a system of three immiscible phases, bitumen, water and sand, the total volume was equal to the sum of the volumes of the different phases.

By accurately measuring the volume of a weighed sample of bituminous sand, the bitumen content, as a percentage of the sample taken, can be readily calculated if the water content is known. The volume of the bituminous sand sample was determined in a calibrated pycnometer flask by mixing with a known weight of toluene. The water content was determined on a separate weighed sample of bituminous sand by distillation with A. S. T. M. dilution naphtha, according to A. S. T. M. method D 95. From the values obtained the bitumen content was calculated on the dry basis. A more complete description of this method will be found in Appendix III.

PREPARATION OF THE STANDARD SAMPLES

The examination of drill cores taken from the Athabasca bituminous sand area revealed a wide range of mixtures of bitumen, sand and clay. Lignite was also occasionally present. To evaluate the suitability of the three analytical methods for estimating the bitumen content of such mixtures, six one hundred pound samples were prepared from drill cores which had been previously analysed. For example, a large number of cores containing 2.5 per cent bitumen were crushed, mixed, and screened to make the composite sample as uniform as possible. In a similar manner standard composite samples of drill cores were prepared having 5, 7.5, 10, 12.5 and 15 per cent bitumen respectively.

The individual samples were analysed in quadruplicate by each

of the three methods and the water determinations were made at the same time. All determinations on a given standard sample were started simultaneously to avoid any changes in moisture content and variation of the sample which might arise due to segregation.

DISCUSSION OF RESULTS AND CONCLUSIONS

The results of analyses by the three methods are shown in Table I while Table II shows the differences in average bitumen content and the probable error of the mean as determined by the three methods.

As mentioned previously, the water content of the six standard samples was determined by two methods, - the A. S. T. M. method D 95 and the toluene extraction method. The toluene extraction method always gave a higher result than the A. S. T. M. method. The difference between the water content as determined by these two methods, varied from 0.9 to 0.4 per cent for the six standard samples with an average difference of 0.6 per cent.

All the bitumen determinations made by the carbontetrachloride extraction and the toluene extraction methods were corrected for silt passing through the extraction thimble, except for the No. 1 sample where silt was not observed in the extract. However, in order to emphasize the error which would be introduced into the determinations if not corrected for the silt, the bitumen content is also shown on the uncorrected basis

for both extraction methods in Table I. It should also be noted that the quantities of silt shown were obtained using double thickness thimbles. Were single thickness thimbles employed this error would have been augmented considerably.

For twenty-four determinations made by the carbontetrachloride extraction method the correction for silt varied from a high value of 1.8 per cent to a low of 0.1 per cent with an average of 0.8 per cent. For twenty determinations made by the toluene extraction method, the correction for silt varied from a high value of 0.7 per cent to a low of zero, with an average of 0.2 per cent. Therefore, if the bitumen content had been reported on the uncorrected basis, that is, uncorrected for silt or mineral matter, the average bitumen content for the carbontetrachloride extraction method would have appeared as 0.8 per cent higher than the corrected value, while the toluene extraction method would have yielded a result 0.2 per cent higher than this value.

In Table II the average values of the bitumen content on the dry basis of the six standard samples as determined by the three analytical schemes may be compared. Also the scatter of the data in arriving at these averages is expressed by the probable error of the mean. It will be observed that the probable error of the mean increases slightly with the bitumen content and that the average value of the probable errors of

the mean are + 0.08 per cent for the carbontetrachloride, + 0.06 per cent for the toluene extraction and + 0.25 per cent for the density method.

The toluene extraction method gave results that were always lower than those obtained by the carbontetrachloride extraction method. On the average for the six standard samples, the difference between these two methods varied from 1.2 per cent to 0.6 per cent with an average difference of 0.9 per cent in bitumen content. As previously noted, the water content determined by the toluene extraction method was, on the average, 0.6 per cent higher than that determined by the A. S. T. M. procedure. Consequently, the difference in bitumen content between the toluene extraction and carbontetrachloride extraction methods was almost entirely due to the difference in moisture content determined by these two methods.

The density method of bitumen assay was of a much lower order of precision than the two extraction procedures and the average values of bitumen determined in the six standard samples were generally somewhat lower than those obtained by the extraction methods. Consequently, the density method should only be considered when it is not possible to use the extraction methods or when a high accuracy is not important.

The toluene extraction method involves the simultaneous extraction of both bitumen and water from the same sample and is to be preferred to the carbontetrachloride method which requires a water determination

by A. S. T. M. method D 95 on a separate sample. The simultaneous extraction of bitumen and water from the same sample has the merit of avoiding any changes in moisture content which may take place in a separate sample through uneven distribution or through losses which may take place during handling. As the bitumen content is determined as the difference between the total weight extracted and the water, any error in the water determination is reflected in the estimated bitumen content. The error in the water determination using dilution naphtha may be due, either to a slightly higher solubility of the water in this medium, or an increased loss of water through the condenser because of its higher boiling point.

TABLE I

Results of Analyses by the Three Methods

Sample No.	Nominal Bitumen Percentages	Carbon Tetrachloride Extraction Method			Toluene Extraction Method			Density Method	
		Water % (A. S. T. M.)	Bitumen (Dry Basis) %		Water %	Bitumen (Dry Basis) %		Water % (A. S. T. M.)	Bitumen (Dry Basis) %
1	2.5%	2.1	2.8		3.0	1.7		2.0	0.7
		2.1	2.8		3.0	1.9		2.0	1.0
		2.1	2.8		2.2	2.3		2.0	1.6
		2.1	2.9		2.4	2.3		2.1	1.8
	Av.	<u>2.1</u>	<u>2.8</u>		<u>2.6</u>	<u>2.0</u>		2.1	2.5
2	5.0%	0.2	6.1	5.5	0.9	5.1	4.9	2.1	3.2
		0.3	6.1	5.6	0.9	5.1	5.1	2.0	3.3
		0.3	6.4	5.8	0.8	5.4	5.2	2.1	4.7**
		0.2	6.5	5.8	0.9	5.6	5.3	2.0	2.4
	Av.	<u>0.2</u>	<u>6.3</u>	<u>5.7</u>	<u>0.9</u>	<u>5.3</u>	<u>5.1</u>	<u>0.3</u>	<u>5.2</u>
3	7.5%	0.4	8.0	7.5	1.1	6.9	6.8	0.4	7.4
		0.4	7.9	7.7	1.2	7.0	6.9	0.4	7.9
		0.4	8.3	7.7	1.2	7.0	7.0	tr.	8.5
		0.4	7.9	7.8	1.0	7.1	7.0	tr.	9.3
	Av.	<u>0.4</u>	<u>8.0</u>	<u>7.7</u>	<u>1.1</u>	<u>7.0</u>	<u>6.9</u>	<u>0.2</u>	<u>8.3</u>
4	10.0%	0.1	10.0	9.2	1.1	8.6	8.3	0.1	8.0
		0.1	10.3	9.4	0.9	8.7	8.5	0.8	8.4
		0.1	10.4	9.8	1.1	8.7	8.5	0.8	8.4
		0.1	10.9	9.9	1.0	9.5	8.8	0.1	8.7
	Av.	<u>0.1</u>	<u>11.2</u>	<u>10.0</u>	<u>1.0</u>	<u>8.9</u>	<u>8.5</u>	<u>0.1</u>	<u>10.2**</u>
5	12.5%	tr.	13.0	12.1	0.5	11.5	11.3	0.1	8.8**
		tr.	13.0	12.2	0.3	11.8	11.7	tr.	11.1
		tr.	12.9	12.3	0.5	11.9	11.7	0.1	11.7
		tr.	14.1	12.3	0.4	12.0	11.8	tr.	12.4
	Av.	<u>tr.</u>	<u>13.7</u>	<u>12.4</u>	<u>0.4</u>	<u>11.8</u>	<u>11.6</u>	<u>tr.</u>	<u>12.6</u>
6	15.0%	tr.	14.5	14.0	0.4	13.8	13.6	tr.	11.0
		tr.	15.0	14.4	0.4	13.8	13.7	0.0	12.4
		tr.	15.1	14.4	1.1	13.9	13.7	tr.	13.4
		tr.	15.6	15.0	0.4	14.3	14.2	tr.	13.6
	Av.	<u>tr.</u>	<u>15.9</u>	<u>15.1</u>	<u>0.6</u>	<u>14.0</u>	<u>13.8</u>	<u>tr.</u>	<u>12.9</u>

Note: All percentages given are on "% by weight" basis.
 * Uncorrected for silt passing through extraction thimble.
 ** "Wild" result, but included in average due to large scatter of results.

T A B L E II

Difference in Average Bitumen Content
as Determined by the Three Methods

Sample	<u>A</u> Carbon Tetrachloride Extraction Method Mean Bitumen Content %	<u>B</u> Toluene Extraction Method Mean Bitumen Content %	<u>C</u> Density Method Mean Bitumen Content %	<u>A-B</u>	<u>A-C</u>
1.	2.8	2.0	2.4	+0.8	+0.4
2.	5.7 \pm .05*	5.1 \pm .06*	5.2 \pm .04*	+0.6	+0.5
3.	7.7 \pm .05	6.9 \pm .04	8.3 \pm .27	+0.8	-0.6
4.	9.7 \pm .09	8.5 \pm .07	8.7 \pm .11	+1.2	+1.0
5.	12.3 \pm .08	11.6 \pm .07	11.3 \pm .51	+0.7	+1.0
6.	14.7 \pm .13	13.8 \pm .09	12.9 \pm .36	+0.9	+1.8

*Probable error of the mean.

APPENDIX I

Laboratory Sampling and Assaying of Bituminous Sands by the Carbontetrachloride Extraction Method

This method of assaying Alberta bituminous sands is divided into four parts:

- (a) Preparation of sample for analysis.
- (b) Determination of water content.
- (c) Determination of bitumen content.
- (d) Screen analysis of sand residue.

PART (a) - Preparation of Laboratory Sample

Scope

The apparatus and procedure, although especially developed for drill-cores, are applicable to other bulk samples that may vary widely in their content of clay partings, sand aggregate, and other mineral matter.

Apparatus

- (1) Pans for air-drying - Enameled steel pans
18 x 12 x 2 in. in depth.
- (2) Balance - A balance or scale having a capacity
of 5 kg., sensitive to 0.5 gms.

- (3) Grinder - A sturdy (household or store) meat grinder capable of being taken apart for cleaning. Figure 1 shows a good grinder arrangement for grinding laboratory samples. This assembly consists of a quarter horse power electric motor, a 48 to 1 speed reducing gear and an Enterprise No. 12 meat chopper, inter-connected by means of flexible leather couplings, solidly mounted on a heavy steel plate.
- (4) Mortar and Pestle - A heavy cast iron mortar of 6 pint capacity (9 inch outside diameter) with accompanying pestle.

Procedure

One quarter (longitudinally split) of a two inch drill core varying in length from 5 inches, or shorter, up to 5 feet and weighing from 100 to 1000 grams is usually taken as a single laboratory gross sample.

An aliquot sample of the drill core is placed on pans and allowed to air dry at room temperature to constant weight. The weight of drill core dried should be a multiple of 100 g. as 50 g. are required for the water determination, and 50 g. for the extraction of the bitumen. Twenty-four hours are usually sufficient for this determination as the main purpose is to stabilize the sample weight to avoid errors due to loss of moisture in the subsequent operations. The air drying loss is recorded.

If the sample contains a mixture of soft and hard constituents, the hard rock-like parts should be picked out and ground with the mortar and pestle. The two parts of the sample are mixed together and passed through the grinder. After grinding, the sample must be very thoroughly mixed to a uniform composition and placed in a closed container.

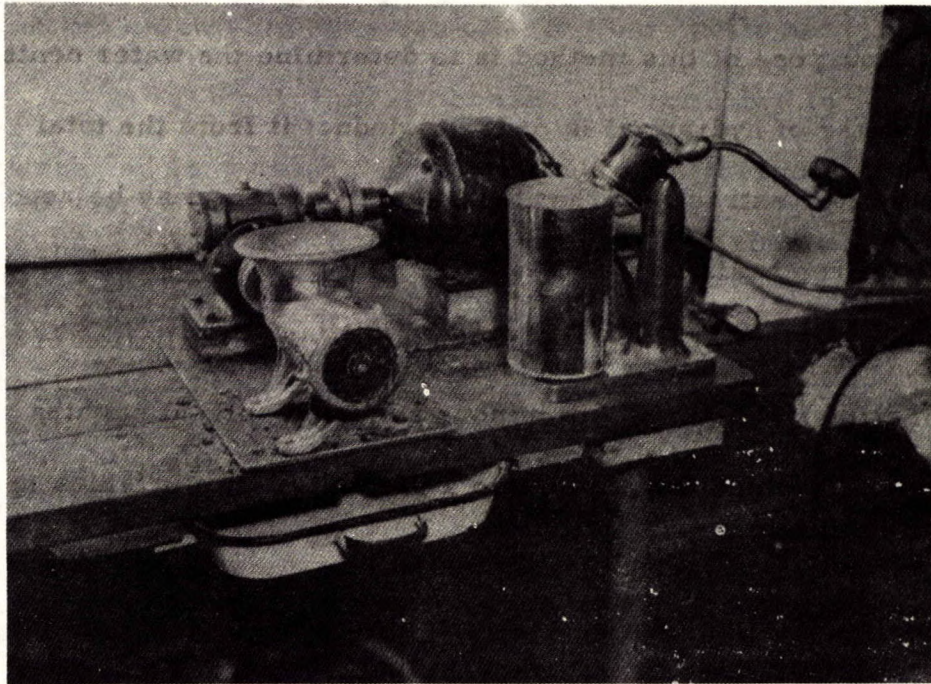


Figure 1 - Power Grinder Assembly for Sample Preparation and Manual Opener for Core Containers.

PART (b) - Determination of Water Content

The method used is essentially the same as the A. S. T. M. Designation D 95-46, which during development (prior to 1921) was known as the Dean and Stark method.

Purpose

The purpose of this method is to determine the water content (other than water of hydration) in order to deduct it from the total bitumen and water extract, so that the bitumen content may be reported on a moisture free basis.

The principle of the method consists in the distillation of the water from a flask containing bituminous sand and solvent naphtha and condensing both naphtha and water into a graduated trap in which the volume of the water can be observed.

Apparatus

Fig. 2 shows a convenient arrangement for multiple determinations of this type.

- (1) Glass flask - Pyrex, round bottom, short neck type, capacity 500 ml.
- (2) Trap - Pyrex, with closed end graduated from 0 to 10 ml. in 0.1 ml. divisions, 18 mm. outside diameter.
- (3) Condenser - Liebig type, 400 mm. long with inner tube 9.5 to 12.7 mm. outside diameter.
- (4) Electric heater - 250 (or 500) watts, rheostat control.

Note:- For convenience, glassware may be purchased with standard taper joints - flask, Corning Cat. No. 4320; trap - Corning Cat. No. 3602; condenser - Corning Cat. No. 2360.

Solvent

A. S. T. M. Dilution Naphtha (see Method D 95-46), a petroleum naphtha conforming to the following distillation requirements: " 5 per cent shall distill at a temperature not below 194°F. (90°C.) nor above 212°F. (100°C.) and 90 per cent shall distill below 410°F. (210°C.)". Oil refinery " Dilution Naphtha" with a distillation range 196° to 273°F. has been found to be a quite satisfactory substitute.

Procedure

Fifty grams, (weighed to the nearest 0.1 gram), of sample are placed in the flask and mixed with 150 cc. of solvent by swirling. Heating is so regulated that the distillate falls from the condenser tip at a rate of from 2 to 5 drops per second. The distillation is continued at the specified rate until no water is visible on any part of the apparatus except at the bottom of the trap.

Between tests it is necessary to clean the apparatus thoroughly to prevent water droplets from adhering to the walls of the trap and condenser. This is accomplished by frequent cleansing with cleaning solution and drying in drying oven.

Calculation

The volume of condensed water measured in the trap multiplied by two (i. e. for a 50 gram sample) is the percentage of water contained in the (air dried) sample tested.

PART (c) - Determination of Bitumen Content

Scope

This method is suitable for the assay of bituminous sands with bitumen contents above one per cent. As a clean sand aggregate is produced, this method may be employed when a screen analysis of the sand is required. In general, this method may be applied to a wide variety of bituminous substances with safety, provided reasonable precautions are taken to ventilate the working area.

Apparatus

Figure 3 shows a convenient arrangement for multiple determinations.

- (1) Soxhlet extraction unit - large size, similar to Corning Cat. No. 3840.
- (2) Extraction thimbles - Whatman, fat free, double thickness, * filter paper, size 43 x 123 mm.
- (3) Electric heater or hot plate.
- (4) Drying oven (electric)
- (5) Muffle furnace (electric)
- (6) Light metal cans to hold thimbles. See Fig. 4.
- (7) Crucibles - 50 ml. capacity
- (8) Desiccators - for metal cans and crucibles
- (9) Evaporating lamps or hot plate
- (10) Analytical balance
- (11) Miscellaneous glassware - graduated 250 ml. glass stoppered graduates, 25 ml. pipette with rubber suction bulb, etc.

* Double thickness is required to reduce silt correction.

Solvent

Carbontetrachloride (CCl₄), technical grade, is used at the Fuel Research Laboratories in this extraction for the following reasons: Carbontetrachloride is not inflammable so the extraction apparatus may be set up on an open bench in a well ventilated room. The relatively high specific gravity of this solvent aids in the suspension of the fine silt coming through the extraction thimbles, making possible a more accurate aliquot of the silt for the estimation of the total mineral aggregate. Carbontetrachloride is also known to be an excellent solvent for a wide variety of bituminous substances. In general, it is superior to benzene in that it is capable of dissolving a slightly greater percentage of the high molecular weight asphaltic substances.

Procedure

The extraction thimble is placed in an open, numbered, tared metal can, with a corresponding lid, and dried in a drying oven at 105 to 110°C. for at least one hour. Then the metal can is removed from the oven, and closed to exclude moisture. After cooling in a desiccator, the metal can is weighed to the nearest 10 mg.

Approximately 50 grams of the sample are then placed in the weighed thimble which in turn is placed in the weighed metal can, the can capped and reweighed in order to determine the weight of the sample.

Changes in weight, due to the hygroscopic nature of the extraction thimbles, can be quite large but are readily controlled by placing the thimble in a light metal can having a closely fitting lid. The aluminum can, shown in Fig. 4, weighing approximately 70 grams, has proven satisfactory for prevention of moisture absorption.

The distilling flask of the Soxhlet extractor is filled with 250 ml. of carbontetrachloride, then the thimble containing the sample is inserted into the upper extraction section of this apparatus. After assembling the apparatus, the boiling rate of the carbontetrachloride is adjusted to avoid overflowing the thimble. The automatic extraction of the bitumen is continued until the extract surrounding the thimble is colourless. The extraction section of the Soxhlet apparatus is then removed from the distillation flask and the thimble is raised above level of solvent until it has drained. If the drained solvent is colourless the extraction may be considered complete.

The thimble from the extraction section is transferred to its respective can and the excess solvent removed under heat lamps in a well ventilated fume hood. When the odour of the carbontetrachloride is no longer perceptible, the open can containing the thimble and sand residue is transferred to a drying oven and dried overnight at a temperature of 105 to 110°C. After drying, the thimble is removed from the oven, and enclosed in the metal can, which is then cooled in a desiccator for one hour, and weighed to the nearest 10 mg.

The loss in weight of the sample on extraction must be corrected for the fine silt passing through the thimble in the following manner. After the extraction has been completed, the contents

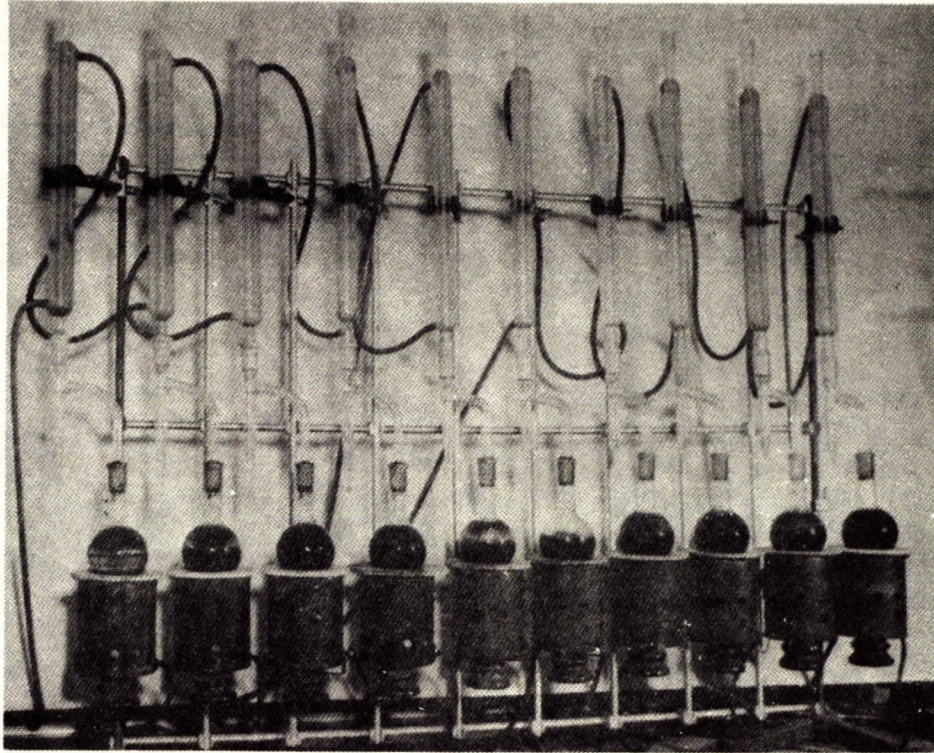


Figure 2 - Multiple Water Determination Apparatus.

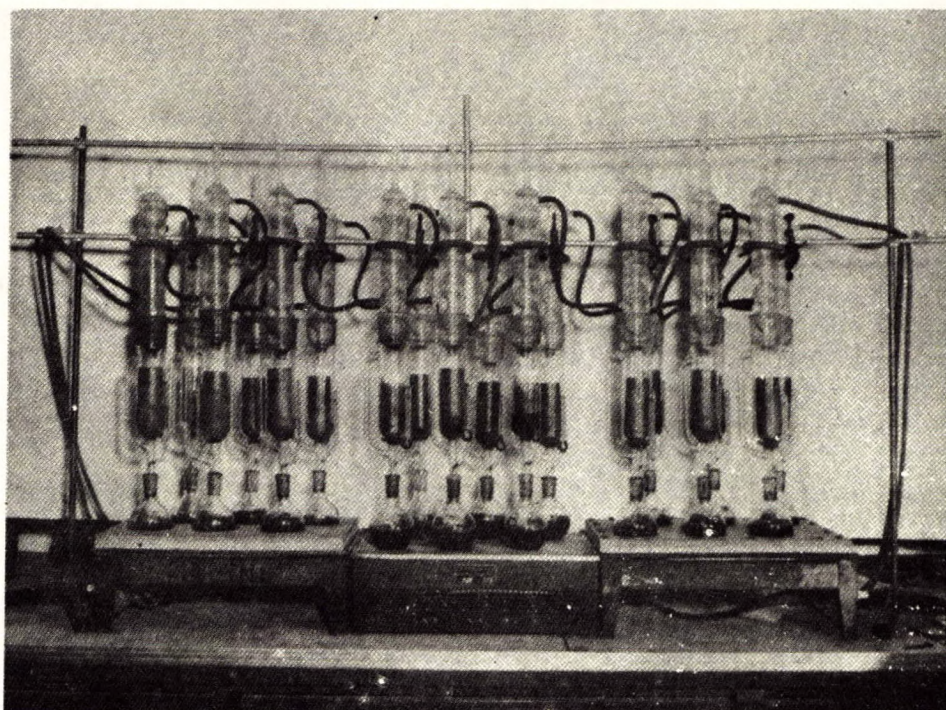


Figure 3 - Multiple Soxhlet Extraction Apparatus

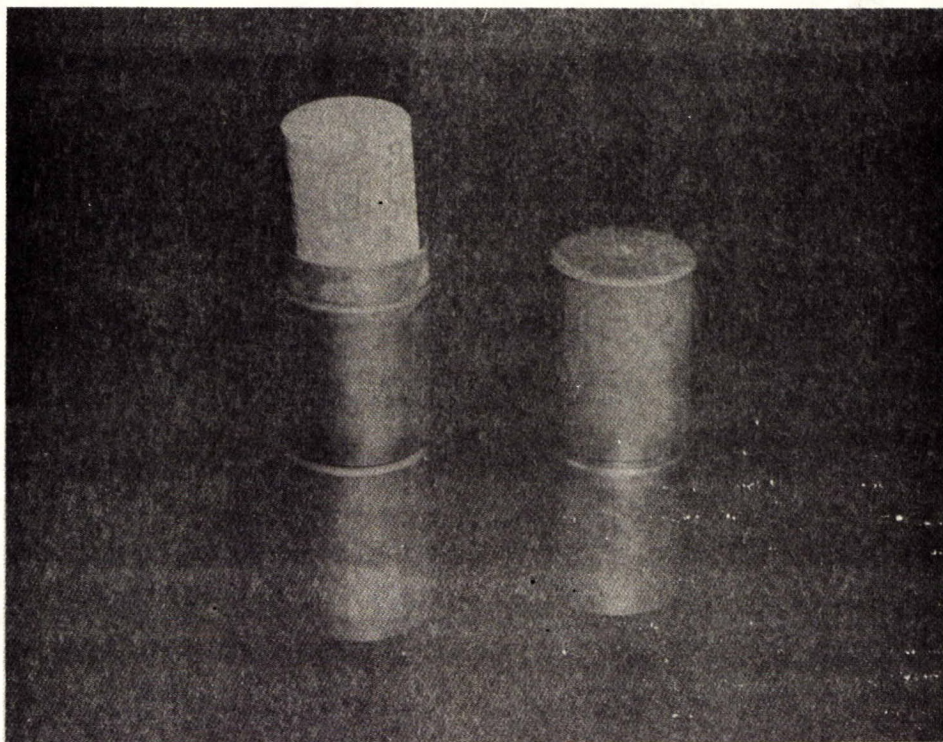


Figure 4 - Metal Holder for Extraction Thimble

of the flask are swirled to bring the finely divided solids into suspension and washed with solvent into a 250 ml. stoppered graduate. After making up the volume to a multiple of 25 ml., the graduate is stoppered and shaken to bring the solids into suspension, and a 25 ml. aliquot is pipetted into a tared crucible and weighed to the nearest 0.1 mg. The solvent is carefully evaporated under heat lamps in a fume hood to avoid spattering. The remaining contents of the crucible are then ashed in a muffle furnace in accordance with the standard procedure for ashing coal or other solid fuel. After removal from the furnace, the crucible is cooled in a desiccator and weighed.

Calculation

Weight of Mineral Aggregate =
Weight of residue in thimble + weight of solids passing thimble.

Weight of solids passing thimble =
Weight of ash in crucible x $\frac{\text{Volume of liquid in graduate}}{\text{Volume of aliquot}}$

$\frac{\text{Weight of Mineral Aggregate} \times 100}{100 - \text{per cent moisture}} = \text{per cent Mineral Aggregate}$
(air dried basis)

100 - per cent Mineral Aggregate (moisture free basis)
= per cent bitumen (moisture free basis)

To facilitate routine calculations the following standard form was adopted.

BITUMINOUS SAND

Date

Soxhlet Extraction with CCl₄

Hole No. Laboratory No.

Can No.

Can + thimble + sample

Can + thimble

Sample

Soxhlet No.

Can + thimble + residue

Can + thimble

Residue

Aliquot

Crucible No.

Crucible + Ash

Crucible

Aliquot ash

Total ash

Residue + ash

Residue + ash, % of sample

Average, residue + ash, % of sample

Average, residue + ash, % of sample, (Moist-free basis)

% of bitumen (Moisture-free basis)

Remarks:

Analyst:

Checked by:

Date:

PART (d) - Screen Analysis of (Extracted) Sand Aggregate

Although a screen (or sieve) analysis of forty grams or so of the sand residue from a fifty gram sample of bituminous sands, extracted in a Soxhlet unit, will give comparable results on a series of samples, it is recommended that the screen analysis be made on a larger sample obtained by combining the residues from duplicate determinations on the same sample.

A. S. T. M. Designation D 451-40 "Standard Method of Test for Sieve Analysis of Granular Mineral Surfacing for Asphalt Roofing and Shingles" is recommended - selecting for use from the set of consecutive sieves specified the 20, 40, 60, 100, 150 and 200 mesh sieves. A Tyler Ro-tap shaker machine, as installed and used at the Fuel Research Laboratories, is specified as "a mechanically operated sieve shaker, which imparts to the set of sieves a rotary motion and tapping action of uniform speed". Otherwise, the procedure for making the screening test is the same as specified in D 451-40.

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Note: The screen analysis of the extracted sand aggregate is not necessary for the comparison of the laboratory assay methods, discussed in this report, but it is included because it completes the laboratory assay of a bituminous sand sample.

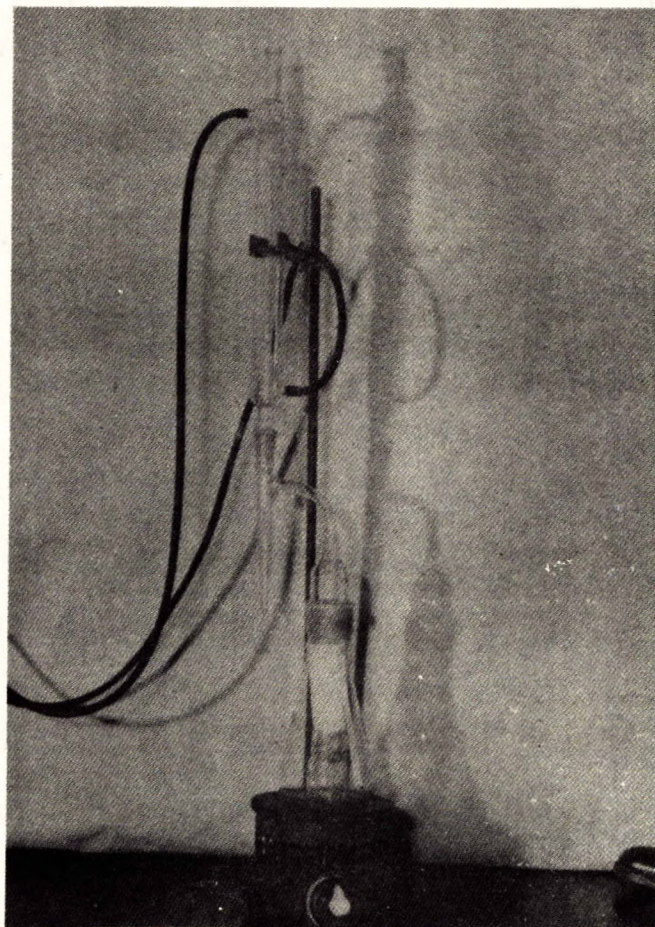


Figure 5 - Modified Toluene Extraction Apparatus

APPENDIX II

Laboratory Sampling and Assaying of Bituminous Sands by the Toluene Extraction Method

This method was developed by the Calvan Consolidated Oil and Gas Company Limited for use in their Athabasca Tar Sands Project. It simultaneously effects a separation of the bituminous sand sample into its three components; water, sand and bitumen. The water is removed by distillation, the bitumen by solvent extraction and the clean sand residue is left in the extraction thimble. As the preparation of the laboratory sample, and the screen analysis of the sand residue have been fully described in Appendix I, Parts (a) and (d), they have been omitted here.

Scope

This method is suitable for the assay of the bituminous sands from Northern Alberta. However, a certain amount of caution should be exercised, in applying this method to bituminous substances in general as some may have a lower solubility in toluene than in carbontetrachloride.

Apparatus

Fig. 5 shows the assembled extraction apparatus.

- (1) Erlenmeyer Flask, Pyrex, Wide Mouth, 1000 ml. capacity.
- (2) Thimble Support Cup - Pyrex Glass - this cup traps a small amount of raffinate above the general solvent level. This enables the progress of the extraction to be assessed visually.
- (3) Trap-Pyrex - Dean and Stark pattern, graduated from 0 to 10 ml. in 0.1 ml. divisions.
- (4) Condenser - Liebig type, 400 mm. long with inner tube 9.5 to 12.7 mm. outside diameter.
- (5) Extraction thimbles - Whatman, fat free, double thickness, filter paper, size 43 x 123 mm.
- (6) Light metal cans to hold thimbles.
- (7) Porcelain crucibles - 50 ml. capacity.
- (8) Desiccators - for metal cans and crucibles.
- (9) Analytical balance.
- (10) Drying oven (electric)
- (11) Muffle furnace (electric)
- (12) Evaporating lamps or hot plate.
- (13) Electric heater or hot plate.
- (14) Miscellaneous glassware - graduated 250 ml. glass stoppered graduates, 25 ml. pipette with rubber bulb etc.

Note: For convenience, extraction glassware should have standard taper ground glass joints which will facilitate assembly and minimize vapour leakage and absorption that would be encountered with a cork joint assembly.

Solvent

Among the many possible solvents that could be used for extraction, toluene has been chosen for its capacity to dissolve the bitumen, its stability with respect to heat and oxygen, and the fact that its boiling point at atmospheric pressure is 10.6°C. above that of water. Thus, the hot toluene vapours that rise through the bituminous sand material are

sufficiently warm to vapourize the water present in the sample. This water vapour is carried along with the toluene into the condenser, where it also is condensed and falls back into the graduated Dean and Stark trap. Because toluene and water are immiscible, the two liquids separate into two distinct layers in the trap. Since water has the greater density it forms the bottom layer and the toluene floats on top and the overflow returns to the extraction flask.

Procedure

The extraction thimble is placed in an open, numbered, metal can with the corresponding can lid, and is dried in a drying oven at 105 to 110°C. for at least one hour. It is then removed from the oven, cooled in a desiccator and weighed to the nearest 10 mg. Approximately 50 grams of sample are placed rapidly in a thimble and metal container, whose combined weight is known. The container is closed and reweighed to determine the weight of sample. (Note:- the Calvan Oil and Gas Company Limited recommended a 30 gram sample but this was increased to 50 grams in order to minimize, as much as possible, differences between this method and the carbontetrachloride extraction method currently used by the Fuels Division.) The thimbles are quite hygroscopic, hence, it is necessary to exercise care throughout the determination to avoid errors due to the accumulation of moisture.

The extraction flask is filled with 200 ml. of toluene, and the thimble containing the sample is carefully placed in the flask so that it is supported in a vertical position above the solvent by the glass support cup. The apparatus is assembled and heat is applied to begin the extraction. The boiling rate of the toluene is carefully controlled to avoid overflowing the thimble. The bitumen extraction and the vapourization of the water is allowed to continue for one hour after the toluene dripping from the thimble into the support cup is colourless and the water level in the trap is constant.

After the extraction is considered complete, the volume of water in the trap is recorded, and the thimble is transferred from the extraction flask to its respective can and excess solvent removed, under evaporating lamps, or on a hot plate, placed in a well ventilated fume hood. When the odour of solvent is no longer perceptible, the can is transferred with its thimble and sand residue to a drying oven and dried at 105 to 110°C. overnight. After drying, the can is removed from the oven, closed, cooled in a desiccator for one hour, and then weighed.

To improve the accuracy, and to enable a strict comparison to be made with the carbontetrachloride extraction method used by the Division of Fuels, it is necessary to make a correction for the quantity of silt passing through the thimble into the extraction solvent. The

following procedure is employed to determine this correction:- The contents of the flask are poured into a 250 ml. stopper-type graduate and any remaining residue is washed from the flask into the graduate with more solvent. The contents of the graduate are made up to a volume which is a multiple of 25 ml., and shaken well to bring solids into suspension. A 25 ml. aliquot is then pipetted into a tared crucible and weighed to the nearest 0.1 mg. This is followed by carefully evaporating the solvent under heat lamps in a fume hood to avoid spattering. The remaining contents of the crucible are then ashed in a muffle furnace in accordance with the standard procedure for ashing coal or other solid fuel. After removal from the furnace, the crucible is cooled in a desiccator and weighed.

Calculation

Weight of Mineral Aggregate =
Weight of residue in thimble + weight of solids passing thimble.

Weight of solids passing thimble =
$$\text{Weight of ash in crucible} \times \frac{\text{Volume of liquid in graduate}}{\text{Volume of aliquot}}$$

Weight of water = Volume of Water in trap

Percent Mineral Aggregate (dry basis) =
$$\frac{\text{Weight of mineral aggregate}}{\text{Weight of sample} - \text{weight of water}} \times 100$$

Percent Bitumen (dry basis) =
100 - percent mineral aggregate (dry basis)

Percent water =
$$\frac{\text{Weight of water}}{\text{Weight of sample}} \times 100$$

APPENDIX III

Laboratory Sampling and Assaying of Bituminous Sands by the "Density" Method

A complete description of this method is given in Bureau of Mines Memorandum Series No. 87, dated January 1944. In this report only Method 2 "The Solvent-Weight Method" described in the above publication was used.

This method of assaying Alberta bituminous sands may be divided into three parts:

- (a) Preparation of sample for analysis.
- (b) Determination of water content.
- (c) Determination of bitumen content.

As parts (a) and (b) are fully described in Appendix I of this report they are omitted here. It will also be noted that this method does not give the dry mineral aggregate which is required for a screen analysis.

Scope

This is a rapid method for the determination of bitumen content. Although designed and developed for testing drill-core samples of bituminous sands, it is applicable to any two component (bitumen-mineral aggregate) system of which each component has a known constant density. As a result of many determinations, the values, of

2.62 and 1.00, were adopted as the densities of the mineral aggregate and bitumen components respectively. For the purpose of this test, the combined bitumen and water contents are considered as a single component.

Apparatus

Figure 6 shows a volumetric flask with interchangeable filling funnel and calibration head.

- (1) Calibrated volumetric flasks (pycnometer type) - nominal 250 ml. capacity for 100 to 200 gram samples.
- (2) Balance - a balance with a capacity of 500 grams and a sensitivity of 20 mg.
- (3) Miscellaneous - sample scoop, beakers, dropping pipette.

Solvent

Pure toluene of specific gravity 0.8660 at 20°/4°C. (68°F.) and with a thermal coefficient of expansion of 0.00085 cc. per °C. (or 0.00047 cc. per °F.) was used for this series of determinations, but technical grade toluene of known specific gravity and thermal coefficient of expansion may also be used.

Procedure

The sample should be at, or close to, room temperature before proceeding with the determination to avoid temperature-volume changes.

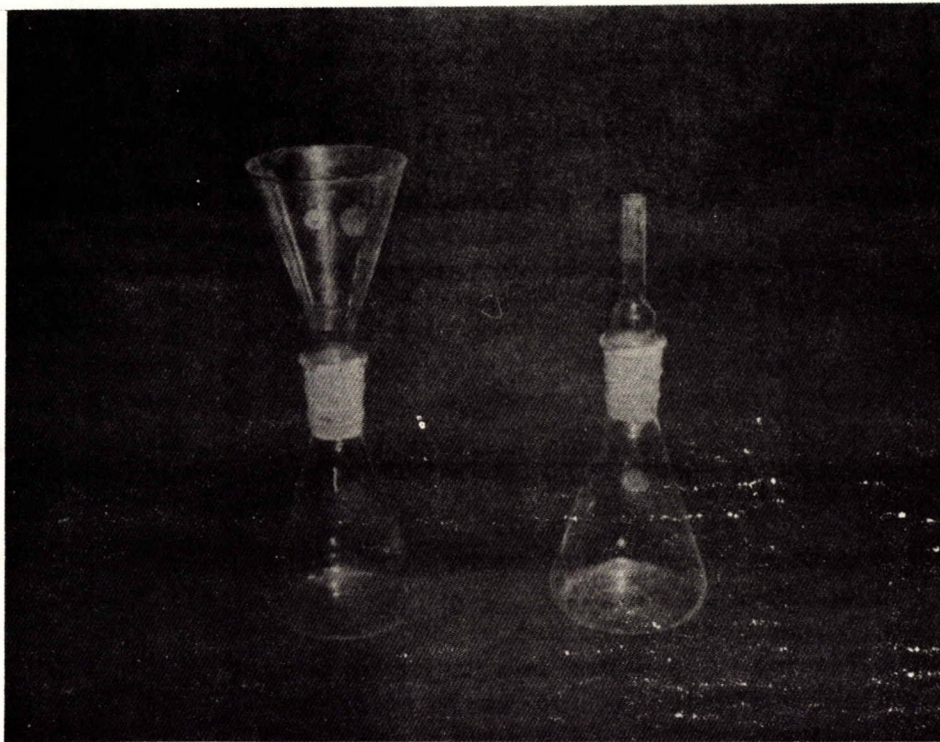


Figure 6 - Calibrated Volumetric Flask

To simplify the calculations it is convenient to use the same weight for all samples, e. g., 100 grams of bituminous sand. The sample is weighed into a tared volumetric flask. Sufficient toluene is added to cover the sample completely. The mixture is then stirred with a glass rod or suitable mechanical stirrer in order to effect complete penetration of the sample by the solvent and to liberate any air bubbles. Finally, the flask is filled to the calibration mark, and after all bubbles have been expelled, the flask and contents are reweighed. Immediately after weighing the temperature of the flask and contents is determined.

Formula Derivation

Let W = weight of sample, grams
 w = weight of bitumen and water, grams
 B = % bitumen by weight
(moisture free basis)
 b = % bitumen and water in sample by weight
 d_1 = density of mineral aggregate, gm/cm³
 d_2 = density of bitumen and water, gm/cm³
 V_1 = volume of mineral aggregate, cm³
 V_2 = volume of bitumen and water, cm³
 V = volume of sample, cm³

$$V_1 + V_2 = V \quad (1)$$

$$d_1 V_1 + d_2 V_2 = W \quad (2)$$

Multiplying (1) by d_1 and subtracting (2)

$$V_2 (d_1 - d_2) = d_1 V - W \quad (3)$$

Rearranging (3)

$$V_2 = \frac{d_1 V}{d_1 - d_2} - \frac{W}{d_1 - d_2} \quad (4)$$

$$b = \frac{w}{W} \times 100 = \frac{V_2 d_2}{W} \times 100 \quad (5)$$

Substituting for V_2 in (5)

$$\begin{aligned} b &= \left(\frac{d_1 V}{d_1 - d_2} - \frac{W}{d_1 - d_2} \right) \times \frac{100 d_2}{W} \\ &= \frac{100 d_1 d_2 V}{(d_1 - d_2) W} - \frac{100 d_2}{d_1 - d_2} \quad (6) \end{aligned}$$

d_1 and d_2 are considered as constants equalling 2.62 and 1.00 respectively so equation (6) reduced to

$$b = 161.7 \frac{V}{W} - 61.73$$

∴ the % Bitumen (moisture free basis) is given by

$$B = \frac{\left(161.7 \frac{V}{W} - 61.73 - \% H_2O \right)}{100 - \% H_2O} \times 100 \quad (7)$$

Calculations

Known or directly determined properties

1. W_f - weight of flask
2. V_f - volume of flask
3. $W_f + W$ - weight of flask plus sample. From this calculate W .
4. $W_f + W + W_t$ - weight of flask plus sample plus toluene
5. T - temperature of toluene
6. % H₂O - determined by ASTM method D 95
7. Specific Gravity of Toluene at 20°C.
8. Specific Gravity Coefficient of Toluene

Calculate

Volume of Toluene

= weight of toluene + specific gravity at T °C.

Volume of Sample = V

= Volume of flask - Volume of toluene

Percent Bitumen (moisture free basis) is found by substituting the values obtained for V , W and % H₂O in equation (7)

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