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Total Analysis of Mineral Wastes Containing Bitumen, Solvent, Water and Solids.*

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Abstract. Compared with the existing methods of analyses a quick and more reliable procedure has been developed to determine the bitumen, solvent, water and solids content of mineral wastes, in order to serve efficiently both plant operations and research needs. Bitumen and hydrocarbon solvent in the samples are extracted using solvents that do not absorb in the CH_3 group region of the ^{1}H NMR spectrum. Bitumen is then determined spectrophotometrically, and the process solvent by quantitative ^{1}H NMR. Water is dissolved in methanol and subsequently determined using a Karl Fischer titrator. Solids are measured gravimetrically. This procedure was used to analyse mineral tailings from the centrifuge stage of the hot water process for the extraction of bitumen from oil sands. Results for all four components; bitumen, process solvent, water and solids, had relative standard deviations much lower than the ones obtained using a modified Dean-Stark method. Mineral agglomerates obtained after the extraction of bitumen from oil sands using the solvent extraction-spherical agglomeration method, were also analyzed by both methods. As a result of compaction occurring during solids agglomeration, complete extraction of bitumen by the Dean-Stark method could not be achieved. Extraction of bitumen and precision of results were much improved for agglomerated samples using the proposed method of analysis which is amenable to wastes containing solids, water, bitumen and solvent in any proportion.

INTRODUCTION

The extensive deposits of Athabasca oil sands are assuming an increasing role in supplying Canada's liquid hydrocarbon needs. One commercial plant, Suncor Inc., has operated since 1967, using the hot water process technology for the extraction of bitumen from oil sands. The Syncrude Canada Ltd. plant, which is designed to produce 109,000 barrels of synthetic crude per day, began production in 1978. Fundamental to the successful operation of these extraction plants are reliable analytical methods for the analysis of the various process streams, such as bitumen-rich froth and tailings containing mineral matter, residual bitumen, solvent and water. The bitumen froth collected from the hot water extraction process is treated to remove solid particles and water. The process consists of a diluent addition step to reduce the hydrocarbon density, two stages of centrifugation to remove solids and water, and a diluent recovery step. Analytical inspection of these process streams includes analyses for bitumen, diluent, water and solids. These analyses are essential for process control and material balance calculations.

Typically, the determination of bitumen, diluent, water and solids is performed by separating the sample into the individual components [1]. However, separation of the diluent from bitumen is difficult to achieve and poses problems in the independent determination of the two components. Bitumen is usually determined spectrophotometrically [2] or gravimetrically [3], diluent (naphtha) by difference or by gas chromatography [1]. If naphtha is determined by difference all the errors accumulate in the results for this component. In the GC method errors arise from dilution and the small volume required for injection (1 μl) [1]. Also, the absorption of the asphaltenes from the bitumen on the column packing materials shortens the column life and increases maintenance, making this method rather cumbersome for the estimation of the diluent in the presence of bitumen. The purpose of this investigation was to develop a rapid, simple and accurate analytical procedure for the total analysis of samples containing solvent, bitumen, water and solids.

In this study naphtha and bitumen were extracted using a solvent that does not have methyl or methylene protons, e.g. benzene or carbon tetrachloride. Bitumen

is determined spectrophotometrically and the naphtha by measuring the methyl peak height or area in the ¹H NMR spectrum. Water is determined by Karl Fischer titration and the solids gravimetrically.

EXPERIMENTAL

Sample handling. Three types of samples were used for this study; mineral tailings from the hot water process, mineral agglomerates obtained after the extraction of oil from oil sands using the solvent extraction spherical agglomeration (SESA) process and aqueous tailings from a solvent/bitumen contactor used by Energy, Mines and Resources Canada (EMR). All samples contained bitumen, naphtha, water and mineral matter in various proportions. The first two types of tailings were stored in one gallon metal cans capped securely to minimize losses due to evaporation. Aqueous tailings from the EMR solvent/bitumen contactor were provided in 1 Litre and 250 mL glass jars.

Because the agglomerates were kept under process solvent naphtha, the handling techniques for these samples were different from the other two types of tailings. About 50 g of agglomerates were removed using a perforated strainer to drain excess solvent and placed in a 250 mL glass jar. A rolled kimwipe tissue was placed on top of the agglomerates. The jar was inverted for 10 minutes to remove drainable solvent, 20-30 of these agglomerates were then transferred into another 100 mL preweighed dried glass jar and weighed again to determine the weight of the agglomerates by difference.

There was no solvent drainage step for the centrifuge tailings. These tailings were mixed thoroughly for homogeneity before weighing.

Aqueous tailings were agitated on a reciprocating shaker for 30 minutes to ensure homogeneity. After removing them from the shaker, the contents were kept shaken by hand until transferred into a preweighed glass jar.

Extraction of bitumen and diluent. A 50 mL sample of the analytical solvent was introduced into the sample jar which was sealed tightly with a screw cap containing a polyethylene insert. The solvents tested for extraction included; carbon tetrachloride, benzene, toluene, tetrachloroethylene, dioxane, hexanol, isopropanol/toluene, benzene/phenol and benzene/methanol. The jars were agitated using either a reciprocating shaker, paint shaker, Spex mixer or a Waring blender. Mixing times were varied depending on the mode of agitation. Five min. were found to be sufficient for good mixing with the Spex mixer or Waring blender. The paint shaker required 15-30 min., whereas much longer times (1-4 h) were found to be necessary on a reciprocating shaker.

Quantitative ¹H NMR. The use of ¹H NMR for quantitative purposes is based on the principle that when the spectrometer performs ideally and measurements are made in a prescribed manner, the area under an absorption band is directly proportional to the number of hydrogen atoms contributing to the absorption. The same correlation exists between peak heights and the number of hydrogens for a well defined sharp peak [7]. Because the number of hydrogens of any particular type in a molecule is proportional to the concentration of that molecule, an indirect correlation exists between the concentration of a molecule and the peak height or peak area of a particular group of magnetically equivalent hydrogens in the ¹H NMR spectrum.

¹H NMR measurements. ¹H NMR measurements were performed on a Varian EM-360 NMR spectrometer (60 MHz); 500 μL of solution in a 5 mm outer diameter tube was used in each case. Gain and amplitude were adjusted to give integrations/peak heights within the range of the chart paper using lowest and highest concentrations. Once adjusted all the parameters were kept constant for subsequent measurements. Both peak heights and integrated areas of the methyl peak at about 1 ppm downfield from TMS (Figure 1) in the
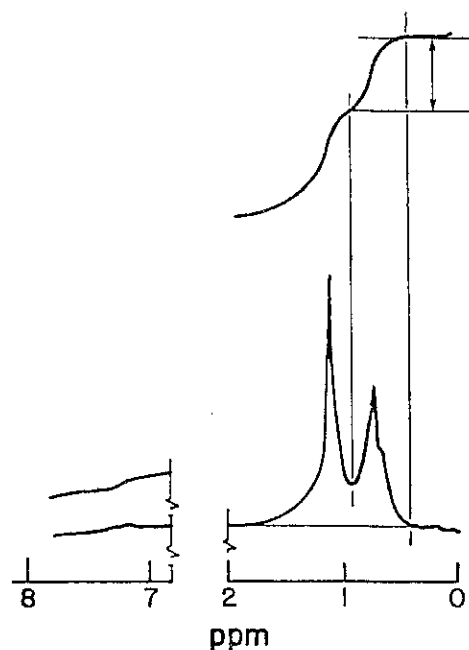

Figure 1. Proton NMR spectrum of bitumen, illustrating the measurement of the area of methyl peak.

¹H NMR of bitumen, naphtha and varsol were employed in the quantitative determinations.

Preparation of the standard bitumen samples. Standard bitumen samples were prepared for calibration curves by extracting oil sand feeds for SESA and EMR solvent/bitumen contactor processes using toluene as solvent [4]. Non filterable solids were removed from the bitumen solution by centrifugation. The solvent was removed at 100°C first in a Brinkmann rotary

evaporator under reduced pressure and later in the Brinkmann SC/24 R sample concentrator under nitrogen at 80°C. The amount of residual solvent was then measured using infrared spectroscopy [4] and proton NMR[5].

One standard sample of bitumen was obtained from the Alberta Research Council sample bank. This was a sample of coker feed bitumen from Suncor, prepared for use in a round robin study of bitumen analyses [6]. This sample contained an unknown amount of residual naphtha. An attempt to estimate this naphtha content was made by comparing the transmittance of a known solution of the bitumen in toluene with a calibration derived for a well characterised bitumen of a similar type. This comparison indicated a naphtha content of 0.4 w/w%.

Calibration curves.

Bitumen – Three standard samples of bitumen obtained as outlined above, were used for the calibration curves. The amount of residual process solvent, quantitatively determined by infrared and ¹H NMR, was applied as a correction to the bitumen content. Bitumen samples, accurately weighed to 0.1 mg, were used to prepare stock solutions (≈ 30.0 % W/V) in various solvents for analysis. Serial dilutions of the bitumen stock solutions were then prepared in the concentration range 0.5 - 30 % for NMR and 0.01 - 0.1 % for spectrophotometry in the visible spectral region. For NMR calibrations, the peak height and the area of the methyl peak at ca. 1.0 ppm downfield from tetramethysilane in the ¹H NMR spectrum were measured for each concentration. For spectrophotometric determinations, absorbances at 530 nm were determined in the 0.01 - 0.1 % range. Plots of the per cent bitumen vs absorbance or peak height and peak area produced straight lines passing through the origin.

Diluent – Measurements were made for two bitumen diluents, namely naphtha and varsol (Stoddard solvent). Solutions of both naphtha and varsol ranging in concentrations from 0.2 - 60 % W/V were prepared in CCl_4. The height and the area of the methyl peak at ca. 1.0 ppm downfield from tetramethylsilane were determined for each concentration as described above for bitumen. The plots of the per cent naphtha vs peak height and peak area produced straight lines passing through the origin.

Benzene and toluene – Calibration curves were also prepared for benzene and toluene in order to determine their residual amounts in the standard bitumen samples. Carbon tetrachloride solutions of toluene and benzene were prepared ranging in concentration from 0.1 - 10 %. Areas and peak heights of the methyl peak for toluene and aromatic signal of benzene were measured from their ¹H NMR spectra. Plots of the per cent concentrations vs areas and peak heights produced straight lines in both cases.

Determination of varsol / naphtha + bitumen in a mixture – The methyl peak height or the area, measured as outlined above, represents the total peak height or peak area due to contributions from both diluent and bitumen. Bitumen concentration was separately determined spectrophotometrically by measurements of absorption at 530 nm [2]. From the concentration of bitumen thus determined, the peak heights or peak areas due to the methyl groups in bitumen can be calculated. Subtracting the value for the methyl absorption due to the bitumen from the total value for the mixture gives the peak height or area due to the process diluent, naphtha or varsol.

Water determination – Water was determined using the Fisher Scientific model 392/395 Automatic Karl Fischer Titrator. Karl Fischer reagent was standardized using sodium tartrate ($Na_2C_4H_4O_6 \cdot 2H_2O$). Standardization was checked once a week. However, the titre value for the Karl Fischer reagent in each bottle could be significantly different. Therefore, whenever replacing a new bottle of Karl Fischer reagent, it should be standardized. We have also noticed that standard water solutions give reproducible results of high accuracy and precision only when prepared freshly or obtained from a sealed bottle. Measurements using sodium tartrate on the other hand are accurate, precise and reproducible at all times. The procedure for the determination of the water content of the tailings was as follows: a weighed amount (20-30 g) of the sample was transferred to a preweighed 100 mL glass jar. Methanol (50 mL) was then added to the tailings in the jar. The jar was tightly capped and then placed on a paint shaker and the tailings/methanol mixture shaken for 5 minutes. After removing the jar from the shaker, it was allowed to stand upright for 10-15 min. to settle the mineral solids. Aliquots of the resultant extract solution were filtered using a small fine porosity fritted glass tube and then analysed for water content. Filtered aliquots of 500 µL were used for water determinations. A 500 µL sample of methanol was also titrated for blank moisture determination.

Subsampling was found to give differences of 4-10% in the measured values for water content. Consequently, most water determinations were done on the same sample after removal of a known volume for bitumen and naphtha determination.

Solids determination – After the aliquots of sample extract solution were removed for water, bitumen and diluent analyses the remaining extract was filtered to separate the solids using a fine pore glass frit filtering funnel containing a layer of Celite hyflo super-cel filter aid. The solids were transferred quantitatively to the filter funnel and washed with several portions of solvent blend until the effluent appeared colorless. The clean solids were finally washed with acetone to aid in drying. The funnel and solids are dried in the oven at 110°C, allowed to cool and then reweighed.

RESULTS AND DISCUSSION

Extraction of bitumen and diluent from tailings. Choice of solvent and mode of agitation. The results for a number of solvents and agitation modes are given in Table 1. Because the bitumen/naphtha recoveries obtained using a reciprocating shaker were poor, these results are not included in the Table. Best recoveries were obtained with a short period of vigorous agitation on a Spex mixer followed by a more gentle agitation on a paint shaker to reagglomerate the solids. Also, the results were much more reproducible when obtained with a Spex mixer than with the Waring blender or paint shaker, as shown by the smaller values of the standard deviations. Reagglomeration of the solids occurred on shaking. However, the new agglomerates formed in the paint shaker were much larger than the original agglomerates and were not of uniform size. Reformed agglomerates on the Spex mixer were, on the other hand, about 100 times smaller and more uniform than the original agglomerates. The Waring blender did not always completely break down the solids. These results demonstrate that the initial breakdown and the uniform distribution of the agglomerates is very important for complete mixing and subsequent recovery of bitumen and diluent from agglomerates.

For hot-water process aqueous and mineral tailings, the mode of agitation was not as significant as for mineral agglomerates, in terms of total recoveries of bitumen and diluent. However, the time required for the total recovery of the organic material from the tailings varied considerably: from about 1 h in a reciprocating shaker to 5 min. in a Spex mixer. About 15 min. were required in a paint shaker.

The choice of solvent for the extraction of organic material from aqueous effluents and mineral agglomerates is limited because of the requirement that it should not absorb in the region of interest of the ¹H NMR spectrum. In the case of bitumen, naphtha and Stoddard solvent this region is 0.5 to 2.0 ppm downfield from tetramethylsilane. Inspection of the data in Table 1 indicates that greater extraction of bitumen and naphtha occurred when using 15% phenol in C_6H_6 or 10% methanol in C_6H_6. The presence of phenol or methanol in benzene increases the water miscibility of the solvent which appears to be important in order to obtain the good dispersion of the solid phase required for effective extraction.

It is generally believed that the composition of the bitumen extracted using different solvents will be different. More polar solvents will be expected to dissolve some of the toluene insoluble, polar organic matter adsorbed on the clays present in oil sands. Since bitumen is usually defined as the toluene-soluble material, the organic matter extracted using solvents other than toluene should be different both in composition and quantity from the toluene-soluble bitumen. This is particularly true for low grade samples where the

Table 1. Concentration[a] of bitumen and naphtha[b] in agglomerated low grade oil sands.

Solvent	Paint shaker (30 min.)			Spex shaker (5 min.)			Waring blender (5 min.)		
	bitumen	naphtha	total	bitumen	naphtha	total	bitumen	naphtha	total
CCl_4	0.79[c] ±0.39	1.13 ±0.16	1.92 ±0.38	1.39 ±0.16	1.43 ±0.14	2.82 ±0.30	0.76 ±0.27	1.19 ±0.44	1.95 ±0.71
C_6H_6	1.09 ±0.15	1.66 ±0.49	2.74 ±0.63	1.25 ±0.05	1.85 ±0.27	3.10 ±0.32	0.84 ±0.22	1.95 ±0.38	2.79 ±0.48
toluene	0.79 ±0.04	—	—	0.98 ±0.03	—	·	0.86 ±0.04	—	—
15% phenol in C_6H_6	1.21 ±0.01	2.01 ±0.11	3.22 ±0.09	1.31 ±0.02	2.01 ±0.09	3.32 ±0.12	0.79	1.34	2.13
10% methanol in C_6H_6	1.40	2.07	3.47	1.48 ±0.01	1.99 ±0.17	3.47 ±0.18	0.35	1.30	1.65

[a] in w/w%

[b] the amount of naphtha determined from total loss in weight at 120°C for two hours, after subtracting the weight of water determined independently by Karl Fischer was found to be 2.23 ± 0.16

[c] 0.79 ± 0.39 w/w% bitumen.

NOTE: No attempt was made to homogenise the total sample of agglomerates. Therefore, the results for the different samples may not be directly comparable.

toluene insoluble fraction represents a much greater proportion of the total organic, compared to a high grade sample. For some samples, therefore, the actual amount of bitumen determined will vary depending on the solvent used.

Spectrophotometric determination of bitumen. Bitumen is a complex mixture of a large number of organic molecules and is therefore difficult to measure quantitatively. The determination of bitumen by the spectrophotometeric method is based on the linear relationship between the absorbance at 530 nm and the concentration of the bitumen solution. However, the amount of the colored material giving rise to absorbance at 530 nm can vary in different samples of bitumen depending upon the oil sand deposit or treatment of the bitumen. This is shown in Figure 2, which is a plot of the concentration versus transmittance at 530 nm for 3 bitumen samples in toluene. It is obvious that a calibration curve prepared for one bitumen type obtained from one particular site of a sand deposit cannot be used to determine the bitumen content of a sample from another deposit area if high accuracy in bitumen determination is required. However, in the present investigation when bitumen was determined using a calibration based on either the bitumen actually present in the sample or on a clean
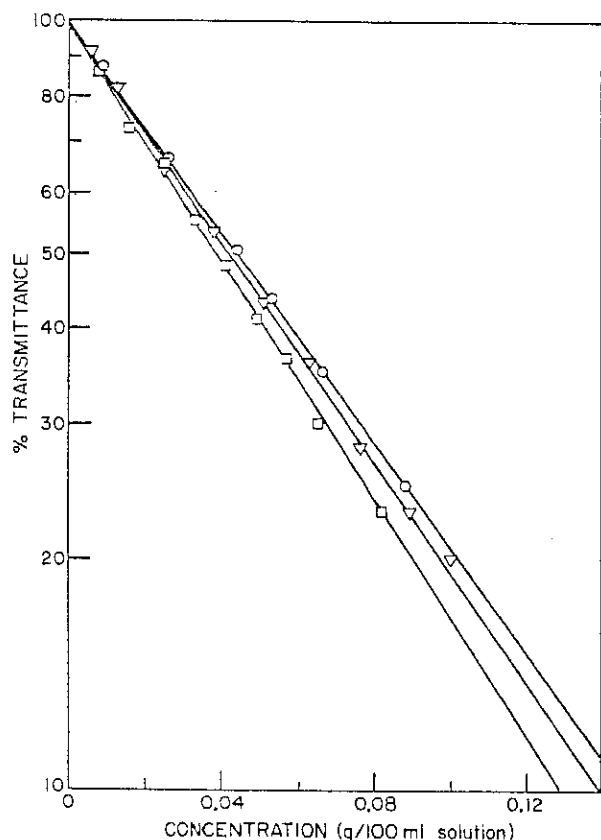
bitumen obtained from the Alberta Research Council the two results fell within ± 2%.

The asphaltene content of the various bitumen samples used in this study was plotted against the slope of the spectrophotometric calibration curves. However, no correlation was found, suggesting that the calibrations do not depend upon the asphaltene content of the bitumen. Obviously the quantity of the material absorbing at 530 nm varies in different bitumen samples.

The choice of solvent is an important consideration in the spectrophotometric determination of bitumen. Using the same solvent for calibration and the actual determination is important because the calibration for the same bitumen sample in other solvents could be quite different. This is evident from Figure 3 which shows calibration curves for the same type of bitumen in various solvents. The reasons for these differences are uncertain but may be related to the concentration units used. For example a plot using w/w% gives much closer coincidence of the curves than the illustrated data using w/v%.

Determination of residual solvents in bitumen. The procurement of unaltered standard samples of bitumen

Figure 2. Spectrophotometric calibrations for 3 bitumen samples in toluene. Measurements made at 530 nm with a cell path length of 1.2 cm.
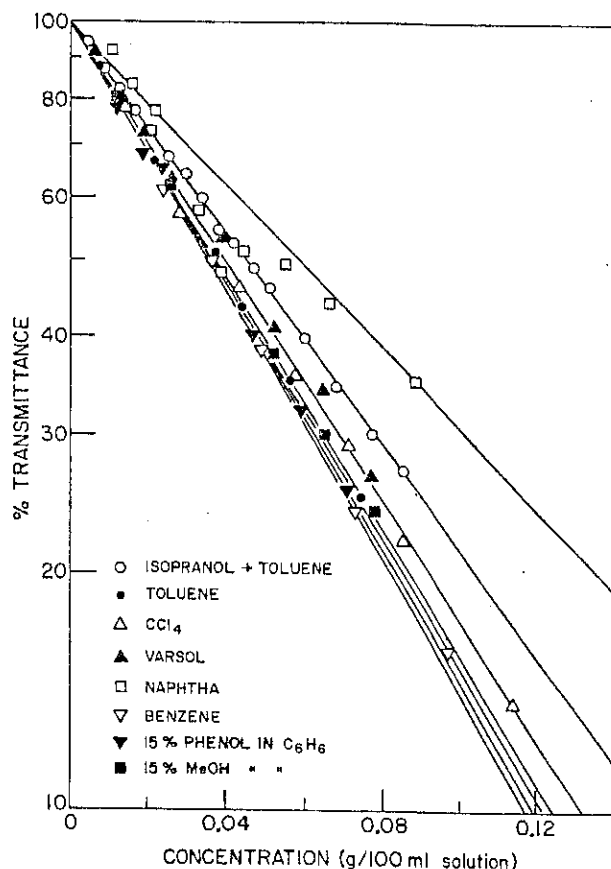

Figure 3. Spectrophotometric determination of bitumen. Calibration curves for the same bitumen samples in various solvents. Measurements made at 530 nm with a cell path length of 1.2 cm.

from oil sands is a serious problem, recognized by Clark in 1950 [8]. Oil does not separate from the native sands and water without the use of either chemical aids, solvent, heat or extreme mechanical force, all of which may significantly alter the oil. Since no method of separation that can guarantee an oil sample free from alteration exists, the first problem encountered in obtaining a standard sample of bitumen is the development of an acceptable separation procedure. Of the various separation methods, solvent extraction of bitumen from oil sands has been recommended as the most suitable method for this purpose [4].

The major drawback of the solvent extraction method is that it is not practical to remove completely all the residual solvent from the bitumen. Hence, analytical techniques are required to determine quantitatively the amount of residual solvent in bitumen. Commonly used solvents for the extraction of bitumen from oil sands are benzene, toluene and methylene chloride. All of these have sharp signals well separated from most bitumen signals in the ^{1}H NMR. Quantitative determination of these solvents in bitumen should therefore be possible if a correlation between the peak areas and concentrations can be found. A plot of % concentrations against the areas of the methylene peak of methylene chloride, the methyl peak of toluene and the aromatic peak of benzene is shown in Figure 4. All three plots are good straight lines with zero intercepts, indicating linear correlations between the peak areas and w/v% concentrations.

Estimation of bitumen naphtha/Stoddard solvent using ^{1}H NMR. For the quantitative determination of bitumen in various solvents, correlations between the % con-
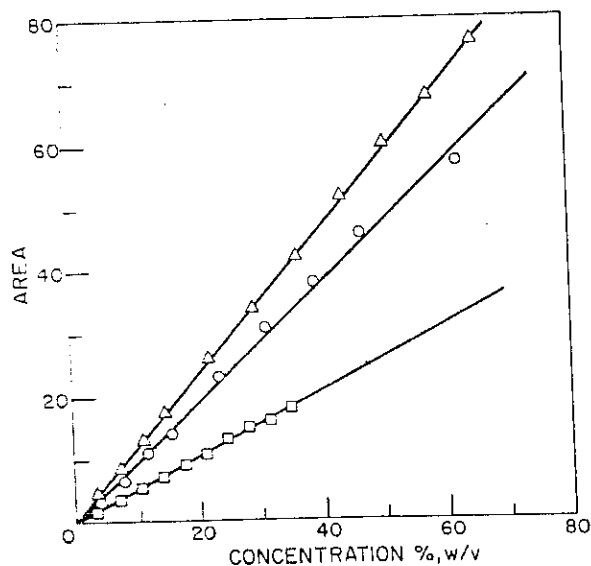
centrations and peak height and peak areas of methyl peaks at ca. 1.0 ppm downfield from TMS, were investigated. Linear correlations were indeed obtained for both as seen from the plots in Figure 5. The reproducibility of peak heights and peak areas was checked over a period of two weeks. A standard deviation of 2.8 – 3.9 % for peak height and 2.7 – 2.9 % for peak area was found. Similar correlations were found for naphtha and Stoddard solvent.
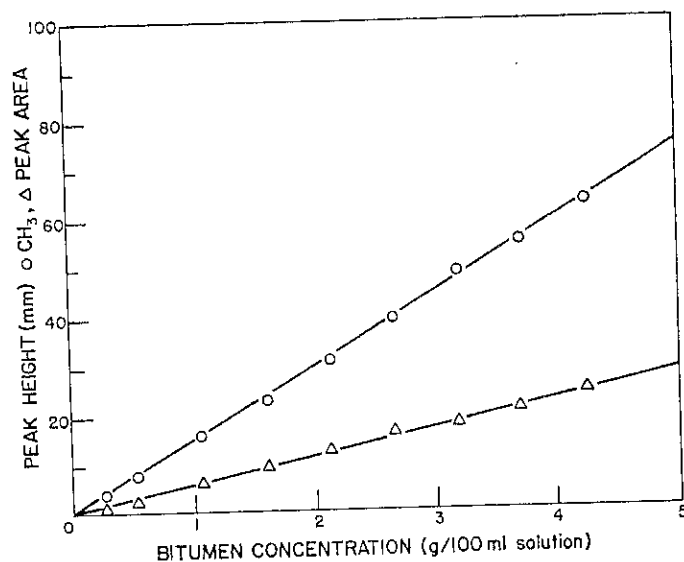

Figure 5. Plot of the % concentration against O, methyl peak height, and △, methyl peak area of bitumen in CCl_4.

A calibration curve prepared for a particular sample of bitumen can be used for the quantitative determination of bitumen from the same general area of the mining site. However, separate calibration curves might
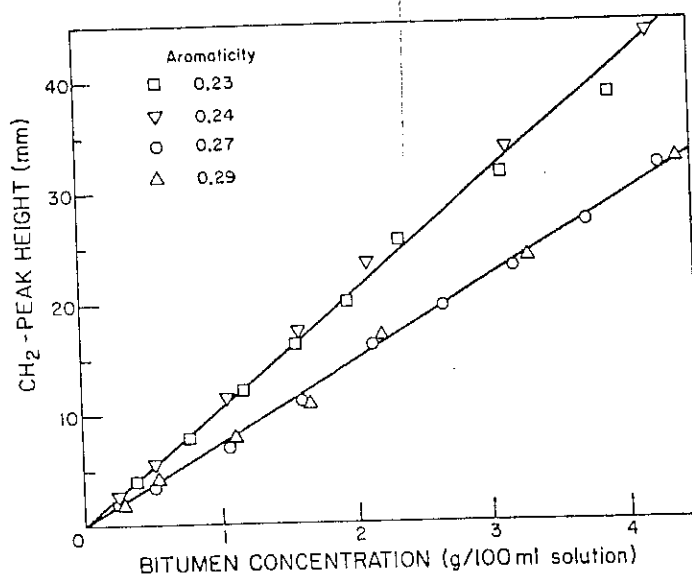

Figure 4. Calibration curves. Plot of the % concentrations against peak areas. Benzene, O; Toluene, □; Methylene chloride, △.

Figure 6. Proton NMR calibration curves for four samples of bitumen in CCl_4.

be required for samples from other deposits. This is demonstrated in Figure 6, which is a plot of the methylene peak heights against wt% concentration for four different kinds of bitumen. Two of the more viscous samples with higher aromaticity as determined from ^{13}C NMR fall on one line while the other two samples with low viscosity and lower aromaticity fall on the other line.

For the same bitumen sample both the peak heights and the peak areas were found to be independent of the choice of the solvent as shown in Figure 7.
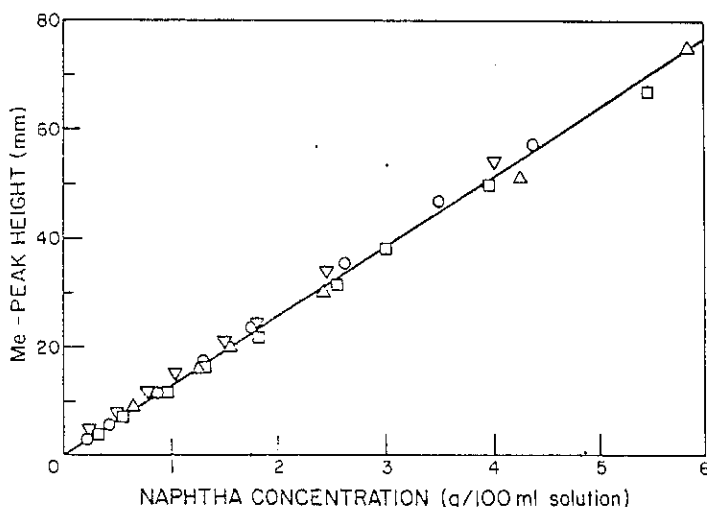

Figure 7. Plot of the methyl peak height of bitumen against % concentration in various solvents. O, CCl₄; □, C₆H₆; △, 10% methanol in C₆H₆; ▽, 15% Phenol in C₆H₆.

Estimation of naphtha/Stoddard solvent in the presence of bitumen. Because the ¹H NMR spectrum of bitumen overlaps the spectrum of the diluent, the independent determination of one in the presence of the other is not practical. However, by combining the spectrophotometric determination of bitumen with the ¹H NMR determination, the quantitative estimation of both can be achieved.

Table 2 contains results for the determination of Suncor naphtha. At the higher bitumen levels the naphtha contents, calculated from the methyl peak heights, were less accurate than those obtained from the methyl peak areas. This is caused by the presence of bitumen, resulting in broadening of the peaks thereby affecting peak height but having no effect on the total area of the peak. However, if the two values for the highest bitumen concentrations are excluded, then the relative standard deviations of ±2.25% and ±6.35% for peak height and peak area indicate greater precision for the peak height measurements. Therefore, bitumen concentration will be the deciding factor in the choice of calculation method.

Determination of water The Karl Fischer method of

Table 2. Determination of suncor naphtha in a mixture of bitumen and naphtha

Sample #	Concentration/W/V %				
	actual		found		
	bitumen	naphtha	bitumen[a]	naphtha[b]	
				height	area
1	0.33	0.81	0.33	0.81	0.73
2	0.93	1.95	0.93	1.88	1.80
3	2.08	1.27	2.08	1.21	1.21
4	6.61	0.90	6.62	0.65	1.02
5	0.97	5.77	0.96	5.82	6.11
6	0.11	1.95	0.11	1.91	1.88
7	4.88	5.09	4.88	4.47	4.98

[a] using the spectrophotometric method.

[b] from methyl peak

water determination was chosen because it is a fast and reliable way to obtain water measurement of high accuracy and precision [3]. Methanol was used as a solvent to dissolve water. The reproducibility of the titre value was excellent, with a standard deviation of ±0.2%.

Solids determination Samples containing large proportions of fine material filter easily with no detectable loss of fines using the filter aid Celite hyflo supercel to separate the sample solids from the extract solution.

Total analysis of oil sands mineral waste obtained from the solvent extraction spherical agglomeration process. Table 3 contains data for the bitumen/diluent/water and solids analysis by the proposed method as well as a modified Dean-Stark method [1] for subsamples of oil sand mineral wastes obtained from the SESA process [9]. It appears that complete extraction of the bitumen from agglomerates is not achieved in the modified Dean-Stark method. This is understandable because most of the residual bitumen in agglomerates is entrapped and is not released unless the agglomerates are broken down to smaller size. The relative standard deviation for the bitumen results obtained using the modified Dean-Stark method was also much higher than the 5% recommended by the Canadian Petroleum Association Tar Sands Council [10]. Disaggregation of the agglomerates in the proposed method of analysis results in improved contact between solvent and bitumen in the sample, yielding better reproducibility in the measured bitumen concentration.

In the modified Dean-Stark method, naphtha is determined by difference and because the bitumen content tends to be underestimated by this method the naphtha content is much higher than that determined

Table 3. Total analysis of oil sand agglomerates

Method	No. of samples analyzed	W/W % (average ± std. dev.)				
		bitumen	naphtha	water	solids	total
modified Dean-Stark	8	0.23 ± 0.06	3.25 ± 0.54	12.49 ± 0.55	84.03 ± 0.25	100
this method[a]	10	0.98 ± 0.02[b] (1.31 ± 0.02)	2.01 ± 0.09	12.83 ± 0.09	84.12 ± 0.27	99.94 ± 0.27 (100.27 ± 0.27)

[a] solvent used for the extraction of bitumen and naphtha = 15% phenol in benzene; mode of agitation = Spex mixer for 5 min.

[b] toluene soluble bitumen, uncorrected values given in parentheses.

by the proposed method. The results for water and solids contents by the two methods compare favorably although the standard deviation for the water results is much lower by this method compared to the Dean-Stark method.

The precision of the analyses of all four components by this method is well within the 5% relative standard deviation limit suggested by the Canadian Petroleum Association Tar Sands Council [10]. In the Dean-Stark method the mass balance is assumed to be 100 and thus the total organic material is determined by difference. In our method of analysis all four components are determined individually. The resulting mass balance is excellent with a very small relative standard deviation.

Total analysis of solid tailings from the centrifuge stage of the hot water process. In order to check whether this method of analysis was suitable for other types of tailings, mineral waste from the centrifuge stage of the hot water process was also analyzed by both methods. The results are shown in Table 4. In this case comparable results for all four components were obtained by both analytical procedures. This improvement could arise owing to the better dispersibility of the mineral tailings from hot water process compared with the agglomerates from the SESA process. Also, the entrapment of bitumen and solvent in the highly compacted agglomerates makes complete extraction difficult. The amount of fines (<44μ particles) present in these tailings could also affect the recovery, because both bitumen and solvent are strongly absorbed by clay and require vigorous treatment to effect their release.

Although the average values for bitumen, naphtha and water determined by the two methods compare favorably, the relative standard deviations were much higher than 5% for the modified Dean-Stark method, whereas the results for the proposed method were all within ±5%.

Aqueous tailings from EMR solvent/bitumen contactor. In order to confirm that our proposed method of analysis is applicable for the analyses of wastes containing water, solids, bitumen and naphtha in all proportions, we also analysed aqueous tailings from an EMR solvent/bitumen contactor by both methods. The results are shown in Table 5. Solids and bitumen concentrations determined by the two methods were comparable. However, the water and naphtha results from the two methods differ significantly. The total of water, solids and bitumen determined by the Dean-Stark method amounted to ≈ 102%, preventing the determination of naphtha in the sample. However, analysis by the new procedure indicated the presence of about 1% naphtha.

These results clearly demonstrate that our method for the analysis of tailings streams is more accurate

Table 4. Total analysis of solid tailings from centrifuge stage of hot water process

Method	No. of samples analyzed	W/W % (average ± std. dev.)				
		bitumen	naphtha	water	solids	total
modified Dean-Stark	8	2.63 ± 0.29	1.07 ± 0.63	6.36 ± 0.65	90.11 ± 0.22	100
this method[a]	10	2.58 ± 0.13[b] (2.27 ± 0.13)	1.21 ± 0.08	6.76 ± 0.06	89.75 ± 0.33	100.31 ± 0.28 (99.99 ± 0.28)

[a] solvent used for the extraction of bitumen and naphtha = 15% phenol in benzene; mode of agitation Spex mixer for 5 min.

[b] toluene soluble bitumen, uncorrected values given in parentheses.

Table 5. Total analysis of aqueous tailings from EMR solvent/bitumen contactor.

Method	No. of samples analyzed	W/W % (average ± std. dev.)				
		bitumen	naphtha	water	solids	total
modified Dean-Stark	8	1.24 ± 0.12	—	98.75 ± 1.03	1.72 ± 0.11	101.71 ± 1.03
this method[a]	10	1.29 ± 0.12[b] (1.27 ± 0.12)	1.15 ± 0.12	95.85 ± 0.43[c]	1.71 ± 0.35	

[a] solvent used for the extraction of bitumen and naphtha = CCl_4; mode of agitation = paint shaker for 15 min.

[b] toluene soluble bitumen, uncorrected values given in parentheses.

[c] water content was determined by difference.

than the modified Dean-Stark method. This is particularly true for the determination of small amounts of residual bitumen and diluent.

SUMMARY

A new and simpler method has been developed to measure the bitumen and diluent content of mineral tailings within a 45 minute turnaround time. The bitumen and diluent in the sample are extracted by agitating the sample with a known quantity of an appropriate solvent that does not absorb in the 0.5 to 2 ppm range of the ¹H NMR spectrum. An aliquot of this extract is filtered and then used for the determination of bitumen by a spectrophotometric method and solvent by quantitative ¹H NMR spectroscopy. Water is extracted with reagent grade methanol and is subsequently determined using a Karl Fischer titrator. Before the percentages of each component are calculated the volume of the solvent used is corrected to take into account dissolved bitumen, solvent and water. Solids are routinely filtered, dried and weighed so that a mass balance check is obtained on the analysis. The elapsed time for the analysis of a single sample (solids by difference) is 45 min. and the total elapsed time for a set of 10 samples (solids by difference) is 4-5 h. The determination of the solids content of a set of 10 samples requires an additional 1 h.

This method is a fast and reliable method for determining the bitumen, solvent, water and solids content of waste samples. Analytical results can be obtained in a significantly shorter time than with the conventional Dean-Stark method, and with much better accuracy and precision.

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