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Rapid Determination of Bitumen, Varsol and Other Solvents
Using Proton N.M.R.

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Introduction

The extensive Athabasca oil sands are assuming an increasing
role in supplying Canada's liquid hydrocarbon needs. One commercial
plant, Suncor Inc., has operated since 1967. It extracts bitumen
from the oil sands and subsequently upgrades to synthetic crude oil.
Syncrude Canada Ltd. which is designed to produce 109,000 barrels of
synthetic crude per day, began production in 1978. Fundamental to
the successful utilization of this oil sand resource and to the
economic operation of the extraction plant is a reliable analytical
method for the analysis of bitumen rich froth collected from the hot
water extraction process. This froth must be further treated to
remove solid particles and water. The purification process consists
of a diluent addition step to lighten the hydrocarbon density, two
centrifuging stages to remove solids and water, and a diluent
recovery step. Analytical inspection of these process streams
includes analysis for bitumen, diluent, water and solids. The
analyses are needed for process control and material balance
calculations.

The current determination of bitumen, diluent, water and
solids is performed by separating the sample into the individual
components. The solvent/hydrocarbon solution must be further
analyzed for diluent (naphtha) and bitumen content. Bitumen is
usually determined spectrophotometrically while diluent (naphtha) is
either determined by difference or by G.C. (2). The most common
problems with these methods are the greater sources of errors
involved (2). If the naphtha is determined by difference all the
errors will accumulate in the results for this component. In the
G.C. method errors will arise from dilution and the small volume
required for injection (1 µl) (2). Also the adsorption of asphalt-
enes from bitumen on the column packaging materials limits the use
of G.C. for the estimation of the diluent in the presence of
bitumen.

In this paper we report the proton nmr results for the
quantitative estimation of bitumen and a diluent (naphtha or varsol)
in the presence of toluene, benzene or methylene chloride, three
commonly used solvents for the extraction of bitumen from oil sands.

Experimental Methods

a) Proton nmr measurements were performed on a Varian EM-360 nmr
spectrometer (60 MHz); 500 µl of solution was used in each case in a
5 mm internal diameter tube. Carbon tetrachloride or tetrachloro-
ethylene was used as solvent. Gain and amplitude were adjusted to
give integrations within the range of the chart paper using lowest
and highest concentrations. Once adjusted all the parameters were
kept constant for subsequent measurements. Integration limits for
the aromatic region of benzene, CH_2-group of methylene chloride and

the CH_3-group of to
measured. However,
the integration for
at ca. 1.0 ppm down
the overlap of the
decided to take the
methylene) as the s
for methyl regions
Proton nmr spectra
benzene, methylene
+ varsol + benzene
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b) Preparation of
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from a 100 gram sa
was then measured

c) Calibration Cur
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(2) Diluent: Mea
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(3) Toluene, Ben
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the CH$_3$-group of toluene are well defined and can be easily measured. However, it is difficult to decide the starting point for the integration for the methyl region of bitumen, varsol or naphtha at ca. 1.0 ppm downfield from tetramethylsilane. This is because of the overlap of the methylene and methyl regions. It was therefore decided to take the mid point of the two peaks (methyl and methylene) as the start for the integration. The integration limits for methyl regions were therefore as illustrated in fig. 8a. Proton nmr spectra for bitumen, varsol, bitumen + varsol, toluene, benzene, methylene chloride, bitumen + varsol + toluene and bitumen + varsol + benzene are shown in figures 6-8 to illustrate the portions integrated for calibration curves.

b) Preparation of Standard Bitumen Solution: Bitumen was extracted from a sample of high grade oil sand using toluene in a Soxhlet apparatus (2). Non-filtered solids were removed from the bitumen solution by passage through a 0.45 μm millipore filter paper. The solvent was removed in a Brinkmann rotary evaporator at 100°C under reduced pressure. The total time required to remove the solvent from a 100 gram sample was less than one hour. The residual solvent was then measured using infrared spectroscopy (3) and proton nmr.

c) Calibration Curves: (1) Bitumen: - A standard sample of the bitumen required for the calibration curve was prepared as outlined above. The amount of the residual toluene quantitatively determined by infrared and proton nmr, was applied as a correction to the bitumen content. A stock solution (35.0% w/v) of bitumen in carbon tetrachloride and another in tetrachloroethylene were prepared from the standard bitumen accurately weighed to the nearest 0.0001 gram. Serial dilutions of bitumen, ranging in concentration from 3-35%, were prepared and the areas of the methyl peaks were determined from the integration of the peaks at ca. 1.0 ppm downfield from tetra- methylsilane in the proton nmr spectrum. A plot of the per cent bitumen vs area of the methyl peak produced a straight line passing through the origin, with a slope of 0.51.

$$\% \text{ Bitumen} = \frac{\text{Area of the methyl peak}}{0.51}$$

(2) Diluent: Measurements were made for two bitumen diluents, namely naphtha and Varsol (Stoddard solvent). Solutions of both naphtha and Varsol ranging in concentrations from 3-60% w/v were prepared. Areas of the methyl peaks at ca. 1.0 ppm downfield from tetramethylsilane were determined as described above for bitumen. The plots of the per cent naphtha and Varsol vs area of the methyl peak produced straight lines passing through the origin. Slopes for the two plots were 1.17 and 0.95 for % w/v concentrations and 0.85 and 0.75 respectively for % v/v concentrations. The concentration of the diluent was determined as follows:

$$\% \text{ Diluent} = \frac{\text{Area of methyl peak}}{\text{Slope}}$$

(3) Toluene, Benzene and Methylene Chloride: Carbon tetrachloride solutions of toluene, benzene and methylene chloride were prepared ranging in concentrations from 1-20% (10% in the case of benzene). Areas of the methyl peak for toluene, CH$_2$-peak for methylene chloride and aromatic peak of benzene were measured from their proton nmr spectra. Plots of per cent concentration vs areas were straight lines in each case. The concentrations were calculated using the following equations.

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$$\% \text{ (v/v) of Toluene} = \frac{\text{Area of the methyl peak}}{5.64}$$

$$\% \text{ (v/v) of Benzene} = \frac{\text{Area of the peak from proton nmr}}{13.75}$$

$$\% \text{ (v/v) of Methylene Chloride} = \frac{\text{Area of } -CH_2 \text{ peak}}{5.64}$$

(d) Determination of Varsol/Bitumen in a mixture.

Area of the methyl peak, measured as outlined in 1 or 2 above, represents the total area due to contributions from both diluent and bitumen. Bitumen concentration was separately determined photometrically by measurements of absorption at 530 nm. Knowing the concentration of bitumen the area of the methyl peaks due to bitumen can be determined from the equation in 1 above.

$$\text{Area of the methyl peaks in bitumen} = 0.51 \times \% \text{ (w/v) Bitumen}$$

Concentration of the diluent can then be calculated as follows:

$$\frac{\text{Total Area of the methyl peak} - \text{Area due to bitumen } CH_3 \text{ group}}{\text{slope}}$$

Results and Discussion

The calibration curves for benzene, toluene, methylene chloride, bitumen and diluents (Suncor naphtha and Varsol) are shown in figures 1, 2 and 3. All plots are good straight lines with zero intercepts. This is indicative of the existence of a linear correlation between the per cent concentrations and the area of the proton nmr signals emphasising the usefulness of proton nmr in the quantitative estimation of concentrations.

The measurements involving bitumen and diluent were performed independently in two solvents, carbon tetrachloride and tetrachloroethylene. Results were found to be independent of the solvent indicating no loss due to evaporation of the carbon tetrachloride during the period of measurement. Benzene, toluene and methylene chloride were only studied in carbon tetrachloride.

Procurement of unaltered standard samples of bitumen from oil sands is a serious problem recognised by Clark in 1950 (1). Oil does not separate from the native sands and water without the use of either chemical agents, solvent, heat or extreme mechanical force, all of which may significantly alter the oil. Since no method of separation exists that can guarantee an oil sample free from alteration, 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 (3).

The major drawback of solvent extraction methods is the fact that it is not practical to completely remove all residual solvent from the bitumen. Hence analytical techniques are required to determine the residual solvent concentration. Again proton nmr is found to be very useful for determining commonly used protonated solvents such as toluene, benzene and methylene chlorides.

Concentrations of toluene, benzene and methylene chloride determined from proton nmr compare reasonably well with the actual

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References:

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(2) Syncrude Ana
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(3) L.D.L. Vornd
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values. Accuracy of the nmr method is evident from the values of the standard deviations of ± 0.116, ± 0.177 and ± 0.318 respectively. A plot of Actual vs Found concentrations is shown in fig. 4. In the case of benzene or toluene the zero intercept and slope of 1 are indicative of good accuracy. In the case of methylene chloride significant errors are introduced because of the high volatility of this solvent (b.p. 39.8°C) which makes it difficult to prepare standard solutions because of evaporative losses. Hence a much higher relative standard deviation of ±1.033 with respect to least squares plots of data at different concentrations. To remedy the problem of evaporation of the solvents from the nmr tubes we find it helpful to use teflon stoppers rather than regular plastic caps. Besides reducing evaporation the teflon caps are more resistant to solvent attack, particularly by the chlorinated solvents.

Rapid and reliable determination of diluent (Varsol/Naphtha) in bitumen/diluent mixtures is essential for process control and material balance calculations both in hot water process and solvent extraction spherical agglomeration process for the extraction of bitumen from oil sands. The traditional methods for the determination of diluent do not give the required degree of accuracy. The concentrations of Varsol as determined from proton nmr measurements are shown in fig. 5 as a plot of the actual concentrations against calculated concentrations. Zero intercept and a slope of 1 indicates a very good linear co-relation. A standard deviation of ±0.281 (wt.%) was calculated for these results. This again demonstrates the accuracy of the nmr method. Advantages of the nmr method include higher precision, shorter analysis time (actual analysis time ca. 2 minutes), broader range of applicable concentrations (0.2-70%) and small quantity of the non-consumable sample needed for analysis (500 µl).

Bitumen and diluent can be determined separately by proton nmr, in all the common solvents, e.g. benzene, toluene, methylene chloride, carbon tetrachloride and other non-protonated solvents. The results are at least as accurate as obtained by other methods.

One of the peaks of the diluent spectrum overlaps with the methyl peak for toluene. Also, there is an overlap between the aromatic region of the benzene and diluent. Hence, an accurate determination of the concentrations of benzene or toluene in presence of diluent is not possible using this method. However, the presence of toluene or benzene does not effect the determinations of the concentrations of bitumen or diluent.

References:

(1) Ward, S.H. and Clark, K.A., Report No. 57. Alberta Research Council, (1950).
(2) Syncrude Analytical Methods for Oil Sand and Bitumen Processing. 1979.
(3) L.D.L. Vorndran, A.J. Serres, J.K. Donnelly, R.G. Moore and D.W. Bennion. Can. J. Chem. Eng. Vol. 58, 1980, p. 580.
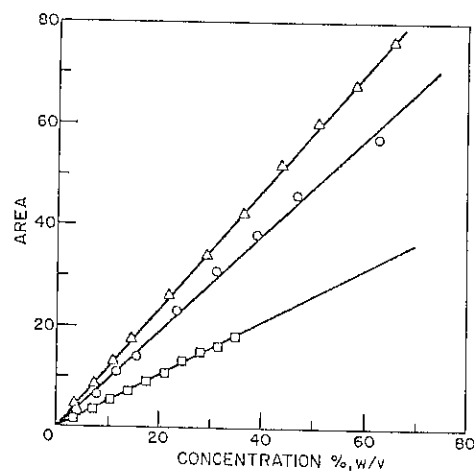
Acknowledgment

Fig. 1. Calibration Curves. Concentrations ($\frac{v}{v}$%) vs area of the ^{1}H nmr peaks. Benzene ◯ ; Toluene ☐ ; methylene chloride △ .
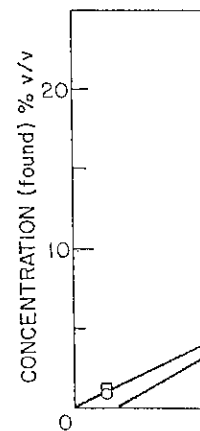
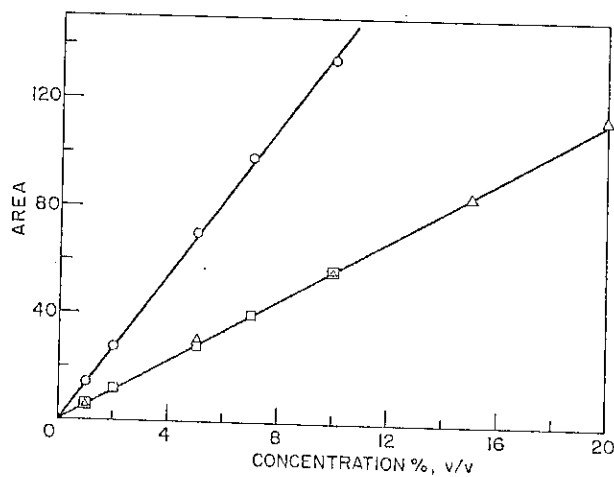

Fig. 2. Calibration Curves. Concentrations ($\frac{w}{v}$%) vs area of the methyl proton nmr peaks. Bitumen ☐ ; Stoddard solvent ◯ ; Suncor Naphtha △ .
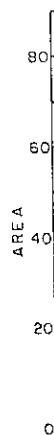
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Fig. 4. Plot o
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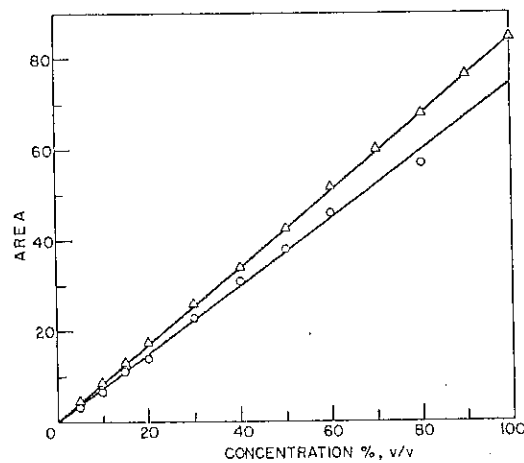
Fig. 3.   Calibration Curves.   Concentration ($\frac{V}{V}$%) vs area of the methyl proton nmr peaks.   Varsol $\bigcirc$; Suncor Naphtha $\triangle$.
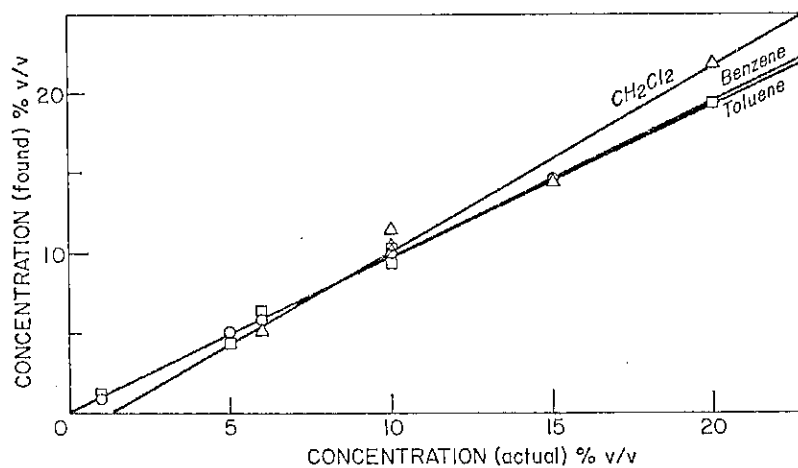
Fig. 4.   Plot of the concentrations ($\frac{V}{V}$%), Actual vs Found. Benzene $\bigcirc$; Toluene $\square$; methylene chloride $\triangle$.
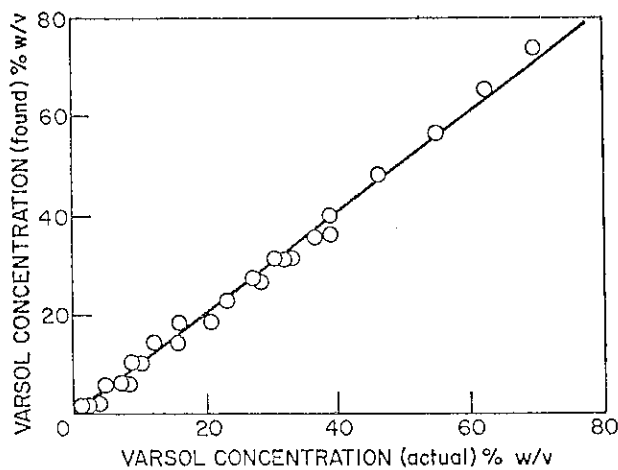
Fig. 5.   Plot of the Varsol concentration actual vs Varsol
concentration found.
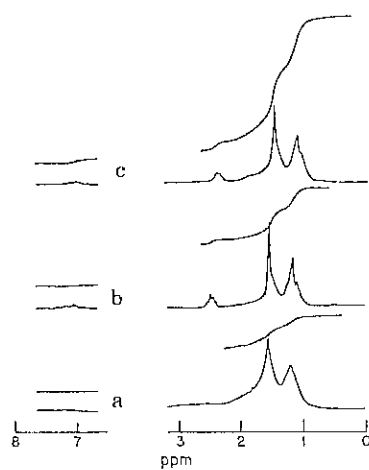
Fig. 6. ^{1}H n.m.r. spectra of a) Bitumen   b) Stoddard solvent

c) Bitumen + Stoddard solvent.
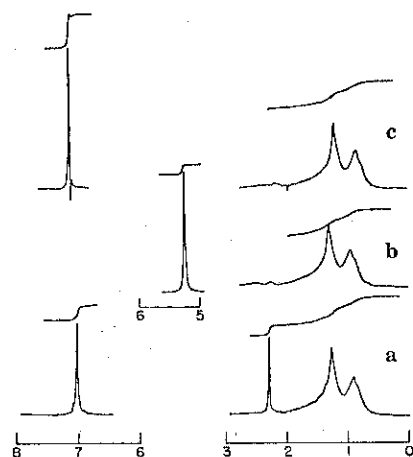
Fig. 7. ^{1}H n.m.r. spectra of a) Bitumen + Toluene b) Bitumen + methylene chloride c) Bitumen + Benzene.

ppm
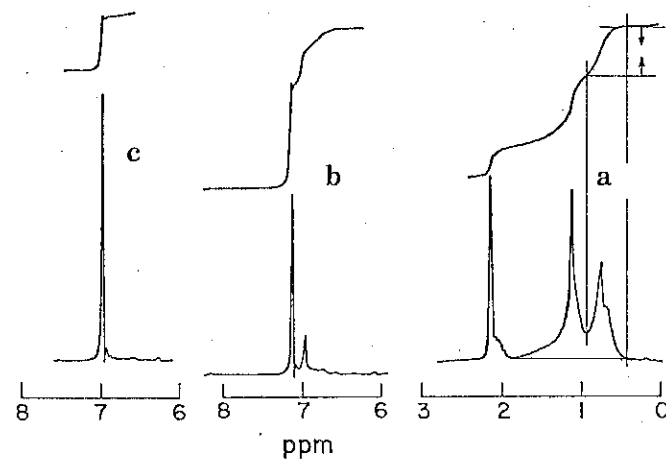
Fig. 8. ^{1}H n.m.r. spectra of a) Bitumen + Toluene + Stoddard solvent b,c) Bitumen + Benzene + Stoddard solvent.

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