

**GEOLOGICAL
SURVEY
OF
CANADA**

DEPARTMENT OF ENERGY,
MINES AND RESOURCES

R. G. McCrossan

PAPER 72-36

**IDENTIFICATION OF PETROLEUM SOURCE ROCKS USING
HYDROCARBON GAS AND ORGANIC CARBON CONTENT**

(Report, and 9 figures)

L.R. Snowdon and R.G. McCrossan

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Price: \$2.00

Catalogue No. M44-72-36

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ABSTRACT

A method of examining hydrocarbon gas and total organic carbon data from drill cuttings has been used to identify potential petroleum source rocks and to indicate the level of thermal diagenesis of the organic matter contained in the sediment. As the mechanical disaggregation of the cuttings and the extraction and analysis of the hydrocarbon gases are both rapid and inexpensive, the analyses can be completed almost concurrently with sample collection. Calculation of the regression equations and correlation coefficient for the least squares line of a plot of gas concentration against organic carbon content classifies the gaseous hydrocarbons as either epigenetic or syngenetic. Source potential is evaluated from a consideration of the abundance and composition of the total released gas. The data also may be used to select samples for more exhaustive analyses.

RÉSUMÉ

Une méthode d'étude des gaz d'hydrocarbures et du carbone organique à partir de déblais de forage a été utilisée pour identifier les roches mères potentiellement pétrolifères et pour montrer le niveau de diagénèse thermique de la matière organique contenue dans le sédiment. Comme la désagrégation mécanique des déblais et l'extraction et l'analyse des gaz d'hydrocarbures sont rapides et peu dispendieuses, on peut effectuer ces analyses presque en même temps que la collecte d'échantillons. Le calcul des équations de régression et du coefficient de corrélation pour tracer par la méthode des moindres carrés la courbe de concentration de gaz par rapport à la teneur en carbone organique classe les hydrocarbures gazeux en épigénétiques ou syngénétiques. Le potentiel de la roche mère est évalué à partir d'une étude de l'abondance et de la composition de la totalité du gaz libéré. Les données peuvent aussi être utilisées pour sélectionner des échantillons afin d'en faire une analyse plus poussée.

IDENTIFICATION OF PETROLEUM SOURCE ROCKS USING HYDROCARBON GAS AND ORGANIC CARBON CONTENT

INTRODUCTION

An ideal analytical system for evaluating source rocks and level of diagenesis of organic matter should be economically efficient and permit a rapid output of data. Owing to the time and cost involved, conventional analytical systems can be applied only to geological sections that have been separately and previously proposed as potential source rocks. Solvent extractions and column chromatography can be avoided by using the total organic carbon content and the mechanically extractable (ME) hydrocarbon gas concentration as the measured parameters. Quantitative determination of these is rapid, precise and simple.

Hydrocarbon gas analysis has been used in conjunction with petroleum exploration and sediment characterization for a number of years. Many service companies¹ monitor the hydrocarbon gases extracted from drilling fluids or perform on-site analysis of "cuttings gas" using hot wire detectors for total gas, and gas chromatography with either flame ionization or thermal conductivity detectors for the individual gaseous components. The gases are released from the samples using mechanical disaggregation for cuttings and either mechanical agitation or heat for drilling fluids. However, gas chromatography performed under controlled laboratory conditions on cuttings samples that have been hermetically sealed on the drill site is preferable to on-site analysis. The samples can be semi-permanently sealed and stored in cans and examined and analyzed at the convenience of the technician. A number of wells being drilled simultaneously can be collected by on-site personnel and returned to the laboratory. Flame ionization detectors have the following advantages over thermal conductivity detectors: (1) higher sensitivity for hydrocarbon gases, (2) zero response to fixed gases (N_2 , O_2 , H_2S , CO_2 and water vapour), (3) no oxidative destruction of the detector due to air in the samples, and (4) wider linear range. This last feature is important because the quantity of gas extractable from cuttings varies considerably and both low and high values are of interest.

¹Baroid of Canada Ltd., Geoservices North America Ltd., Continental Laboratories Inc., etc.

Manuscript received: June 15, 1972

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Evans and Staplin (1971) have shown that valuable information can be derived from cuttings canned at the drill site. They have used gas analysis data generated in the laboratory from such samples to classify organic metamorphic facies and demonstrated the correlation between the wet gas to dry gas ratio (C_{2+}/C_1) and other parameters such as the colour of kerogen, and the C_4 - C_7 and C_{15+} hydrocarbons. (C_{2+} = ethane, propane, iso-butane, and normal butane; C_{15+} indicates the fraction of which the lightest n-paraffin contains 15 carbon atoms).

The basic advantage of using the hydrocarbon gas content instead of the other standard analyses as the measured parameter for source rock determination is that no separation prior to gas chromatography is necessary and, because no solvents are used, only the components of interest are detected. Furthermore, the extraction time is decreased from the hours or days required for the extraction of heavier hydrocarbons to minutes required for the gases.

According to Evans and Staplin (1971), immature sediments are characterized in the C_1 - C_4 range by the dominance of methane and only trace amounts of ethane, propane and the butanes. Extremely metamorphosed sediments also will contain predominantly methane produced by the thermal cracking of the higher molecular weight hydrocarbons in the subsurface environment. In the intermediate or mature zone, the sediment can be expected to contain "wet" gases, gasoline- and kerosene-range hydrocarbons. These are the result of temperature levels of the sediment sufficient to alter the kerogen to petroleum but insufficient to crack the petroleum to methane and graphite.

The authors have found up to about 95 per cent of the total ME gas present may be in the C_{2+} range and, in relatively well understood geological areas, these correspond to oily or petroliferous sections. Evans and Staplin (1971) reported a high correlation between wet gas and the C_4 - C_7 range hydrocarbons and the present data show a significant correlation amongst the C_{2+} gases. Therefore, an extrapolation from the wet gas concentration, which is actually determined, to the gasoline- and kerosene-range hydrocarbons, which are of more interest to an oil explorationist, is probably reasonable in most if not all cases, and sediment may be classified as immature, oily or mature, or metamorphosed. To be a potential source rock, it must contain a sufficient amount of organic material to enable it to generate significant amounts of hydrocarbon. Background information on source rocks and hydrocarbon gases is available in Cerchez (1967), Erdman (1961), and Louis (1967); and on organic geochemistry in general in Breger (1963) and Eglinton and Murphy (1969). Various lower limits have been suggested in the literature (Ronov, 1958; Schrayner and Zarella, 1963) but it is probably unrealistic to preclude any sections below a rigidly established minimum. The present data show that sections containing significant quantities of ME gas have at least 0.4 per cent organic carbon. However, zones ultimately classified as potential source rocks contained more than 1.57 per cent organic carbon. The total organic carbon parameter should be used as an indication of relative overall potential of a section to generate petroleum hydrocarbons.

The problem of differentiating between potential source rocks in the mature zone and sections containing migrated hydrocarbons is resolved by plotting the ME gas concentration against the organic carbon content. This is a modification of the method first suggested by Philippi (1957), who examined the correlation coefficient of heavy hydrocarbon (C_{15+}) concentration and total organic carbon content. In the case in hand, however, the least squares slope rather than the correlation coefficient

is used to characterize the hydrocarbon gases as either epigenetic or syngenetic. When only syngenetic hydrocarbons are present, higher gas contents should be paralleled by increased amounts of organic matter, resulting in an approximately constant gas to organic carbon ratio. However, introduction of significant quantities of epigenetic hydrocarbons will cause this ratio to increase, resulting in a steeper slope on the gas versus organic carbon plot. Thus, higher slopes indicate the presence of epigenetic hydrocarbons, whereas low slopes correspond to syngenetic hydrocarbons and hence source rocks.

The correlation coefficient of the least squares line is used as a guide to the validity of the linear curve selected as the slope. A high correlation coefficient does not necessarily imply that a section is a source rock rather than a reservoir rock. Notwithstanding the objections to the idea of a localized source, or source rock, Hodgson and Hitchon (1966) point out that accumulation of petroleum may be due to solubility fractionation between water and organic phases, and the initial "seeding" may be due to in-place organic material. As a result, a high correlation between epigenetic hydrocarbons and syngenetic organic matter is possible.

In order to isolate sections of the sedimentary sequence which contain abnormal amounts of ME gas and are potential source rocks, a downhole log of the gas and total carbon data is plotted. Peaks are then selected on the basis of adjacent background levels or in terms of standard deviations above the overall mean. The gas data from the individual samples in the peak are then plotted against the carbon data. Only peaks in which methane makes up less than about 50 per cent of total gas present are selected as being in the mature zone. However, methane alone could presumably be classified as syngenetic or epigenetic by the same method.

ACKNOWLEDGMENTS

The authors would like to acknowledge the assistance of Mobil Oil Canada Ltd., Anderson Exploration Ltd., Dome Petroleum Ltd. and Shell Canada Ltd. in obtaining canned samples of drill hole cuttings; and Imperial Oil Ltd. for its assistance in setting up the laboratory, and its guidance in establishing a geochemical program. The authors also wish to acknowledge the thorough and helpful critical reading of the paper by Drs. N. J. L. Bailey and G. W. Hodgson.

EXPERIMENTAL ANALYSES

GASEOUS HYDROCARBON AND TOTAL ORGANIC CARBON ANALYSES

Samples of fresh drill cutting (500-800 g.) were taken at 30-foot intervals and sealed in tin cans at the drill site. Lacquered cans prevented some corrosion due to salt water and did not noticeably affect the measured gas values. The samples were covered with water to maintain a standard head space volume of approximately 100 millilitres. In the laboratory, the samples were stored at room temperature for periods from one month to two years. Samples in cans with large head space volumes (>200 ml.), a broken seal, or without water contained noticeably lower gas concentrations than adjacent samples.

Six hundred millilitres of distilled water were placed in a stainless steel blender jar with a 100-millilitre aliquot of the cuttings (measured by displacement of the water). The samples were blended for 2 minutes on a Waring Model 5011S Blender, reducing the cuttings from 3- to 6- millimetre particles to sand size for the hard material and to clay size for shale and unconsolidated samples. 1.25 millilitres of the blender head space gas were injected into a gas chromatograph using a 6-port nut-type gas sample valve. A 1/8" x 5' column, packed with 100- to 120-mesh Porapak Q was used, and the temperature programmed isothermally at 80°C for 4 minutes, 15°C/minute for 2 minutes, 20°C/minute for 4 minutes and then held at this temperature for 1 to 6 minutes to flush the C₆-C₈ hydrocarbons out of the column. The pentanes were eluted in less than 10 minutes. The gases up to normal butane were measured quantitatively using a digital integrator and the C₅ and C₆ isomers noted qualitatively. Room temperature and final blender temperature greatly affected the observed concentration of the latter 2 components. Compensation for instrument attenuation and detector response to the various gases was made within the computer program prior to plotting.

The organic carbon content was determined for each sample with a Leco carbon analyzer. A portion of the blender sample was air dried at 70°C for 48 hours, pulverized to particles about 100 microns in diameter, weighed into a combustion crucible, treated with 6N HCl at about 80°C in a sand bath to remove carbonates, and dried prior to combustion.

EFFECTS OF SAMPLING DELAY AND LONG-TERM STORAGE

Control samples were taken to examine the effects of delay between collecting the samples and sealing them in cans, and also of long-term storage of samples at room temperature prior to analysis. Cuttings samples were taken over a 10- to 15-minute interval for four separate formations (Colorado, Second White Specks, Viking and Mississippian) and allowed to stand exposed to normal atmospheric pressure and temperature fluctuation for a period of up to four hours. (Temperature range was about 5-25°C). Aliquots were sealed in cans at various time intervals and analyzed at a later date. The data for the two formations plotted in figure 1 are representative of the two other formations not plotted and indicate that the results are not significantly affected by delays of at least 3.5 hours.

To examine the effects of storage in cans, triplicate samples from each of three formations were canned and stored at room temperature for 1 month, 5 months and 15 months. In the case of the Viking and Colorado Formations, a small change in the total amount of ME gas was noted, but the difference was not significant relative to the intensity of a normal signal peak above baseline (see Fig. 2). However, the sample from the Second White Specks actually yielded more gas as the length of the storage period increased.

Thus, reasonable time differences prior to canning and analysis can be ignored, as their effect upon the results is not of sufficient magnitude to affect the interpretation.

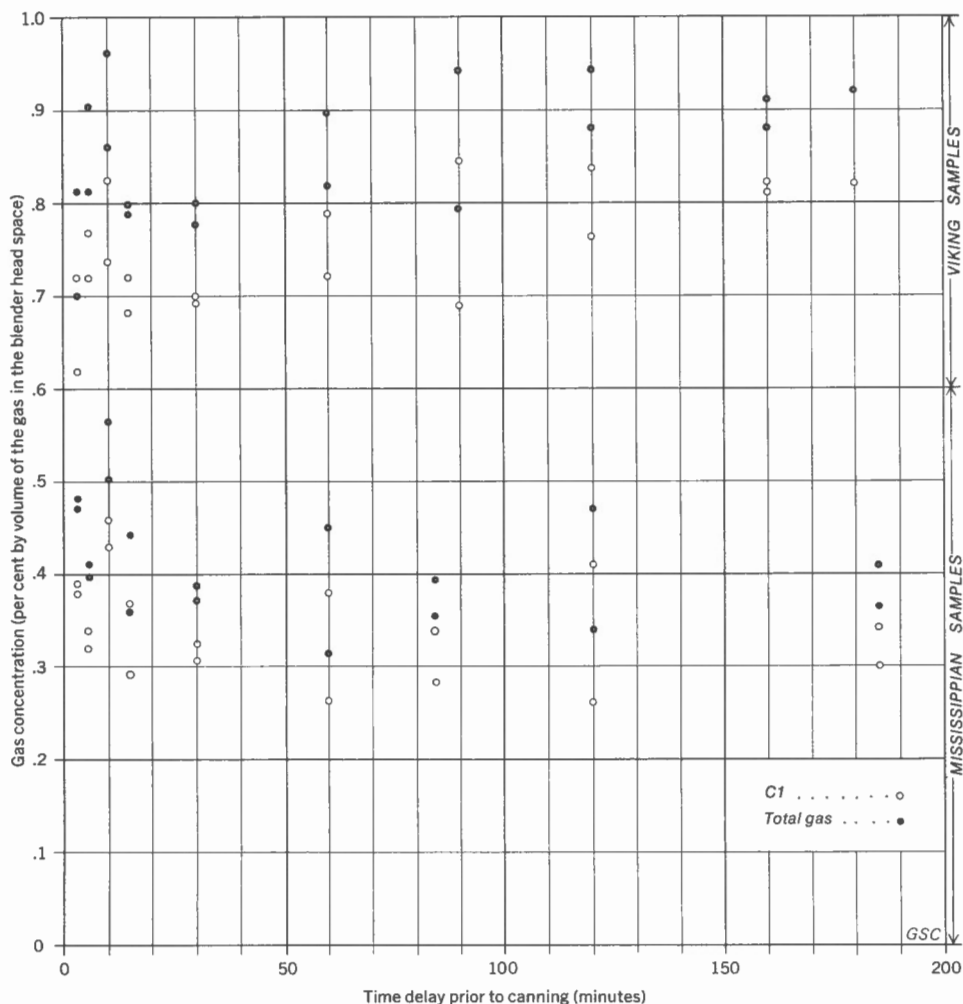


Figure 1. Effect of delay prior to canning on the mechanically extractable gas concentration for the Viking and Mississippian Formations at GPD Noel CPOG Beiseker well (11-31-28-26W4)

RESULTS AND DISCUSSION

The data are displayed on a downhole log of organic carbon (plotted as "+") against methane (x) and total C_1 - C_4 gas (*). The gases are plotted as per cent by volume of the 380-millilitre head space in the blender jar with full scale equal to 1.0 per cent, and the organic carbon as per cent by weight of the rock with full scale equal to 5.0 per cent.

Figures 3, 5 and 7 are examples of downhole logs, and interpretations drawn from them using the criteria stated previously are presented below.

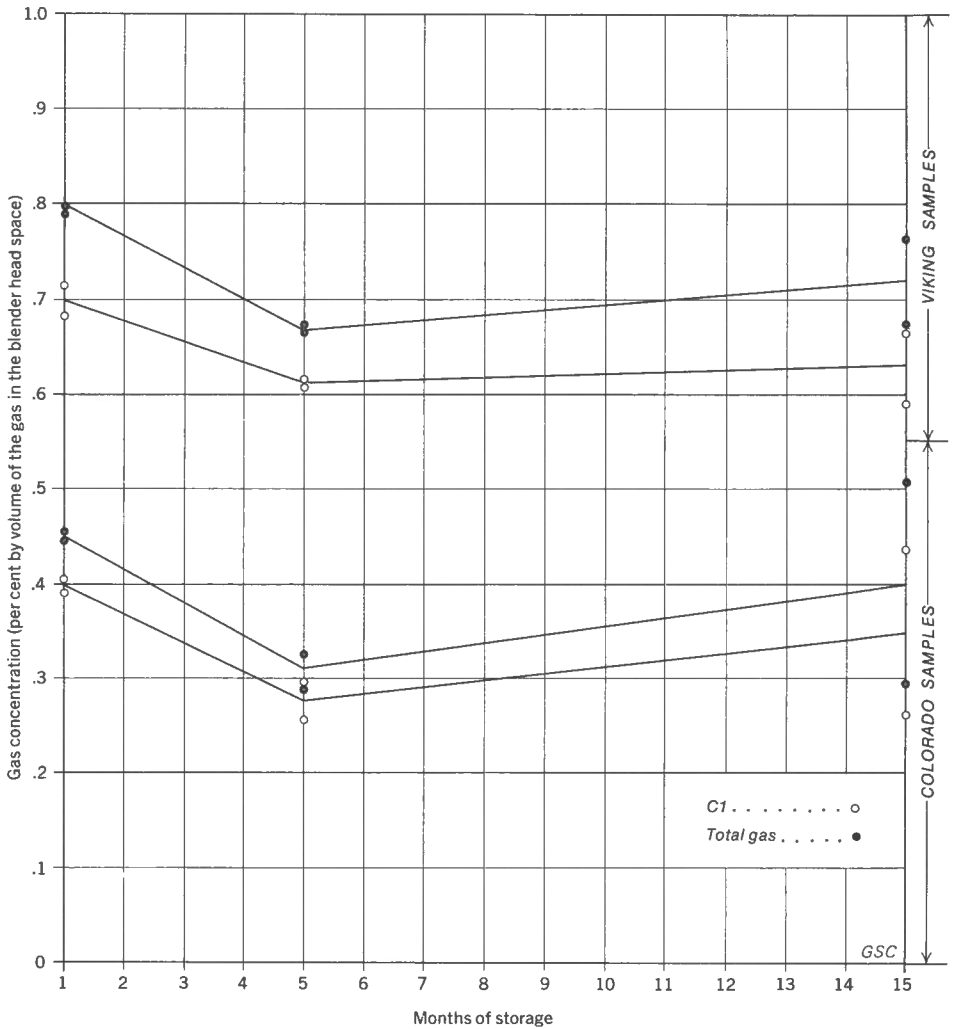


Figure 2. Effect of storage on mechanically extractable gas concentration of canned samples from the Colorado and Viking Formations at GPD Noel CPOG Beiseker well (11-31-28-26W4)

Mobil et al. James River well (8-14-34-7W5)

The samples for the Mobil et al. James River well are taken from depths of 1,400 to 10,200 feet and from 13,100 to 13,800 feet at about thirty-foot intervals. No samples are available for the 3,000-foot gap between 10,200 and 13,100 feet.

As can be seen in the gas log for this well (Fig. 3), no significant wet gas concentrations are present above the Lea Park Formation indicating that, through the Belly River Formation, the sediment is immature and/or the original organic material is unsuitable for the generation of hydrocarbons in the C_2 - C_4 range. This is consistent with what might be expected from a continental deposit containing coaly material. In the Lea Park Formation (7,040' - 8,235'), there are several small gas peaks (7,500', 7,820', 8,100') that are not significantly above the mean but are appreciably above the apparent baseline. These peaks are largely wet gas, indicating that the sediment contains some heavier hydrocarbons. These peaks may represent epigenetic or syngenetic gas and the gas-carbon plot fails to resolve this due to the low gas concentrations and the poor correlation with organic carbon. If the gases extracted from the Lea Park are syngenetic, then the formation is probably thermally mature; however, if the gases are epigenetic, they indicate the level of maturity of some other formation and thus no information is available concerning the level of thermal alteration for the Lea Park. The Lea Park peaks are overshadowed by the massive wet gas peak in the Cardium Formation where the total gas values are off scale (1.05%, 1.39%, 1.02%, 1.68%, 1.39%) and methane, which is less than 0.2 per cent, makes up only 5 to 18 per cent of the total gas present.

The least squares line fitted to the gas-carbon plot of the interval from 8,850 to 9,330 feet (Cardium Formation; Fig. 4) has the steepest slope yet observed in this laboratory. It is concluded, therefore, that the wet gas and oil in the Cardium

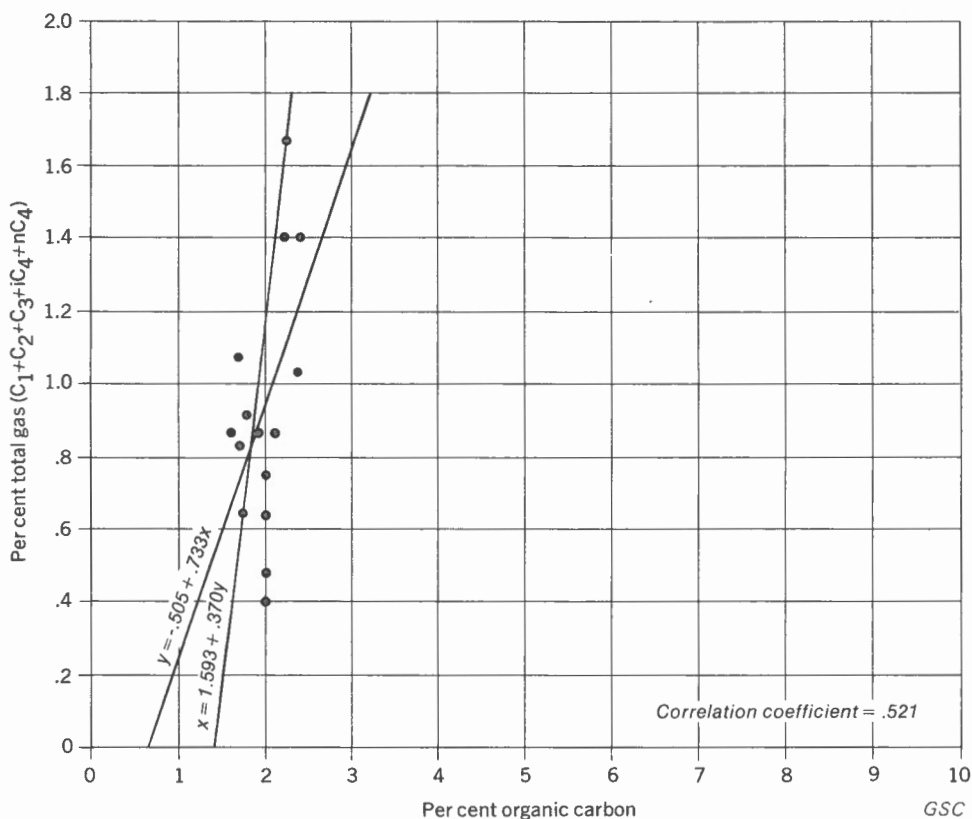


Figure 4. Gas-organic carbon plot for Mobil et al. James River well (8,850 - 9,330 feet)

Formation are epigenetic and have migrated from elsewhere. This is the same conclusion obtained by Philippi (1957), who used solvent extraction and C₁₆-C₂₅ range hydrocarbon concentration on the ordinate axis. The irregularity of the gas curve throughout the Base of Fish Scales Zone, Viking Formation, and down to the Blairmore coal seam is probably due to contamination by sidewall cavings from the gas-rich Cardium Formation.

Below the sampling gap, the ME gas is almost entirely methane indicating that the organic matter in the Duvernay Formation and below is metamorphosed, precluding the occurrence of indigenous oil or wet gas. The crossover from the mature to the metamorphosed state is apparently within the sample gap.

Anderson et al. Dunvegan well (10-17-80-3W6)

Samples were collected at ten-foot intervals from a depth of 2,800 to below 4,600 feet from a well drilled by Anderson Exploration at 10-17-80-3W6.

Two predominantly methane peaks represented by only one datum point each occur in the Gething Formation at depths of 2,960 and 3,010 feet. As these peaks are given by only one sample, it is difficult to decide whether they are true values or due to contamination, but the organic carbon content rises abruptly at the same depth and it is likely that the peaks are due to the presence of small coal seams.

The Fernie Formation contains a relatively large concentration of organic carbon ($\approx 2.0\%$), but only a small amount of gas (predominantly methane). This indicates that the organic material present is immature and/or not suitable for generating C₂-C₄ range hydrocarbons.

The Nordegg Member, however, contains large amounts of gas which is dominantly wet (10-20% methane) and an organic carbon peak. The large C₂₊/C₁ ratio suggests that the organic matter in this formation is mature, and the low slope of the least squares line fitted to the gas-organic carbon plot (Fig. 6) indicates that the hydrocarbons are syngenetic. Hence, the Nordegg is probably a mature source rock.

The high gas and organic carbon values at the top of the Triassic strata are due possibly to contamination by cavings or incorrect depth labelling of the samples due to lag time errors. In the remainder of the Triassic, both the organic carbon and ME gas concentration decrease. There is a significant proportion of wet gas present in all samples below the Nordegg, indicating that this entire section contains mature organic matter.

The gas log of another set of samples from a well in the same area (Dome Chiefco Belloy 7-28-78-1W6) is virtually identical through the Nordegg Member.

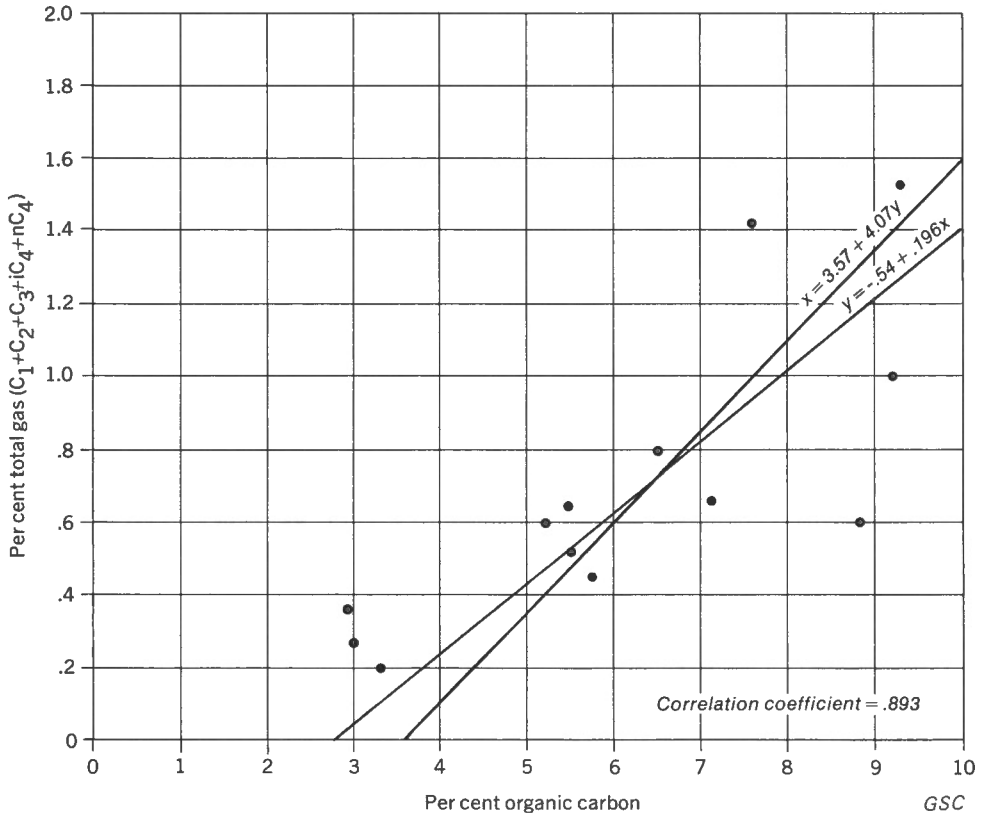


Figure 6. Gas-organic carbon plot for Anderson et al. Dunvegan well (3,340 - 3,750 feet)

Shell Arctic Red River 0-27 Well

(N66°45'56.032"-W132°49'35.881")

A complete set of samples from the surface to a depth of 7,100 feet was analyzed from the Shell Arctic Red River 0-27 well in the Mackenzie Delta.

The section of the gas log (Fig. 7) between 100 and 800 feet contains a large proportion of wet gas which, although fairly typical of the entire section down to 3,800 feet, is unusual at such shallow depths. There are two possible explanations: (1) hydrocarbons have migrated into this section, or (2) the organic material is mature. The 'gas to organic carbon plot' test again fails to resolve these options because the correlation is so low that the least squares line relative to the x-axis is completely different from the least squares line relative to the y-axis. (A correlation coefficient of zero and mutually perpendicular least squares lines result if the data is distributed rectangularly.) From 880 to 1,250 feet, the gas concentration is very low, possibly due to unconsolidated or very coarse-grained sediment which would lose any gas present in the interval between drilling and canning, or into the headspace of the can. Below this depth and down to 3,200 feet, there is a predominantly wet gas

section with peaks occurring at 1,350 feet and particularly at 1,890 feet. Because the organic carbon content is relatively small and constant throughout, the slope of the gas-organic carbon plot (Fig. 8) is high, indicating that the light hydrocarbons are epigenetic. The wet gas peak from 3,200 to 3,550 feet, however, corresponds to a definite increase in the total organic carbon content. The resulting lower slope on the gas-organic carbon plot (Fig. 9) suggests that the gas is syngenetic and that this is probably an excellent mature source rock.

The sharp drop in both total gas and the proportion of wet gas below 3,800 feet may be due either to the nature and low amount (<0.5%) of the organic material present, or to a high level of thermal alteration. In either case, there is no mature source rock in the section below 3,800 feet.

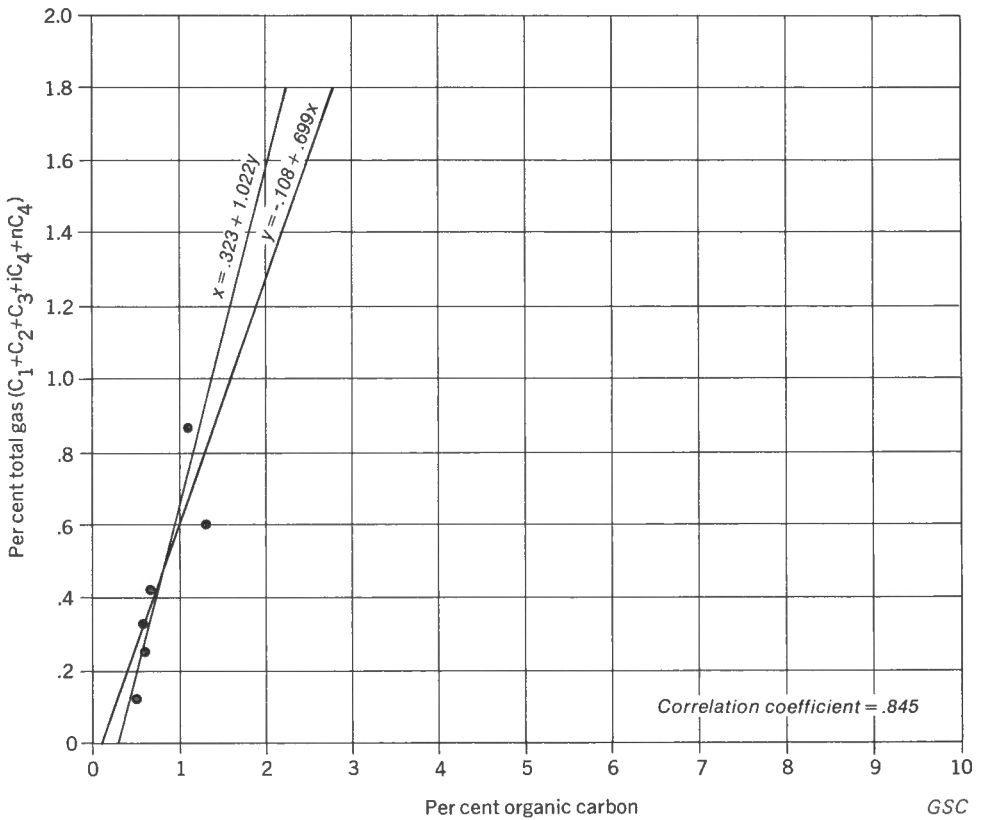


Figure 8. Gas-organic carbon plot for Shell Arctic Red River O-27 well (1,820 - 1,970 feet)

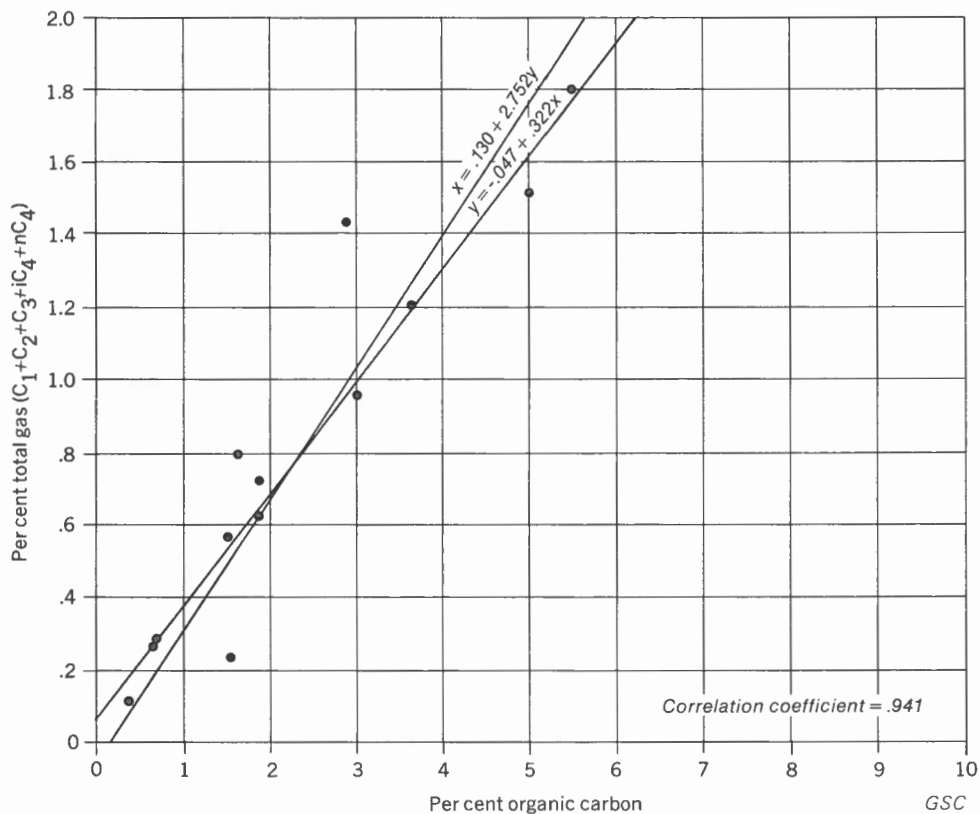


Figure 9. Gas-organic carbon plot for Shell Arctic Red River O-27 well (3,170 - 3,560 feet)

CONCLUSIONS

The mechanically extracted gas concentration and total organic carbon content of sediments can be determined rapidly and at low expense. These data are useful in determining the level of thermal diagenesis of the organic matter in sediment and in identifying potential petroleum source rocks. By using an extractable gas concentration versus organic carbon content plot, and observing the slope and correlation coefficient, the light hydrocarbons present in a high ME gas zone can be classified as epigenetic or syngenetic. In cases where the slope of the least squares line on the gas-carbon plot is unreliable and the epigenetic or syngenetic nature of the hydrocarbons cannot be resolved, the downhole log of the gas and carbon data can be used as a pilot for more extensive chemical analyses.

BIBLIOGRAPHY

- Breger, I. A.
1963: Organic Geochemistry; Pergamon Press, Macmillan Company, New York.
- Cerchez, V. T. L.
1967: Recherches sur L'Identification des roches mères d'hydrocarbures; Revue de l'Institut Français du Pétrole XXII #12.
- Eglinton, G., and Murphy, M. T. J., eds.
1969: Organic Geochemistry: Methods and Results; Springer-Verlag, Berlin, New York.
- Erdman, J. G.
1961: Some chemical aspects of petroleum genesis as related to the problem of source bed recognition; Geochim. Cosmochim. Acta, v. 22, p. 16-36.
- Evans, C. R. and Staplin, F. L.
1971: Regional Facies of Organic Metamorphism, Proc., 3rd International Geochemical Exploration Symposium, Toronto, April 16-18, 1970, Can. Inst. Mining Met., Special Volume 11, p. 517-20.
- Hodgson, G. W. and Hitchon, B.
1966: Research Trends in Petroleum Genesis, 8th Commonwealth Mining and Metallurgical Congress, Australia and New Zealand (1965), v. 5, Proc. - Petroleum.
- Louis, M.
1967: Cours de géochimie du Pétrole; Technip., Paris.
- Philippi, G. T.
1957: Identification of Oil Source Beds by Chemical Means; Proc. International Geological Congress, 20th Session, Mexico (1956), Section III - Geology of Petroleum.
- Ronov, A. B.
1958: Organic Carbon in Sedimentary Rocks (in Relation to the Presence of Petroleum); Geochemistry, v. 5, p. 510-36, translated from Russian Geokhimiya.
- Schrayer, G. J. and Zarella, W. M.
1963: Distribution of Organic Matter in the Siliceous Mowry Shale of Wyoming; Geochim. Cosmochim. Acta, v. 27, p. 1033-40.