

COMPARISON OF ANALYTICAL DATA RELATING TO THE
GEOCHEMISTRY OF QUALITY CONTROL TEST SAMPLES UNDERTAKEN
BY BOTH GEOCHEM LABS (UK) LTD. AND BP.

by S.P. Lowe and G.P. Cooles

Ten sediment samples together with two GC standard samples were submitted for inclusion into the Geochem Laboratories analytical work on the North Sea Norwegian Sector Well 30/4-1. It was intended that these samples would be coded with depths and fed into the work programme at discreet intervals as normal samples. However, this was not accomplished and they were all analysed by Geochem Labs as a single batch of control samples. It was not disclosed to Geochem Labs that the 10 sediment samples were duplicated samples derived from only five standards. The two GC standards were also duplicates of a single saturate fraction isolated from a crude oil.

The accompanying geochemical data tables collate results obtained by Geochem Labs with BP standard values for the sediments. In some instances the crude laboratory data supplied by Geochem Labs has been redefined into the appropriate form for the geochemical interpretation (eg TSE/TOC indices, etc.) that BP use.

Vitrinite Reflectance values obtained by Geochem Labs for two sets of duplicates (A/I and B/J) were themselves in good agreement with each other. However, they do not agree with the BP accepted standard values. This was especially true of the values quoted for B/J. BP would take the Geochem Labs R_0 value of 0.52% as indicating that this sediment was almost mature, whilst our own value of 0.44% strongly indicates immaturity. The remaining two sediments, where R_0 duplicate results were reported showed widely different values. Visual Kerogen sporomorph colour observations were also used by both laboratories to estimate the thermal maturity of these sediments. There was good agreement in the duplicate values obtained by the consultants. However, only two of these duplicate estimations agreed reasonably with the corresponding BP standard values (Table 1). Spore colour estimations for the duplicate samples D and G by Geochem Labs suggested this sediment to be "moderately immature". This was in complete contradiction to the Vitrinite Reflectances of 1.66 and 1.19% (indicating a high level of maturity) quoted for the same sediments. Geochem Labs concluded that the spore colour was giving the valid maturity indications, while the R_0 values were made on dominantly reworked material. In fact this is not the case. BP found this sediment to be over mature for liquid hydrocarbon formation. The difference in interpretations may be explained by the fact that Geochem Labs have taken results from each measurement in isolation, whereas BP use a multiparameter approach in which



SØRFLÅTVEIEN 11, P.O. BOX No. 3077 MARIERO, 4001 STAVANGER

Statoil
P.O. Box 300

4001 STAVANGER

Attention: Mr. J. Bleie

Our reference
DS/asc-9/80
626/1/043

Your reference

Telephone
10451 89580
Telex
33339 BPEXPB

Date
15th January 1980

Dear Sirs,

ORGANIC GEOCHEMISTRY CONTROL WORK WELL 30/4-1

We attach a copy of a brief report on the quality control work undertaken by BP Sunbury for the contract geochemical work done by Geochem Labs. Ltd. The report suggests that the analytical results should be treated with caution.

This work was undertaken in addition to the standard geochemical study and should not therefore be included in any trade of geochemical results.

Yours faithfully,
for BP PETROLEUM DEVELOPMENT LTD., NORWAY

F. Howitt
Exploration Manager

cc: F.R. Aamodt, NPD
D. South
D.C. Harding

Enc.

results from various measurements are taken into account, where any judgment is necessary. The latter is often the case in resolving the vitrinite distributions shown in the raw data and especially on poor samples where a lot of reworked material is present. Owing to the low abundance of suitable organic matter in the sediments C/F and E/H, no estimation of maturity level by spore colouration could be made.

Whilst a pyrolysis study on ground sediments was undertaken by Geochem Labs on the main 30/4-1 Well samples, no such work was reported on the control samples and therefore no direct comparison can be made. However, it seems that Geochem Labs appear to use a Rock Eval pyrolysis instrument in the same manner as BP, as a rapid indicator of source rock richness. They also include peak pyrolysis temperatures in their data, which we find disturbing. This suggests that they may also use the instrument as a maturity indicator, which BP believe does not give true results. Our judgment is based on the fact that the range of temperature over which these measurements vary is too small to provide an accurate measurement on which to base a major conclusion, with any reliance.

Soluble Extract studies showed that consistently larger amounts of solvent extractable material were obtained by Geochem Labs, than by BP. These lead to misleadingly high TSE/TOC values for these sediments, which are well above those expected by BP. According to the consultants, Type Analysis of these TSE's showed a predominance of "asphaltenes", with only a low proportion of saturate alkanes. However, their figures are not reproducible for the sample pairs (Table 2). BP find these extracts to be low in asphaltenes. It is understood that Geochem Labs precipitate asphaltenes from a TSE in n-pentane, while BP precipitate in n-heptane. This difference in solvent could result in minor differences in asphaltene figures between the laboratories, but not to the degree observed. We consider that the differences observed are too large to arise from balance error and must therefore suggest poor technique. The Geochem Labs gas chromatograms of saturate fractions from TSE's all show unresolved humps beneath the range of n-alkanes and predominantly in the n-C₁₉ to n-C₃₀ alkane region. This can be observed to be present in almost every case, but these humps are not repeated in each of the duplicates (Fig 1). This would suggest poor liquid chromatographic separation of the original extract into fractions after precipitation and removal of the asphaltenes. It is suspected that gravity fed chromatographic columns were used for this purpose, or else uncontrolled HPLC. BP use the more efficient technique of controlled HPLC for all chromatographic separation of extracts into fractions, following a very rigidly adhered to technique to maintain column activation. The Geochem Labs gas chromatograms of duplicate saturate fractions also show differences in the distribution of n-alkanes, especially in the lower boiling range. This is due to the loss of lighter components during solvent evaporation. This loss extends beyond pristane and phytane and thus the ratio of these two components with each other, and even with adjacent n-alkanes, cannot be used reliably as a geochemical parameter. Carbon Preference Indices (CPI's) calculated in the alkane range n-C₁₈ to n-C₃₂ would obviously also be affected and therefore are unreliable.

The two GC standards included in this work package were, in fact, two identical saturate fractions isolated from a crude oil and sampled from the same bottle. The n-alkane contents of these two fractions are known precisely by multiple analysis and by two different techniques. These fractions are used by BP for calibration purposes and are run daily to verify that the instruments are consistently giving accurate results. Comparison of GC1 with duplicate standard GC2 shows the inconsistency of Geochem's gas chromatography technique. The n-alkane distributions are quite dissimilar and neither has n-C27 as the highest alkane peak, although it has been established by us to be the major alkane component (Figure 2). The pristane/phytane ratios were exceptionally low, being approximately half the standard BP value. A point of interest noted with regard to the GC2 chromatogram, is an additional series of sharp peaks between the n-alkanes in the region n-C21 to n-C32. As the peaks are sharp in appearance and occur either side of the n-alkanes it would tend to suggest that sample contamination has occurred. Since these samples were supplied in sealed vials, we would suggest that it was introduced by a dirty syringe.

Duplicate Total Organic Carbon (TOC %wt) content values of the control samples reported by Geochem Labs had no more than a fair agreement with each other. We would expect a far higher level of reproducibility of TOC values, than those shown. Although the figures quoted are of the same magnitude as BP values, the general disagreement is of the order of 10%. A very low TOC value was obtained by Geochem Labs for Sample C (0.13% wt), which was also widely different from the value of its duplicate F (0.73% wt). The TOC value for F however, compares very well with the BP standard value. Results of carbonate (HCl soluble) contents of the sediments were not reported by Geochem Labs.

In conclusion, the quality of analytical data supplied by Geochem Labs is no worse than we have learned to expect from geochemical consultants and they should not therefore be unfairly criticised. However, they do fall down badly with their chromatographic technique, when dealing with sediment soluble extract material. It was unfortunate that Geochem Labs did not submit pyrolysis results for comparison, but since BP uses its own Rock Eval pyrolysis instrument for rapid screening purposes only, this was no great loss.

GPC/JMP
22nd November 1979

TABLE 1

QUALITY CONTROL SAMPLES

COMPARISON OF THERMAL MATURATION ESTIMATIONS

SAMPLE	VITRINITE REFLECTANCE (R_o) Z	VISUAL KEROGEN SPOROMORPH COLOUR	
		BP SCALE	GEOCHEM LABS "TMI"
BP A/I	0.41 (15)	2 - 3	
A	0.48 (5)		2- to 2
I	0.48 (11)		2- to 2
BP B/J	0.44 (20)	2 - 3	
B	0.50 (5)		2- to 2/2
J	0.52 (6)		2
BP C/F	1.27 (3) 1.88 (22)		
C	1.66 (8)		2- (?)
F	1.19		2/2 to 2+
BP D/G	1.94 (12), 2.56 (23)	6 - 7	
D	1.04 (1), 1.34 (8)		2- to 2 (??)
G	2.61 (21)		2- to 2 (??)
BP E/H	no determination possible	lean	
E	no determination possible		2 (??)
H	no determination possible		2-/2- to 2 (?)

Figures in parentheses represent the number of separate determinations.

TABLE 1 (Continued)

COMPARATIVE SCALE OF ALTERATION TERMINOLOGY
USED FOR THE VISUAL KEROGEN SPORE COLOUR

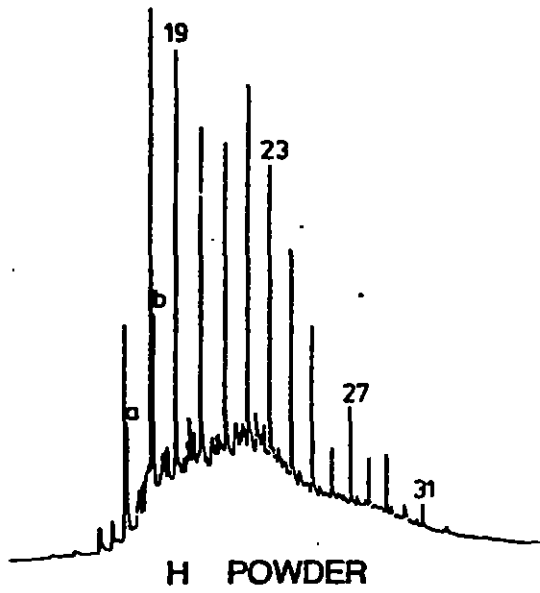
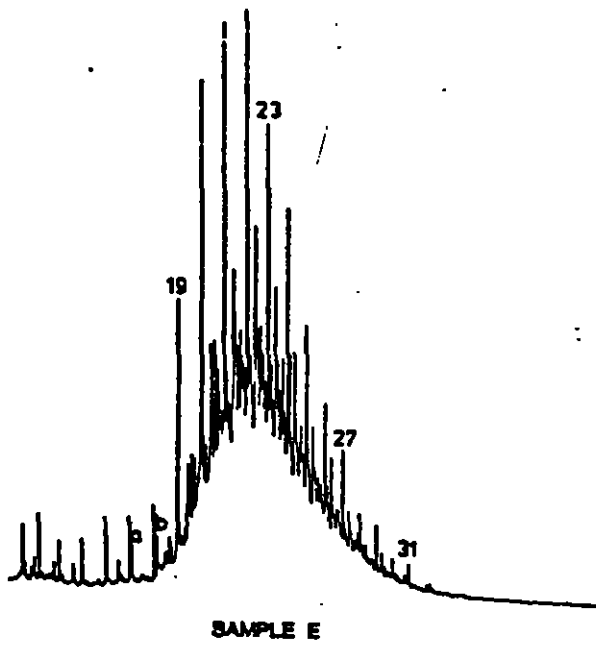
GEOCHEM LABS "TMI"		COMPARABLE BP VALUES
1	immature	1
1+	immature	
1+ to 2-	immature	
2-	moderately immature	2
2- to 2	moderately immature	
2	moderately mature	3
2 to 2+	moderately mature	
2+	mature	3/4
2+ to 3-	mature	4
3- to 3	mature	
3 to 3+	very mature	
3+	very mature	5
4-	severely altered	6
4	severely altered	
5	metamorphosed	7

TABLE 2

QUALITY CONTROL SAMPLES - COMPARISON OF GEOCHEMICAL DATA BETWEEN GEOCHEM LABS AND BP

SAMPLE	SAMPLE TYPE/ MAIN LITH.	TOC (% wt)	TSE (% wt)	TSE/TOC Index %.	SAC/TOC Index %.	TSE			
						SAC(% wt)	CPI "A" "B"	PRISTANE/PHYTANE RATIO	ASPHALTENES (% wt)
BP A/I A I	Outcrop/ Calc. Shale	4.70	0.083	18	3	17.3	1.44	0.36	
		4.28	0.251	59	4	7.1	1.40 1.05	0.44	80.8
		3.68	0.316	86	6	6.7	1.50 1.27	0.99	68.6
BP B/J B J	Core/ Calc. Mudst. /Shale	2.70	0.028	10	2	18.8	1.55	1.07	
		2.58/2.53	0.160	63	6	9.7	1.16 1.12	0.74	79.8
		2.17	0.127	58	3	4.8	1.26 1.25	0.81	64.2
BP C/F C F	Core/ Carbonaceous Sandstone	0.76	0.001	2	0.3	13.2	1.09		
		0.13	0.014	110	12	10.5	1.06 1.23	0.21	61.3
		0.73	0.016	22	1	4.9	0.99 1.18	0.94	73.6
BP D/G D G	Core/ Muddy Limestone	0.59	0.002	3	0.8	25.5	1.06	0.49	
		0.55	0.007	13	2	16.1	1.01 1.18	0.64	50.0
		0.50	0.028	56	4	6.7	1.03 1.33	0.67	70.6
BP E/H E H	Core/ Red Shale	0.01	0.006	unrealistic	unrealistic	35.7	1.04	0.51	
		0.11	0.008	unrealistic	unrealistic	32.3	1.01 1.26	1.00	41.8
		NIL	0.018	unrealistic	unrealistic	5.2	1.08 1.94	0.54	69.4

FIGURE 1



a = pristane
b = phytane

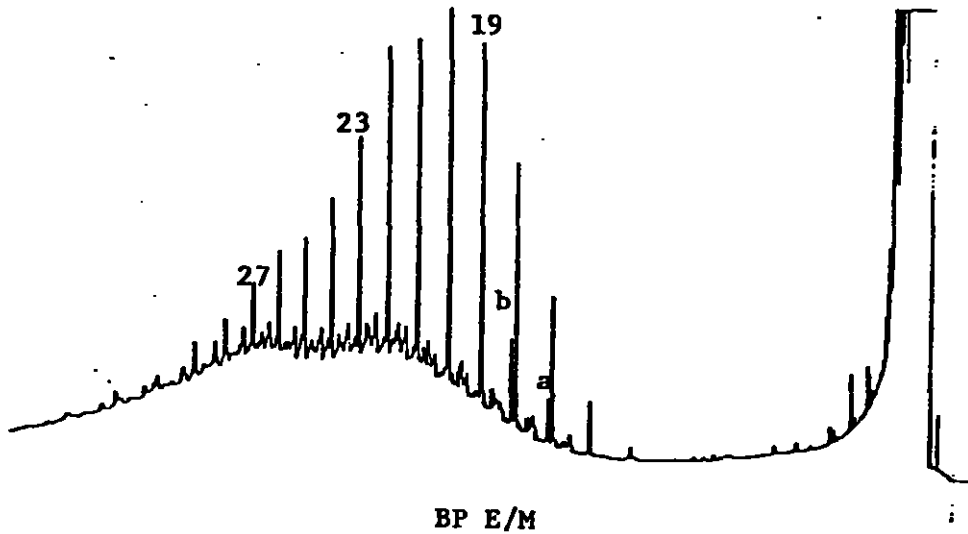
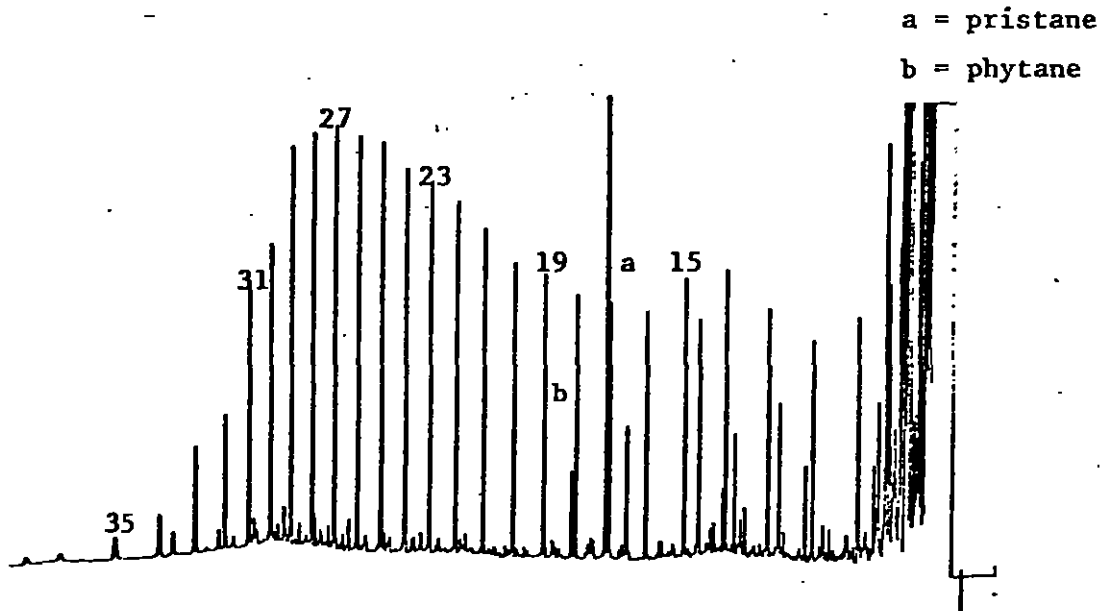
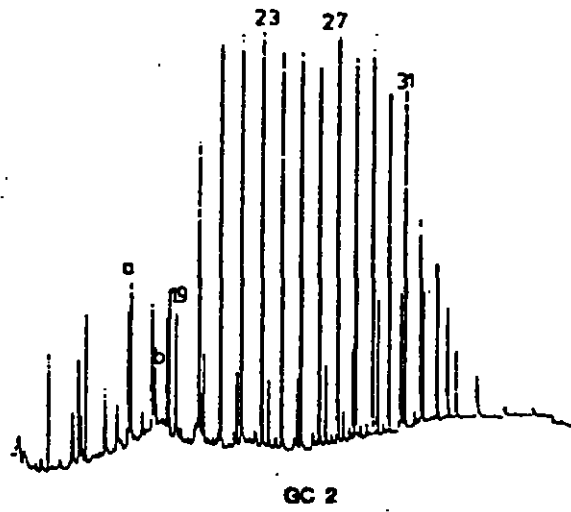
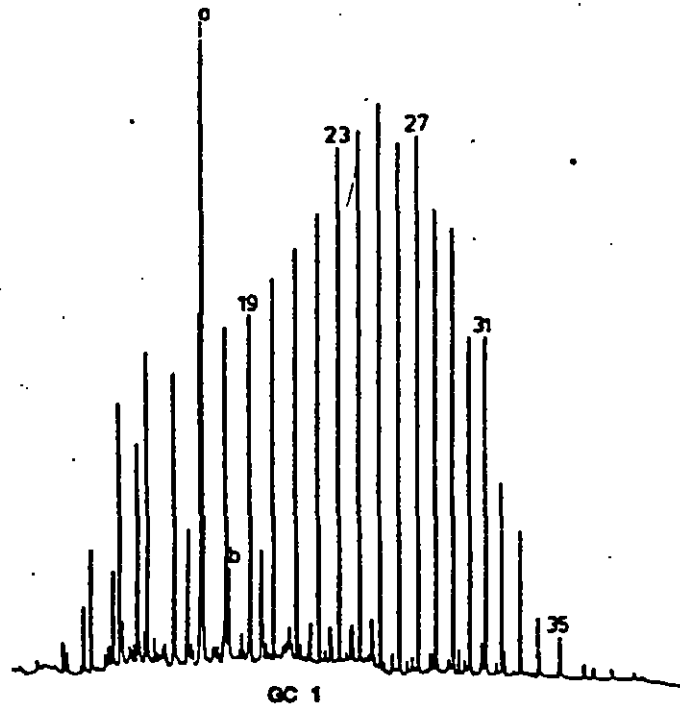


FIGURE 2



a = pristane
b = phytane